THE JOURNAL

OF THE

American Chemical Society

VOL. L

JULY—DECEMBER
1928

EASTON, PA.
MACK PRINTING COMPANY
1928

The Journal of the
American Chemical Society

VOL. 50 JULY, 1928 No. 7

AN AUTOMATIC SAMPLE COLLECTING VACUUM PUMP[1]

BY E. R. WEAVER[2] AND MARTIN SHEPHERD[3]

RECEIVED SEPTEMBER 15, 1927 PUBLISHED JULY 6, 1928

The mercury displacement pump, which has been generally abandoned for the simple production of high vacua in favor of the more rapid mercury vapor pump, is still of value when the gas pumped is to be collected for further investigation. Numerous automatically operated pumps of the Töpler type have been described.[4] Without discussing the ingenious features of these systems, several of which are quite useful, it may be said that the majority of them have one or more of the following faults: (1) vortices are formed in the bulbs during operation; (2) the mercury entering the pump head when low pressure prevails is not sufficiently controlled to prevent fracture occurring here or in the delivery tube; (3) in order to avoid the first two faults, the operation of the pump is made excessively slow; (4) the mercury delivered from the pump has to be returned to the system by hand; (5) the mercury in the pump is not well enough protected from contamination and oxidation to permit the continued operation of the pump for long periods of time.

A pump designed by the senior author a number of years ago eliminates these and other faults and at least three pumps have been built and put into successful operation. The third pump to be constructed has been in continuous use for the past three years, and its behavior has proved entirely satisfactory. The design and operation of this unit will be described.

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[1] Publication approved by the Director of the Bureau of Standards, Department of Commerce, Washington, D. C.

[2] Chemist, Bureau of Standards.

[3] Associate Chemist, Bureau of Standards.

[4] Beutell and Oberhopper, *Chem.-Ztg.*, 43, 705 (1919); *C. A.*, 14, 662 (1920); Bianu, *Bull. sec. sci. acad. Roumaine*, 5, 58 (1916); *C. A.*, 14, 1769 (1920); Johnson, THIS JOURNAL, 34, 909 (1912); Klein, *J. phys.*, 9, 44 (1910); *Compt. rend.*, 148, 1181 (1909); Maass, THIS JOURNAL, 37, 2654 (1915); Morley, Sill. J., 47, 439 (1894); Parnfil, *J. chim. phys.*, 11, 801 (1914); Porter, *Ind. Eng. Chem.*, 16, 731 (1924); Stedman, *Trans. Roy. Soc. Canada*, 15, 93 (1921); Steele, *Chem. News*, 102, 53 (1910); *Phil. Mag.*, 19, 863 (1910); Maass, THIS JOURNAL, 41, 53 (1919).

The pump control is by mercury displacement in a separate cycle made to operate on the suction of a water aspirator or any of the mechanical

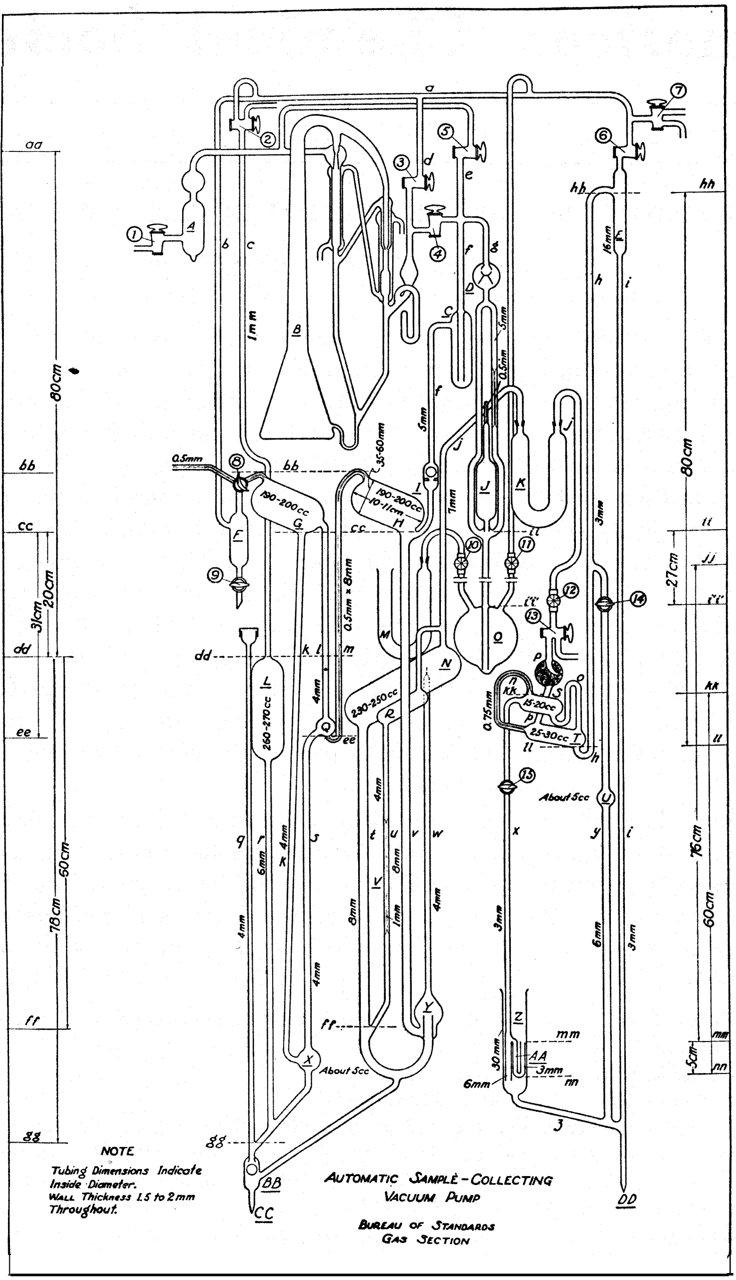

Fig. 1.—Automatic sample collecting vacuum pump.

vacuum pumps commonly on the market. Its operation may be described with reference to the line drawing (Pig. 1) while details of construction and assembly are apparent from a study of the photograph (Fig. 2).

The line drawing has been simplified by the following lettering system. (1) Figures designate stopcocks. (2) Capital letters designate bulbs or other major parts of the unit. (3) Lower case letters designate tubing connecting these parts. (4) Double lower case letters indicate dimensional levels.

The space to be evacuated is connected to the pump through cock 1 and drying tube *A* containing phosphorus pentoxide sublimed onto class wool. The gas may enter the displacement pump directly through *5* or through a mercury vapor pump of the Stimson[5] type located at B. The Stimson pump is capable of producing a high vacuum in an apparatus of reasonable size within a few minutes, with the comparatively high backing pressure of 2 to 4 cm. The displacement pump itself has, then, a very small volume to evacuate, that is, merely the connections f and g and bulb *C* and trap D.

In case gases condensable at liquid air temperatures are to be pumped, condensation bulb *C* is used. After condensation, stopcocks 4 and *5* are closed and the condensate is vaporized into H and *G* or by-passed to a storage system. This step often saves much of the time ordinarily spent in pumping.

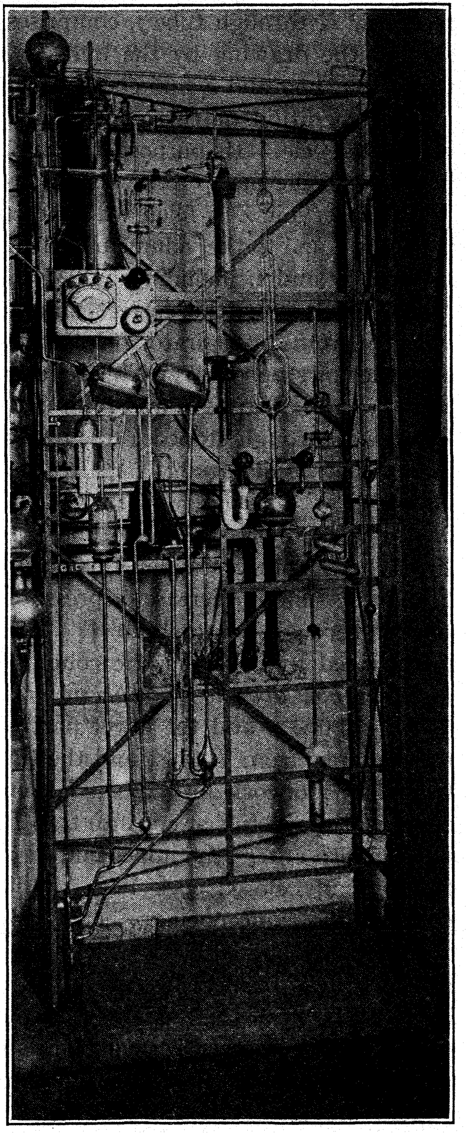

Fig. 2.—Automatic sample collecting vacuum pump.

A McLeod gage, represented with its connections by *J*, *O*, D, *M*, *g*,

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[5] **Stimson,** *J. Wash. Acad. Sci.*, **7,477 (1917).**

10 and *11,* permits the operator to know the pressure at the inlet *f* of the displacement pump proper.

The controlling or actuating system, which connects to the pump reservoir N through tube *j,* comprises the system represented at the right side of the drawing by the bulbs *S* and *T*, reservoir *Z,* interconnecting tubes *h, i,* x, *y* and *z,* and cocks 12, 13, 14 and 15.

The operation of this control unit may be described by tracing one complete cycle. Its purpose is to apply alternate vacuum and atmospheric pressure to the pump reservoir N.

The reservoir *Z* is filled with mercury until the volume above level *nn* is nearly equal to the volume of bulb *S* and tube x, and barometric columns in tubes y and *i,* including bulb U. The mercury must fill *Z* somewhat above level *mm;* the correct amount may be determined by trial. A vacuum from an aspirator or other vacuum pump is maintained through one inlet of stopcock 7. This reduced pressure is communicated through tube *h,* bulb *T*, tube *n* and bulb *S* to tube x, drawing the mercury from *Z* into *x*, through stopcock 15, by which its flow may be regulated, into bulb S. *Simultaneously, this reduced pressure is communicated through the cycle h, T, p, mercury trap and dust filter* P, *and tube* **j** *to the pump reservoir N*. The mercury seal in U-tube ***AA*** is not broken until the mercury in *Z* reaches level *nn*. When this occurs, air rushes through ***AA*** and *x* into *S* and the sudden increase of pressure in *S* causes the mercury to begin to siphon through o into bulb T. The suction through 7 is immediately interrupted by a barometric column in *h*. *The main reservoir, N, of the pump is now open to atmospheric pressure through* ***AA,*** *x, S,* n, T, P, *and tube j*. Tube *y* and the lower part of *h* now serve as a siphon to return the mercury from *T* to *Z,* and the time required for this operation is controlled by stopcock 14. When *T* is empty, air enters *h*. The slug of mercury in *h* above **jj** is swept into trap E, from which it returns to *Z* through ***i***. Air also enters the upper end of y. Mercury flows but slowly through the partially closed cock 14. Air flows many times as fast as mercury through the same opening, hence, when air reaches 14 the mercury in y and *U* drops suddenly, covering the open end of ***AA*** and preventing the mercury in *Z* from being carried up in small portions by an "air lift" as it would be if all the mercury returned slowly to *Z*. When ***AA*** has been sealed over, the starting condition is restored and the cycle repeats itself. The air admitted to N is dried in K to prevent fouling of the mercury.

The displacement pump proper comprises the reservoirs N and R discharging through tubes *t* and *u* and air trap Y into pump chamber *H,* which in turn delivers the gas through fall tube *m* and trap Q into the sample storage reservoir G, whence mercury from *L* may be made to displace the gas through stopcock 8 for delivery to any other apparatus sealed to 8. A system terminating in float valve *BB* and connected through tubes *q, r, s,* and trap X effects the automatic return to the reservoir N of mercury delivered on the compression stroke from the pump head *H* to the collecting bulb *G*.

Very pure mercury is introduced into the system through tube *q,* which may then be closed or left open to the air through a drying tube and dust filter. The amount of mercury must be just sufficient to fill the interconnecting tubes k, l, *m,* ***r,*** *s, t, u,* ***v, w,*** trap *Y,* the reservoir G with a slight excess in L, and the pump head *H* when N and R are just empty. The amount of mercury should be finally adjusted by trial, operating with needle valve 12 nearly closed to avoid breaking the pump head if too much mercury is in the system. When correct adjustment is obtained, the mercury from N, which empties quickly through the large tube *t* just fails to fill the pump head *H* and so avoids fracturing this part. The small bulb R contains just a little more mercury than is required to complete the displacement stroke, and discharges slowly through tube *u* containing a capillary stricture V of sufficiently small bore to prevent the mercury striking sharply against the pump head.

Before beginning to collect a sample, vacuum applied through cock 7, tube *a*, mercury trap F and stopcock S is made to draw mercury from reservoir L, connected to the atmosphere through cock 2, into reservoir G. When G is completely filled, *8* is closed, 2 turned to connect L to the vacuum and mercury withdrawn from G into L, leaving a barometric vacuum in G into which gas from H is discharged. This arrangement permits placing the pump reservoir N below H, the chamber into which it discharges, and the consequent operation of the pump by vacuum and atmospheric pressure rather than vacuum and positive pressure.

The gas delivered from H is effectively prevented from returning by trap Q, which also prevents gas bubbles being carried down tube *s*. The mercury which follows the gas through delivery tube *m* automatically returns to the pump through valve *BB*[6] when vacuum is again applied to N. The reservoir N is made of a tube approximately ***35*** mm. in diameter and **30** cm. in length, sloped at an angle of about 30° from horizontal to prevent the vortex action invariably observed in the usual reservoir. Bulbs S and T in the control system must be relatively narrow inclined tubes for the same reason. The delivery tube *m* must be constructed of tubing of 0.5–0.7mm. bore, in order to be completely effective. Larger bores do not deliver the discharged gas properly, leaving films which prevent the obtaining of high vacua. It is perhaps superfluous to note that the construction of H and m presents an exacting problem to the glass blower, since any surface approaching the horizontal is apt to trap a gas film and ruin the efficiency of the pump.

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[6] The float valves BB and I are solid glass balls ground perfectly spherical and fitting against a 45° ground seat. Floats of this type do not fail as long as they remain clean.

It should be noted that the specified levels indicated by the double letters are quite significant to successful operation of the pumping cycle as well as the control cycle. The level *aa–dd* need not be 80 cm. unless the pump is made to operate on a barometric valve in tube *f*. The glass float *I* is to be preferred at this point. Construction should closely adhere to the other levels specified.

It is apparent that pumping ceases when the pressure in *H* equals that in *G*. At this point the pump runs automatically without further transfer of gas from the pump head to the storage reservoir. The pump is then stopped at the termination of a compression stroke by turning cock 13 to the air, and the pumped gas transferred from *G* by mercury displacement from *L*, cock 2 being turned to the atmosphere for this purpose.

It is worthy of particular comment to note that the pumping cycle contains no stopcocks except the outlet cock No. 8. This is a very important feature, since stopcock lubricant will foul the mercury and make impossible the obtaining of high vacua. The mercury in contact with 8 is carried forward from the pump, and never backward into *G*. No lubricant can therefore be carried into the pumping system. The pump is so arranged that mercury must be added to the Töpler cycle through *q*, never through 8. In actual use, an original filling of pure mercury was perceptibly fouled at the end of two years' operation. If the outlet of *q* and inlet of *N* had been provided with suitable drying tubes, as suggested herein, it is believed the small amount of fouling that occurred over this long period might have been prevented. It is required, of course, that the mercury does not come into contact with a corrosive gas.

For draining and cleaning either the controlling or the pumping system, outlets are provided in the form of drawn-out glass tips at *CC* and *DD*.

The pump was mounted, as shown in the photograph, on a frame of angle iron, the bulbs containing heavy weights of mercury being set into plaster of Paris in suitable metal forms. This type of mounting is desirable when a permanent unit is to be set up. In the event of breaking any part, the whole is easily accessible to a hand torch.

The pump operates readily at a rate of one or two cycles per minute.

Summary

The automatic sample collecting vacuum pump here described has been in successful operation for several years. The pump is an automatic Töpler, which acts as the backing unit to a high speed mercury vapor pump. The automatic control is accomplished by an arrangement of mercury displacement within an auxiliary cycle, which can be operated by a water aspirator or any motor driven vacuum pump commonly on the market. No pressure above atmospheric is required for the operation of the pumping unit. The design incorporates features which prevent

fracture of the Topler pump chamber and delivery tube. Stopcocks have been eliminated from the pumping cycle and a minimum quantity of dried and filtered air comes in contact with the mercury in the pump reservoir; the mercury is consequently not fouled through contact with lubricants or moist air. The mercury delivered by the Töpler pump is automatically returned to the cycle, while the gas pumped is automatically collected and may be transferred as desired to other units.

The control system is entirely independent of the vacuum pump and may find other applications in which alternating vacuum and pressure are desired.

WASHINGTON, D. C.

[CONTRIBUTION PROM THE HUNTINGTON FUND POR CANCER RESEARCH, MEMORIAL HOSPITAL, New YORK CITY]

SOME PROPERTIES OF COLLOIDAL LEAD

BY HELEN QUINCY WOODARD

RECEIVED OCTOBER 14, 1927 PUBLISHED JULY 6, 1928

In the course of the preparation of colloidal lead suitable for clinical use a number of the properties of lead sols prepared by the Bredig method[1] have been studied. The more outstanding of these properties are presented below.

Apparatus and Method.—The apparatus was the same as that described by the author elsewhere.[2] The anode was $^1/_{16}$-inch commercial sheet lead from the National Lead Co. The cathode was a roll of "Pueblo" lead foil from the American Smelting and Refining Co. Baker's "C. P." reagents and Eimer and Amend's "C. P." and "Tested Purity" reagents were used and were not further purified. The approximate currents used at different times are given below, temporary fluctuations up to *10% of the values given being caused by irregularities in the arc: 1.4 amps., 40 volts; 3.8 amps., 50 volts; 7.0 amps., 60 volts. The temperature range was 10–35°.

Properties.—The colloidal lead was dark gray and fluorescent when first prepared, turning blue-black after being centrifuged or being allowed to stand for a few hours. It was brown by transmitted light. The particles carried a positive charge, as shown by their migration in an electric field. When a current passed directly through a sol, the lead coagulated to tree-like growths on the electrodes.

When protected from air by paraffin seals about 5 mm. thick the sols would keep for from three to nine weeks before coagulating. If, however, they were left with a large surface in contact with the air, they rapidly

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[1] Bredig, Z. *angew. Chem.*, 12,951 (1898).

[2] Woodard, *Ann. Sur.*, 607, Oct., 1927.

developed an area of clear supernatant liquid, as observed by Stenstrom and Reinhard.[3] Sols left uncovered in this way soon settled out,

The colloidal lead was readily coagulated by electrolytes. Sulfuric acid, sodium carbonate, sodium bicarbonate, potassium hydroxide and sodium chloride, when added to sols stabilized by potassium hydroxide in amounts sufficient to bring the final concentration of added electrolyte to 0.001 N or higher, caused visible coagulation in a few minutes. The electrolytes mentioned had about equal precipitating power in equinormal concentrations, but acetic acid had much less effect. The coagulation time could not be determined accurately but was roughly inversely proportional to the age of the sol.

All the sols could be coagulated by shaking with air or with carbon dioxide. The time of shaking required to coagulate a sol under given conditions decreased with increasing age of the sol.

Series of sols were made by arcing in different electrolyte solutions. The concentrations of stable colloidal lead prepared under different conditions are shown in Table I, the criterion of stability being the ability of the sol to withstand centrifuging for five minutes at a force of 1000 X gravity. The average deviations from the average concentrations of sols in each electrolyte series are rather large in comparison to the differences in the average concentrations of sols in different series. Nevertheless, a comparison of the different series brings out the following relationships fairly clearly.

TABLE I

Electrolyte	PH of initial soln.	Current, amps.	Number of sols	Average concn., % Pb	Average dev. from av., %
0.00025 M HCl	3.6	1.4	15	0.038	±20
.000125 M H_2SO_4	3.6	1.4	5	.039	±19
.00022 M CH_3COOH	5.2	1.4	6	.050	±24
H_2O only	5.5	1.4	6	.050	±14
.000124 M NaCl		1.4	6	.082	±11
.00025 M NaCl	5.6	1.4	6	.100	± 8
.00050 M NaCl		1.4	5	.091	±18
,00099 M NaCl		1.4	3	.040	±12
.000125 M $NaHCO_3$	8.3	1.4	5	.083	±17
.000125 M Na_2CO_3	9.2	1.4	5	.098	±13
.00011 M KOH	8.8	1.4	5	.104	±15
.00022 M KOH	10.0	1.4	63	.122	*15
.00044 M KOH	..	1.4	6	.130	±14
.00087 M KOH	..	1.4	3	.067	±12
.00022 M KOH	..	3.8	13	.152	*19
.00022 *M* KOH	..	7.0	29	.187	±18

(1) The concentration of colloidal lead stabilized by 0.00022 M potassium hydroxide at currents of 1.4-7.0 amps. is directly proportional to the current used.

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[3] Stenström and Reinhard, *J. Biol. Chem.*, 69, 607 (1926).

(2) For the entire range of electrolyte solutions examined with the exception of the neutral salt sodium chloride, the concentration of colloidal lead stabilized by equinormal solutions of different electrolytes is a function of the PH of the initial solution; see Fig. 1. (Note that the *P*H values given in the table were obtained from solutions that had cooled from the boiling point in the apparatus in contact with the electrodes. Considerable lead is dissolved under these conditions.)

(3) For the electrolytes potassium hydroxide and sodium chloride, the concentration of stable colloidal lead dispersed by a given current rises with increasing electrolyte concentration up to a maximum which is reached in the neighborhood of 0.0003 *M*, and then falls; see Fig. 2. It could not be determined whether the curves finally drop to zero, owing to the extreme difficulty of maintaining an are in high electrolyte concentrations, and the latter portions of the curves are ill defined for the same reason.

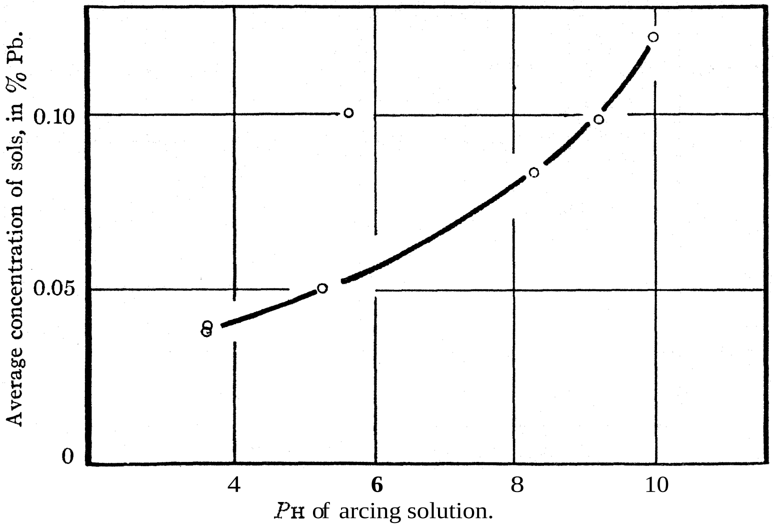

Fig. 1.—Lead sols in approximately 0.00025 *N* solutions of different electrolytes. Relation of concentration of sol to PH of arcing solution.

The relation of the concentration of lead sols to the weight of lead disintegrated from the cathode during the preparation of the sols offers an interesting contrast to the relationship found by the author and others for the similar sols of gold, silver and platinum.[4] Thus, the concentration of gold, silver and platinum sols rises to a maximum during arcing, and then, on further arcing, falls, sometimes rather rapidly, to zero. With lead sols, on the other hand, the concentration rises rapidly to a maximum during arcing, and further arcing, even when quite prolonged, does not show any tendency to cause the concentration of colloidal lead which is stable to five minutes centrifuging with a force of 1000 X gravity to fall below this maximum. This is true of sols in all the different electrolyte solutions examined. Table II gives a typical example. The relation for uncen-

[4] Briggs, *Dissertation,* Columbia, 1923; Woodard, *Dissertation,* Columbia, 1925; Baeyertz, *Dissertation,* Columbia, 1924.

TABLE II

CENTRIFUGED SOLS IN 0.00025 M NaCl AT 1.4 AMPS.

Lead disintegrated, g.	Concn. sol, % Pb	Lead disintegrated, g.	Concn. sol, % Pb
1.30	0.104	2.13	0.089
1.66	.099	2.69	.110
2.06	.109	3.63	.089

trifuged sols is much less consistent than for centrifuged ones, and the maximum of concentration is reached latex.

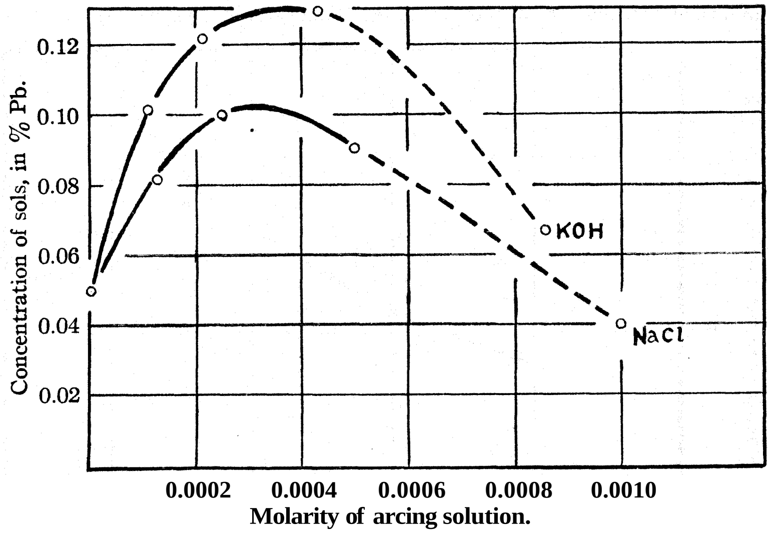

Fig. 2.—Lead sols in solutions of potassium hydroxide and sodium chloride. Relation of concentration of sol to concentration of arcing solution.

The behavior of lead sols under the influence of gravitational force also differs from the analogous behavior of gold sols under centrifugal force, and in general from the settling of dispersions of mixtures of particles of different degrees of stability.[6] This was shown by a study of uncentrifuged sols which were allowed to stand in cylinders 30 cm. high with an internal diameter of 4–4.5 cm. The surfaces of the sols were covered with paraffin. Samples were withdrawn for analysis from the center of the column of liquid from time to time. Typical curves obtained by plotting concentration against time of standing are shown in Fig. 3. These curves show, as expected, an initial rapid drop in concentration as the unstable particles settle out. This is followed by a period of nearly constant concentration, as with colloidal gold. After a time the influence of a cumulative precipitating is apparent. Visible coagulation begins and the con-

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[6] Ayres, *Chem. Met. Eng.*, *16*, 190 (1917); Davidson, *Dissertation*, Columbia, 1924.

centration falls rapidly to zero. This was observed in sols stabilized by acids, neutral salts and alkalies alike. A similar but less marked effect was observed in sols which had been centrifuged for five minutes; see Table III. In view of the readiness with which the sols can be coagulated by shaking with air, it seems probable that the precipitation is caused by the oxygen and carbon dioxide which are absorbed through the paraffin seals.

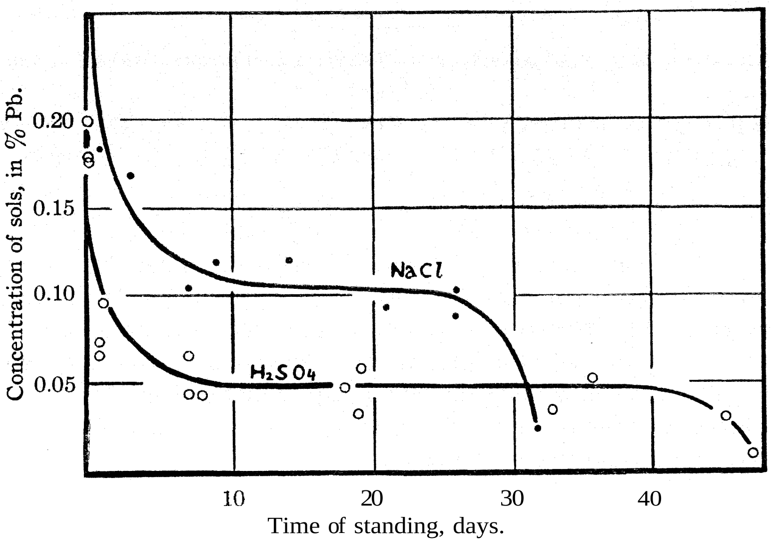

Fig. 3.—Lead sols in 0.000125 M H_2SO_4 and in 0.00025 M NaCl. Change of concentration on standing.

TABLE III

CHANGE IN CONCENTRATION OF CENTRIFUGED SOLS IN 0.00022 *M* KOH AT 7.0 AMPS.

No sols	Time, days	Original concn. remaining, %	No. sols	Time, days	Original concn. remaining, %
8	5	100	5	30	70
8	10	98	5	35	55
8	15	93	5	40	38
8	20	89	5	45	17
8	25	83	5	50	9

Summary

The concentration of stable colloidal lead prepared by the Bredig method has been found to be proportional to the current used in the preparation of the colloid and to the PH of the initial solution in which the arcing is done.

The concentration of colloidal lead has been found to rise to a maximum with increasing concentration of stabilizing electrolyte used, and then to fall as the concentration of stabilizing electrolyte is further increased.

Some properties of Bredig colloidal lead have been compared with the corresponding properties of colloidal gold, silver and platinum.

NEW YORK CITY

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, STATE UNIVERSITY OF IOWA]

THE CONDUCTIVITY AND VISCOSITY OF SOLUTIONS OF LITHIUM NITRATE IN CERTAIN MIXED SOLVENTS[1]

BY J. L. WHITMAN AND S. R. SPENCER

RECEIVED FEBRUARY 8, 1928 PUBLISHED JULY 6, 1928

As part of some investigations being carried on in this Laboratory, it was found desirable to make a series of measurements of the conductivity and viscosity of solutions of lithium nitrate in mixtures of methyl alcohol and ethyl alcohol, and of methyl alcohol and water. Such measurements have previously been made by Jones and Lindsay[2] and by Jones and Carroll,[3] but it seems desirable to report the more extended series of measurements which we have made.[4]

Materials

Lithium Nitrate.—This was prepared from pure lithium carbonate and C. P. nitric acid, was recrystallized five times from conductivity water and was then shown to be free from impurities by a spectroscopic test. The drying of the salt was found to be more difficult than would be indicated from the literature. Anhydrous material could only be obtained by prolonged heating at 150° in a vacuum. This probably accounts for the fact that the values here recorded are uniformly higher than the values previously reported.

Water.—Laboratory distilled water was electrically redistilled from alkaline permanganate and had a conductivity of 1 to 1.2×10^{-6}.

Alcohol.—A good grade of ethyl alcohol was successively treated with lime, metallic calcium, silver nitrate and finally again with lime prepared according to Danner and Hildebrand.[5] Thus prepared it had a conductivity of about 3×10^{-7}, while methyl alcohol prepared in a similar manner had a conductivity of 2×10^{-6}.

Solutions.—Dry lithium nitrate was weighed into a quartz flask, solvent of the required composition then being added to give a solution of the greatest desired concentration. More dilute solutions were made by adding solvent in the required amount to this stock solution.

Apparatus and Measurements

A Leeds and Northrup Kohlrausch slide wire bridge with extension coils, a microphone hummer, tunable head phones, Curtis coil resistance boxes, adjustable air con-

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[1] The data reported in this paper constitute a portion of a Dissertation presented to the Graduate Faculty of the State University of Iowa by S. R. Spencer, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Jones and Lindsay, *Am. Chem. J.*, **28**, 329 (1902).

[3] Jones and Carroll, *ibid.*, 32, 521 (1904).

[4] For a summary and review of the work of Jones in the field of conductivity in mixed solvents see Jones and Kreider, *ibid.*, **45**, 282 (1911).

[5] Danner and Hildebrand, THIS JOURNAL, **44**, 2824 (1922).

densers and the usual sheathings and shieldings were used. The grounded water-bath consisted of a heavy Pyrex vessel of about 12 liters' capacity, the temperature being regulated to 25 ± 0.01°. Washburn pipet cells were calibrated by the method of Kraus and Parker.[6] All other apparatus was carefully calibrated and from 8 to 15 resistance measurements were made on each solution used. All values were corrected for the conductivity of the pure solvent.

Viscosity measurements were made in an Ostwald type quartz viscosimeter.

Experimental

Methyl Alcohol–Ethyl Alcohol **Mixtures.**—The equivalent conductivities of solutions of lithium nitrate of various concentrations and in solvents ranging in composition from pure methyl alcohol to pure ethyl alcohol are recorded in Table I. In every solvent used the equivalent conductivity increases with dilution as is normally the case with water solution, but in no case does the Mass Law hold. For the more dilute solutions the conductivity is almost exactly a linear function of the composition of the solvent, and even for the 0.1 molar solution the deviation is small. The viscosities of a series of mixtures of the two alcohols are given in Table II, referred to water at 25° as unity.

TABLE I

THE EQUIVALENT CONDUCTIVITY OF LITHIUM NITRATE IN METHYL ALCOHOL, ETHYL ALCOHOL AND IN MIXTURES OF THESE SOLVENTS AT 25°

Concn., molar	100% CHaOH	90%	80%	70%	60%	50%	40%	30%	20%	10%	100% C_2H_5OH
0.1	54.27	50.56	45.71	41.83	37.05	33.84	30.16	26.88	23.62	21.01	17.47
.05	63.07	58.10	53.17	49.19	43.87	40.12	35.82	32.04	28.36	24.69	20.74
.025	71.27	65.49	59.30	55.73	49.77	45.95	41.05	36.96	32.75	29.07	24.07
.0125	78.88	72.21	66.30	61.92	56.33	51.49	46.11	41.57	37.05	32.09	27.36
.00625	84.70	78.51	72.36	67.16	61.85	56.35	50.82	45.81	41.17	36.10	30.40
.003125	89.30	83.87	77.91	71.21	64.41	61.03	54.82	49.92	45.06	39.22	33.25
.001562	93.10	87.85	81.84	75.21	69.87	65.09	59.50	53.34	47.40	41.12	35.10
.000781	95.63	91.40	85.16	79.11	73.15	67.52	62.10	56.05	50.05	44.08	38.13
.000391	99.59	94.02	88.10	82.24	76.05	70.51	64.85	59.24	53.19	47.31	41.10
.000195	104.17	98.12	92.18	86.15	80.21	74.31	67.81	62.14	55.91	50.08	44.16

TABLE II

THE VISCOSITY OF METHYL ALCOHOL–ETHYL ALCOHOL MIXTURES AT 25°

CH_3OH, %	Viscosity	CH_3OH, %	Viscosity	CH_3OH, %	Viscosity
100	0.5968	60	0.7800	20	1.0477
90	.6400	50	.8262	10	1.1310
80	.6826	40	.8785	0	1,2530
70	.7249	30	.9618	..	....

In Fig. 1, Curve 1, composition of solvent is plotted against equivalent conductivity for the most dilute solution; in Curve 2 composition is plotted against viscosity for the pure solvent. Viscosity determinations were made for a number of the more dilute solutions but the values obtained differed so little from those for the pure solvents of the same composition that the latter values have been used in all cases.

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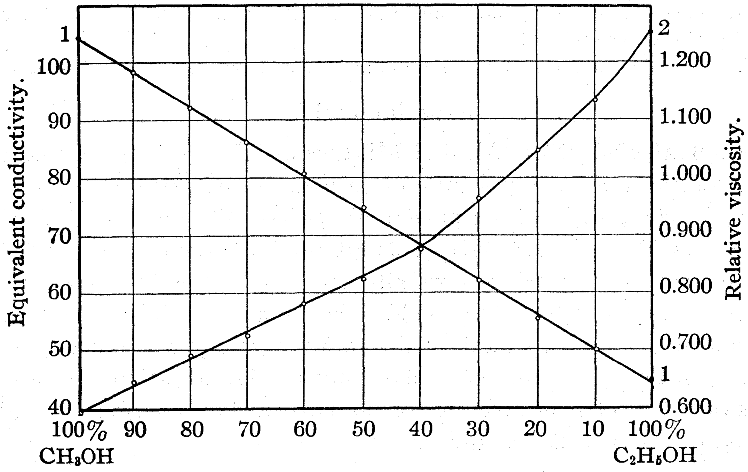
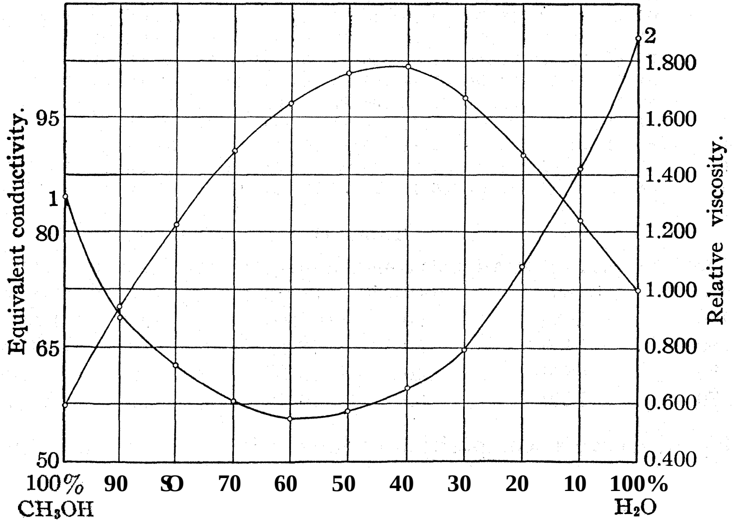
[6] Kraus and Parker, THIS JOURNAL, 44,2422 (1922).

Methyl Alcohol–Water Mixtures.—Table III gives the equivalent conductivities for a series of solutions of lithium nitrate in various mixtures of methyl alcohol and water. Viscosities of the same mixtures are given in Table IV. Dilution was not carried as far as with the methyl alcohol–ethyl alcohol mixtures, since it was found that at a concentration of 0.00625 molar the viscosity of the solution did not differ appreciably from that of the pure solvent. The corresponding curves are shown in Fig. 2.



Curve 1.—Composition–conductivity. Curve 2.—Composition–viscosity.

Fig. 1.—Lithium nitrate in methyl alcohol–ethyl alcohol mixtures.



Curve 1.—Composition–conductivity. Curve 2.—Composition–viscosity.

Fig. 2.—lithium nitrate in methyl alcohol–water mixtures.

TABLE III

THE EQUIVALENT CONDUCTIVITY OF LITHIUM NITRATE IN WATER, METHYL ALCOHOL AND IN MIXTURES OF THESE SOLVENTS AT 25°

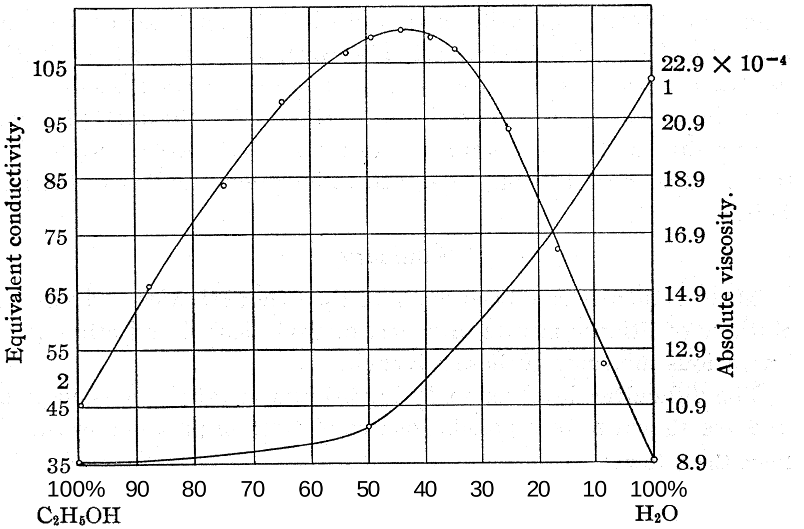
Concn. molar	100% H_2O	90%	80%	70%	60%	50%	40%	30%	20%	10%	100% CH_3OH
0.1	90.56	75.09	64.01	54.95	50.25	47.14	45.50	49.91	47.15	49.82	54 27
.05	94.84	79.31	66.85	57.71	53.07	50.01	48.37	49.21	51.40	54.96	63.07
.025	98.87	83.05	70 04	60.23	55.54	52.40	51.05	52.24	55.20	59.81	71.27
,0125	102.14	85 85	72.77	62 57	57.97	54.70	53.47	55.17	58.99	64.68	78.88
.00625	105.45	88.43	75.91	64.75	60.04	56.60	55.56	58.00	62.95	68.87	84.70

TABLE IV

THE VISCOSITY OR WATER-METHYL ALCOHOL MIXTURES AT 25°

H_2O, %	Viscosity	H_2O, %	Viscosity	H_2O, %	Viscosity
100	1.000	60	1.781	20	1.229
90	1,240	50	1.760	10	0.9473
80	1.466	40	1.656	0	.5969
70	1.667	30	1.483	..	....

Ethyl Alcohol-Water Mixtures.—Data of previous authors are used for ethyl alcohol-water mixtures, conductivity data from Jones and Lindsay[2] and viscosity data from Noack.[7] Graphs are shown in Fig. 3. The conductivity data are unsatisfactory since values are given only for one mixture, that containing 50% alcohol. It is evident, however, and is so stated by Jones and Lindsay[8] that no minimum exists at 25°, although a slight minimum is found for certain concentrations at 0°. An examina-



Curve 1.—Composition-conductivity. Curve 2.—Composition-viscosity.

Fig. 3.—Lithium nitrate in ethyl alcohol-water mixtures.

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[7] John C. Evans, "Physico-Chemical Tables," Griffin and Co., Ltd., London, 1911, p. 651.

[8] Ref. 2, p. 362.

tion of Fig. 3 shows that a decided maximum occurs in the composition–viscosity curve, in this respect being similar to the methyl alcohol–water mixtures.

Discussion

Jones and Lindsay[2] and Jones and Carroll[3] studied solutions of several salts in mixtures of methyl alcohol and water. Measurements were made at various concentrations and at 0 and 25°. They concluded that "the minimum of conductivity is caused primarily by the great decrease of fluidity resulting when the two components of the mixture are brought together."[9] Without considering the many dilutions used, 23 distinct cases were studied, of which 9 show a very pronounced minimum in the conductivity curve, 3 show a slight minimum, while 11 show no minimum.[10] The very marked minimum occurs only in the methyl alcohol–water mixtures, while in the ethyl alcohol–water mixtures the minimum occurs only at 0°, and then only occasionally. For calcium nitrate no minimum* appears under any conditions. These results are difficult to interpret in terms of viscosity, especially in view of the fact that one of the common arguments in favor of the relationship between viscosity and conductivity is that the temperature coefficients of the two are nearly the same.

We have verified and extended Jones' results for the methyl alcohol–water mixtures and have obtained data for methyl alcohol-ethyl alcohol mixtures. The work is being continued to include a number of the higher alcohols.

Summary

1. Measurements have been made of the conductivities and viscosities of solutions of lithium nitrate in water, methyl alcohol and ethyl alcohol, and in various mixtures of these solvents.
2. The difficulties involved in drying lithium nitrate have been pointed out and are shown to be a possible source of error in previous work.

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[9] Ref. 2, p. 553.

[10] Three of this group show a very slight minimum at one concentration. The reader is referred to the original article for a complete comparison.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF HARVARD UNIVERSITY AND OF THE WEST VIRGINIA GEOLOGICAL SURVEY]

THE IODIDE, IODINE, TRI-IODIDE EQUILIBRIUM AND THE FREE ENERGY OF FORMATION OF SILVER IODIDE

BY GRINNELL JONES AND B. B. KAPLAN

RECEIVED FEBRUARY 23, 1928 PUBLISHED JULY 6, 1928

Introduction

U. Fischer,[1] and Braune and Koref,[2] working in Nernst's laboratory, have made measurements of the free energy of formation (A) and heat of formation (U) of silver iodide from its elements. Nernst[3] has measured the specific heat of silver, iodine and silver iodide down to the temperature of liquid hydrogen. Fischer and Nernst regard the agreement between the measured heat of formation and the value computed indirectly from the free energy and specific heats by the aid of the Third Law of Thermodynamics as sufficiently close to furnish support for the Law.

Grinnell Jones and M. L. Hartmann[4] made measurements of the potential of cells of the type Ag, AgI, xKI, xKI + I_2 sat., Pt (similar in principle to the cell used by Fischer but differing in details) at both 25 and 0°. They were thus enabled to obtain a value for dA/dT, or the entropy of the reaction directly from their electromotive force measurements without using thermochemical measurements. They found a value for the entropy nearly twice that found by Fischer and criticize Fischer's work; they also point out that their results and Nernst's data on the specific heats of these substances are not reconcilable by the Third Law of Thermodynamics.

The essence of the Third Law of Thermodynamics is that, for a reaction between solids, the temperature coefficient of the free energy, dA/dT, or the entropy (S) of the reaction is a function solely of the specific heats of the substances involved and can be computed quantitatively if these specific heats are accurately known from absolute zero up to the working temperature. Therefore, as is pointed out by Jones and Hartmann, the sharpest test of the validity of the theory is obtained by comparing the values of dA/dT experimentally determined with that computed from the specific heats of the substances involved. Pischer's method of testing the theory, referred to above, requires not only accurate data on the specific heats and on the free energy of the reaction at one temperature but in addition requires accurate measurements of the heat of the reaction. Therefore, the unavoidable experimental errors in the calorimetric work increase the difficulty of testing the theory by this method. Electromotive force measurements are in

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[1] U. Fischer, *Z. anorg. Chem.*, 78, 41 (1912).

[2] H. Braune and F. Koref, *Z. anorg. Chem.*, *87*, 175 (1914).

[3] W. Nernst, *Ann. Physik.*, [4] 7, 36, 395 (1911).

[4] Jones and Hartmann, THIS JOURNAL, 37, 752 (1915).

general more precise than calorimetric measurements and in the comparison of very similar measurements made at a slightly different temperature, the effect of systematic errors on the temperature coefficient may be largely eliminated.

This point of view is supported by the publications of G. N. Lewis, and especially by the work of R. H. Gerke,[5] which is in our opinion the most rigid test of the validity of the Third Law yet published, and which is based solely on the comparison of measurements of the temperature coefficient of the electromotive force of galvanic cells with the computations based on measurements of specific heat from absolute zero up to the usual working temperature. In the application of this method errors in the potential measurements which vary with the temperature should be guarded against with special care.

If the data of Nernst on the specific heats of silver iodine and silver iodide are correct, and if the Third Law is valid, the value of $\mathrm{d}A/\mathrm{d}T$ should be 2.19 calories per degree.

H. S. Taylor[6] and Taylor and Anderson[7] have discussed this discrepancy between the data of Jones and Hartmann and of Fischer but without definitely locating the cause of the discrepancy. In the meantime G. N. Lewis and his associates have published papers too numerous to refer to in detail which furnish stronger evidence of the validity of the Third Law of Thermodynamics than the numerous papers from Nernst's laboratory. The paper of Gerke[5] referred to above is especially significant. A recent paper by Webb[8] which summarizes and extends the work done on this subject at Princeton also supports the validity of the Third Law.

The discrepancy between the results of Fischer and of Jones and Hartmann has been studied by O. Gerth,[9] a student of Nernst, who duplicated the cells of Jones and Hartmann and of Fischer and repeated the measurements of electromotive force (E_1), and in both cases obtained results which agreed within a few tenths of a millivolt with those of the original authors and also checked the divergent temperature coefficients.

The iodine electrodes prepared either by the procedure of Fischer or by that of Jones and Hartmann were measured by Gerth against each other and agreed within ± 0.02 millivolt. Significant differences were found by Gerth when the two types of silver-silver iodide electrodes were measured against each other. Fischer used pure electrolytic crystals of silver. His silver iodide had been previously fused and then allowed to crystallize on cooling and then broken up into small pieces and added to the silver

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[5] R. H. Gerke, THIS JOURNAL, 44, 1684 (1922).

[6] H. S. Taylor, *ibid.*, **38**, 2295 (1916).

[7] H. S. Taylor and W. T. Anderson, Jr., *ibid.*, 43, 2014 (1921).

[8] T. J. Webb, *J. Phys. Chem.*, 29, 816 (1925).

[9] O. Gerth, *Z* Elektrochem., 27, 287 (1921).

electrodes as a depolarizer. The electrolytes were $N/2$, $N/3$ or $N/10$ solutions of potassium iodide. Jones and Hartmann covered a platinum spiral with silver by electroplating from a cyanide bath. The silver was covered with a paste of pure silver oxide in water, and then heated in an electric furnace to a low red heat to convert the silver oxide completely into spongy metallic silver. The electrodes were then coated with a thin layer of silver iodide by making them an anode in a solution of potassium iodide with a very low current density. These electrodes were then allowed to stand in a fresh solution of $N/10$ or $N/20$ potassium iodide.

Gerth measured silver–silver iodide electrodes of these two types against each other in $N/10$ potassium iodide. His measurements showed that the electrodes made according to the specifications of Jones and Hartmann were positive to those prepared according to Fischer by 0.54 millivolt at 25° and in general the difference is represented by the formula $E = 0.00090 - 0.000015\ t$.

This indicates that the crystalline form of silver iodide used by Fischer is more stable than the form used by Jones and Hartmann. Gerth says "The difference in the silver electrodes found by the preceding measurements explains a part of the discrepancy mentioned at the beginning." This conclusion does not seem to us to be justified because the potential readings of Jones and Hartmann are above those of Fischer, whereas if the only difference between the two types of cell had been that Fischer used a more stable form of depolarizer he should have obtained the higher readings. Thus, if to Gerth's value for the complete cell with the J + H type of electrode, $E_1 = 0.6934 + 0.000258\ t$, there is added the difference between the two kinds of electrodes, $E = 0.0000 - 0.000015\ t$, we obtain $E_1 = 0.6943 + 0.000243\ t$, which should be the same as Gerth's directly measured value for the complete cell of the Fischer type whereas the result obtained by Gerth by actual measurement was $E_1 = 0.6921 + 0.000302\ t$. Thus by taking account of the difference between the two types of electrodes as measured by Gerth, the discrepancy between the measurements of Fischer and those of Jones and Hartmann is made worse instead of being partially accounted for.

Even more important than the discrepancy between the experimental results of Fischer and of Jones and Hartmann is the difference in the computed corrections to allow for the disturbing effect of the formation of tri-iodides in the solution.

The iodide–iodine–tri-iodide equilibrium has been much studied in the past but a detailed review of this earlier work must be omitted to save space.[10] These researches have established that when free iodine is added

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[10] (a) J. L. Gay-Lussac, *Ann. de chemie, 91,* 72 (1814); (b) E. Baudrimont, *Compt. rend.,* 51, 827 (1860); (c) L. Dossios and W. Weith, *Z.* fur *Chemie,* 5, 380 (1869); (d) M. LeBlanc and A. A. Noyes, *Z. physik. Chem., 6,* 401 (1890); *(e)* A. A. Jakowkin,

to a solution of an iodide the principal reaction that occurs is the formation of a tri-iodide according to the reaction $I^- + I_2 \quad I_3^-$. The equilibrium constant of this reaction, $(I^- \times I_2)/I_3^- = k$, is a true constant if the solution is sufficiently dilute in free iodine and iodide, but if the solution is saturated with iodine, especially if the iodide is 0.1 *N* or stronger, there is a decrease in the constant which indicates that some higher complex is present. The iodine electrode is reproducible, constant and reversible to an unusual degree, but in the interpretation of measurements made with it proper allowance must be made for the formation of tri-iodides and the conditions should be so chosen that the formation of higher polyiodides is negligible.

As a result of the formation of the tri-iodides, there is a difference in the concentration of the iodide ion in the two halves of the cell which requires that an osmotic work correction be applied by the Nernst Equation $E_o = RT/F \ln c_2/c_1$. Fischer not only omitted the liquid junction entirely but applied the osmotic work correction in a crude manner because of a lack of accurate knowledge of the tri-iodide equilibrium at the odd temperatures of his measurements. Jones and Hartmann utilized the results of Bray and MacKay[10g] on the tri-iodide equilibrium at 25° and made a study of this equilibrium at 0° themselves[10i] for the purpose. From their measurements with 0.1 *N* potassium iodide solutions, they found $dA/dT = 3.7$ cal. per degree; and from their measurements with 0.05 *N* potassium iodide solutions they found $dA/dT = 4.5$ cal. per degree. They regard the latter as the more reliable.

Gerth made new measurements of the potential of silver–silver iodide–iodine cells similar to those of Jones and Hartmann, using $N/20$, $N/40$ and $N/60$ potassium iodide solutions (E_1) and the results show the same systematic change with concentration.

Gerth then undertook to reduce the disturbing effect of tri-iodides by working with solutions unsaturated with respect to iodine but having a known vapor pressure of iodine. The osmotic work correction and the liquid junction correction are thus substantially reduced and replaced by a correction which can be computed by the Nernst equation $E_p = RT/2F \ln p_2/p_1$, from the vapor pressure of iodine from the solution actually

ibid., 13,539 (1894); 18,585 (1895); 20, 19 (1896); (f) A. A. Noyes and J. Seidensticker, ibid., 27, 357 (1898); (g) W. C. Bray and G. M. J. MacKay, THIS JOURNAL, 32, 914 (1910); (h) W. C Bray, *ibid.*, 32, 932 (1910); W. C. Bray and E. L. Connolly, *ibid.*, 33, 1485 (1911); (i) Grinnell Jones and M. L. Hartmann, *ibid.*, 37, 241 (1915); (j) R. Abegg and A. Hamburger, *Z. anorg. Chem.*, 50, 426 (1906); (k) C. L. Parsons and C. F. Whitternore, THIS JOURNAL, 33, 1934 (1911); (l) G. A. Linhart, THIS JOURNAL, 40, 162 (1918); (m) G. S. Johnson, *J. Chem. Soc.*, 1877, p. 249; (n) H. L. Wells and H. L. Wheeler, *Z. anorg. Chem.*, 1, 448 (1892); (o) H. W. Foote and W. C. Chalker, *Am. Chem. J.*, 39, 561 (1908); (p) C. L. Parsons and H. P. Corliss, THIS JOURNAL, 32, 1367 (1910); (q) E. W. Washburn and E. K. Strachan, *ibid.*, 35, 691 (1913); (r) P. P. Fedotieff, Z. *anorg. Chem.*, 69, 32 (1911).

used (p_1) and the vapor pressure of solid iodine at the temperature of the cell (p_2). This is fundamentally a good idea because as a general rule the activity of un-ionized molecules such as I_2 is very nearly proportional to the vapor pressure and only slightly if at ail influenced by the concentration of the ions present, whereas the activity coefficient of the ions is appreciably different from the degree of dissociation as estimated from the conductivity even in solutions as dilute as 0.05 *N* and widely discrepant in solutions as concentrated as 0.5 N. But if the unsaturated iodine solution can be made sufficiently dilute to reduce the osmotic work correction and the liquid junction to a small figure of the order of one or two millivolts the error in this correction is probably negligible.

To prepare potassium iodide solutions with a small known iodine vapor pressure, Gerth passed nitrogen through a U-tube containing iodine maintained at 0°, thus saturating the nitrogen with iodine vapor at the vapor pressure of solid iodine at 0°. This nitrogen was then bubbled through a potassium iodide solution of known concentration at some higher temperature, until equilibrium had been established. The voltage of a platinum electrode in this solution against a platinum electrode in a solution of the same strength in potassium iodide but saturated with solid iodine was then measured (E_2). The measured potential includes the potential due to difference in iodide ion concentration (osmotic work) and to the liquid junction between the saturated and unsaturated solution as well as the potential due to the difference in the activities of the free iodine in the two solutions. If the vapor pressures are accurately known the latter potential can be computed with precision. This permits the sum of the osmotic work correction and the liquid junction correction to be determined experimentally with a precision greater than they can be computed from the theoretical formulas as was done by Fischer and by Jones and Hartmann. This method does not entirely eliminate the necessity of applying a computed correction for the osmotic work and liquid junction due to the formation of tri-iodides because there still remains a difference in the iodide ion concentration in the pure potassium iodide solution containing no iodine which surrounds the silver iodide electrode and in the solution which is unsaturated with iodine, used by Gerth in his measurements. This potential (E_4) must be computed by the methods criticized above. Gerth attempted to make the unsaturated iodine solution sufficiently dilute so that the error in this correction would be negligible.

Although the basic idea of Gerth's method is good, he lacked the data necessary for its successful execution. This method requires an accurate knowledge of the vapor pressure of iodine at each of the temperatures used in the experiments. Gerth did not determine the vapor of iodine at each of his working temperatures and does not even state directly the values which he used, but he refers to Abegg's "Handbuch," Vol. 4, part 2, p. 350 (1913), where a table of vapor pressures of iodine at various temperatures is given. These data by many different experimenters are obviously inconsistent and lacking in the precision needed for the purpose, as may be readily seen by plotting them on the same sheet with the data given in the "International Critical Tables," Vol. III, p. 201, which are based chiefly on the work of Baxter and Grose. The vapor pressure at 0° is especially important for Gerth's calculations but is so low (0.03 mm. of mercury) that it is difficult to determine with precision and is recorded to only one significant figure. It would seem to be over sanguine to claim that the figures used by Gerth are reliable within 10% and yet an error of 10% makes an error in the computed potential of 1.2 millivolts, whereas Gerth computes the corrections to tenths of millivolts.

Gerth still omits the liquid junction correction (E_j) on the assumption that the potential between the pure potassium iodide around the silver iodide electrode and the unsaturated iodine solution around the platinum electrode is negligible, but this is by no means true as may be seen by inspection of Tables I–V below. Moreover, since these solutions at 11.5' are approximately one-third saturated, and at 25° are only one-tenth saturated, the error due to this omission will have a marked temperature coefficient.

The essential idea of Gerth's new method is to replace the osmotic work correction, E_o, and liquid junction, E_j, which are computed by the Nernst and Planck equations, respectively, involving the concentration of the ions, by a direct measurement, E_2, and a computed correction, E_p, based on the vapor pressure of iodine. This change is partial only and the fraction of the total correction obtained by the old and by the new methods is different at different temperatures. A reference to Table 6 of Gerth's paper will show that at 25° the total correction is —0.0152 volt, of which —0.0133 is obtained by the new method and —0.0019 (or 12% of the total) is computed by the old method. At 11.5° the total correction is —0.0126, of which —0.0056 or 44% is obtained by the old method.

It is apparent that Gerth's new method would fail utterly at 0°, as at this temperature E_2 and E_p would become zero and the total correction would be E_o as computed by the old method (plus the liquid junction correction which Gerth omits). This in effect amounts to applying the correction by the new method at 25° and by the old method at 0° and if the two methods are different in effect, as Gerth contends, this procedure must introduce an error in dE/dT and in dA/dT or the entropy; but as was pointed out above it is especially important to avoid errors in dA/dT in attempts to test the validity of the Third Law of Thermodynamics.

More recently Gerke[11] has made measurements on three different cells

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[11] R. H. Gerke, THIS JOURNAL, 44, 1703 (1922).

which can be combined so that the following results may be obtained indirectly for the reaction $Ag + \frac{1}{2} I_2 = AgI$, at 25°; electromotive force, 0.6858 volt; free energy, 15,825 calories; heat of formation, 14,814 calories; entropy, 3.4 calories per degree. Gerke, unlike any of the investigators referred to above, used precipitated silver iodide. Webb[8] has measured the heat of formation of silver iodide calorimetrically and obtained 14,975 calories. He combines this with the value of 15,767 calories for the free energy (based on the average of the data of Gerke, Gerth, Braune and Koref, Taylor, and Jones and Hartmann) and hence computes the entropy to be 2.6 calories per degree.

Experimental Part

Gerth's fundamental idea of using solutions unsaturated in iodine, thereby replacing the osmotic work correction and the liquid junction correction by another correction dependent on the vapor pressure (or activity) of the iodine, seemed to be a good one if it could be done in a way free from the objections pointed out above in Gerth's procedure. In particular we regard it as essential to use a method equally applicable at 0° and at 25°. We, therefore, undertook a new investigation of the iodine–iodide–tri-iodide equilibrium with special attention to dilute solutions (down to 0.01 N potassium iodide and from 2 to 33% of the amount of iodine necessary to saturate the solution with iodine). The results have been used in a redetermination of the normal potential of the iodine electrode.

Titration gives the sum of the free iodine and of the tri-iodide but does not distinguish between them. Earlier studies of this equilibrium discussed above have been based on the determination of the free iodine either by (1) distribution experiments with a non-miscible solvent such as carbon bisulfide or carbon tetrachloride, interpreted with the aid of data on the distribution of iodine between the solvent and pure water, or (2) analyses of potassium iodide solution saturated with solid iodine interpreted on the assumption that the concentration of the free iodine in the solution containing potassium iodide is the same as the solubility of iodine in water (corrected for hydrolysis).

Since we were interested in studying solutions containing very little free iodine, the second method was inapplicable. The first method was objectionable because the other solvent used is not entirely soluble in the water and thus changes the nature of the medium, and because the distribution ratio is extremely unfavorable. The distribution ratio of iodine between carbon tetrachloride and water is high and varies with the concentration (85–87.9) so that the merest trace of emulsified carbon tetrachloride in the water layer makes serious errors in the analysis. With carbon bisulfide this ratio is even more unfavorable and variable (585–652).[12]

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[12] Jakowkin, *Z. physik. Chem.*, **18**, 586, 588 (1895).

These difficulties were overcome by the invention of a device which we call an equilibrator, which has been described in a separate article because of its suitability for the investigation of many similar problems.[13]

A potassium iodide solution of the desired concentration was prepared by weight, its density and conductivity were determined and one tube of the equilibrator (A) was filled with the solution. Sufficient dry iodine was then added to give approximately the concentration desired. A mixture of water and a saturated solution of iodine in water in the proper proportion to give approximately the desired concentration was placed in the other tube (B) of the equilibrator, and one drop of dilute sulfuric acid was added to prevent hydrolysis. Portions of the potassium iodide solution containing iodine were then blown from tube (A) into a pycnometer to determine its density, into a conductivity cell, into the electromotive force cell and into a weight buret. In a similar fashion the liquid from the water side of the apparatus (tube B) was blown into a pycnometer and weight buret.

The titrations for iodine were made by the Washburn method[14] using arsenite solutions and phosphate buffers with a starch indicator. The end-point is sensitive to 0.01 mg. of iodine. Its principal drawback is that the arsenite solution, if exposed to air, slowly changes its factor by oxidation. We, therefore, found it necessary to maintain an oxygen free atmosphere in the stock bottle. Compressed nitrogen from a steel tank passed through a suitable purifying train to remove all oxygen, then through a wash bottle containing some of the standard arsenite solution to bring it to the proper aqueous vapor pressure and then was delivered to the top of the stock bottle containing the reserve stock of standard arsenite solution.

The titration of the potassium iodide solution from tube (A) gives the sum of the free iodine (I_2) and the tri-iodide ($\Sigma I_3 = I_3^- + KI_3$). The titration of the water from the other tube gives the free iodine (I_2) which at equilibrium is the same in the two tubes. Hence the tri-iodide may be obtained by a simple subtraction, and the iodide remaining may be readily obtained by subtracting the tri-iodide from the original concentration of the solution. The equilibrium constant of the reaction $K^+ + I^- + I_2 \rightleftharpoons K^+ + I_3^-$ may then be readily calculated. This calculation assumes that the activity of the uncharged molecule I_2 is the same as its concentration in the dilute water solution in the other tube of the equilibrator with which it is in equilibrium, and that the activity coefficients of the iodide ion and the tri-iodide ion in the same solution are identical, so that the ratio of the activity of these ions in the common solution is the same as the ratio of their concentrations.

The electromotive force measurements were made in cells of the ground stopper type introduced by Laurie[15] and similar to those used by Jones and Hartmann except that the upper joints were glass stoppers. This type of cell has several important advantages over the other types in common use.

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[13] Jones and Kaplan, THIS JOURNAL, 50, **1600 (1928).**

[14] **E. W.** Washburn, *ibid.*, 30, **31 (1908);** Washburn and Bates, *ibid.*, 34, **1341** (1912).

[15] **A. P.** Laurie, *Proc. Roy. Soc. Edinburgh, 28,* **383 (1908);** *Z. physik. Chem., 67,* **627 (1909).**

(1) It requires only a small amount of the solution used and makes good thermal contact with the constant temperature bath.

(2) It gives readings which are constant for long periods and easily reproducible.

(3) The liquid junction formed by diffusion in the ground joint realizes experimentally the theoretical conditions assumed by Planck in the derivation of the formula for the liquid junction potential and therefore this formula may be used with greater confidence for the computation of the diffusion potential than is possible with other types of liquid junctions which are not so well defined. This type of cell has the disadvantage of a high internal resistance, which greatly diminishes the sensitiveness of the galvanometer, especially if dilute solutions are used. This drawback is probably mainly responsible for the fact that this type has been comparatively little used in the past.

We have invented an improvement in the potentiometer which overcomes this difficulty entirely and makes the sensitiveness of the voltage measurement practically independent of the internal resistance. This improvement consists in adding a large electrostatic condenser in parallel with the galvanometer and its tapping key. Then with the tapping key open, the condenser will be charged to a potential equal to the difference between the potential of the cell and the setting of the potentiometer. A high resistance in the cell cannot prevent this charging of the condenser but can only delay it slightly. If the cell has a resistance of the order of one million ohms it is well to wait about one minute for the condenser to become charged. Then on closing the tapping key the condenser will discharge through the galvanometer but not through the cell and therefore a deflection of the galvanometer will not be influenced by the high resistance of the cell, but will show any slight error in the adjustment of the potentiometer in spite of the high resistance of the cell.

Of course this procedure requires a sensitive ballistic galvanometer in place of the dead-beat instrument commonly used. To bring the instrument quickly and conveniently to its zero reading it is advisable to shunt the galvanometer by a resistance equal to the critical damping resistance of the galvanometer and another tapping key.

The condenser actually used was made by soldering together in parallel enough Western Electric paraffined paper condensers to give a capacity of 44 microfarads (these cost approximately fifty cents per microfarad) mounted in a suitable wooden box carrying a double pole, single throw switch by which the condenser may be disconnected or connected as desired. It is well to have this switch open until an approximate balance (within a few millivolts) has been secured because if a high charge is impressed on the condenser it does not discharge itself completely on a single contact of the discharge key, since with paper condensers the charge is partly "absorbed" in the dielectric and can only be completely removed by tapping the key several times at intervals of a few seconds. Then the switch is closed and the key tapped several times to remove the absorbed charge. The galvanometer is brought to rest at its zero by the key in the critical damping circuit. After waiting a short time for the condenser to become charged (in extreme cases up to one minute) the key is tapped and the deflection of the galvanometer, if any, noted. Then the potentiometer is adjusted until the galvanometer reads zero when the key is tapped.

The effectiveness of the condenser is shown by a typical example. These measurements were made on a cell Ag, AgI, 0.01 N KI, 0.01 N KI + I_2, Pt at 0° in which the liquid junction was made inside of a well ground stopper which was pushed in tightly. The internal resistance of the cell was measured and found to be approximately 1,600,000 ohms, an exceptionally high value.

When the condenser was not used it was necessary to change the setting of the potentiometer by 3 millivolts in order to cause a deflection of 1 mm. on the scale and it was concluded that the potential of the cell was 0.646 volts with an uncertainty of 1 millivolt.

The condenser of 44 microfarads was then connected. It was found that a change in the setting of the potentiometer of 0.1 millivolt made a difference in the galvanometer reading of 3 mm. on its scale—a ninety-fold increase in sensitiveness. At balance the potentiometer reading was 0.64555, volt which was probably correct within 0.02 millivolt. With the condenser the sensitiveness of the potential measurement was found to be nearly independent of the internal resistance. With our potentiometer and galvanometer, which were high-resistance instruments, the condenser is not needed to measure the potential of cells having an internal resistance of 10,000 ohms or less. This modification of the potentiometer overcomes the principal difficulty in the use of cells of the Laurie type for measurement of electromotive force.

The results of the experiments with the equilibrator and the electromotive force measurements are recorded in Tables I–VI, in which the abbreviations have the following significance: CK is the concentration of the potassium iodide solutions used; *M* is the sum of the concentration of the free iodine (I_2) plus the iodine equivalent of the polyiodides present in the potassium iodide solution which is unsaturated with respect to iodine, as determined by titration of the liquid from one tube of the equilibrator; I_2 is the concentration of free iodine in each tube of the equilibrator as found by titration of the tube containing water (plus a trace of sulfuric acid to prevent the reaction $I_2 + H_2O = H^+ + I^- + HIO$). In the later calculations polyiodides higher than I_3, if present, are neglected; $\Sigma I_3 = M - I_2$, $\Sigma I = \Sigma K - \Sigma I_3$, $k = (\Sigma I \times I_2)/\Sigma I_3$, the equilibrium constant of the reaction $KI + I_2$ KI_3.

If it be assumed that the activity coefficient of the iodide ion and of the tri-iodide ion in the common solution is the same, then $k = (I^- \times I_2)/I_3^-$, where the symbols represent the activities of the respective molecular species. This assumption finds support in the following considerations. (1) There seems to be much evidence that activity coefficients are functions primarily of the valence of the ion and of the total ion concentration[16] and there is no change in valence and in total ion concentration due to the reaction $I^- + I_2 = I_3^-$. (2) There is no change in freezing point when iodine is added to a solution of potassium iodide. (3) The degrees of dissociation as computed from the conductivity of KI and of KI_3 are very nearly the same (probably equal within the experimental error as has been shown by Jones and Hartmann, see THIS JOURNAL, **37,** 250–251 (1915)).

The percentage of saturation is obtained by dividing the free iodine (I_2) by 0.00132 at 25° and by 0.000635 at 0°.[17]

E_1 (J. and H.) is the measured potential of the cell of the type, **Ag,** AgI, 0.1 N KI, 0.1 *N* KI + I_2 sat., Pt taken from the paper of Jones and Hartmann. E_2 is the result of our new measurement of the potential of cells of the type, Pt, 0.1 *N* KI + I_2 sat., 0.1 N KI + I_2 unsat., Pt, in which the solution unsaturated with respect to iodine was taken from the equilibrator and is a portion of the same solution whose analysis is recorded in the upper part of the table, and the solution saturated with iodine was made from the same original potassium iodide solution. By adding these two potentials, the osmotic work correction and the liquid junction correction applied by Jones and Hartmann is largely although not entirely eliminated, but a new correction (E_c) must be applied owing to the fact that the iodine around the electrode is unsaturated. This correction is computed by the Nernst formula, $E_c = RT/2F \ln I_2 \text{(sat.)}/I_2 \text{(unsat.)}$.

This computation assumes that the activity of the iodine is proportional to its concentration in its water solution. These solutions are dilute (0.00132 at a maximum) and contain no ions, and therefore the errors involved in this calculation are believed to be less than in the best estimate that can be made in regard to the activities of iodide ions in solutions of potassium iodide up to one-tenth normal.

E_o is the remaining osmotic work correction referred to above, which must be applied because the concentration of the iodide ion in the pure

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[16] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, 1st ed., 1921, p. 374; E. Huckel, *Ergebnisse der exakten Naturwissenschaften,* 3, 243 (1924).

[17] Jones and Hartmann found the solubility of iodine in water to be 0.0006383 mole of I_2 per liter at 0°. From the conductivity of the solution they determined that the hydrolysis of iodine, $I_2 + H_2O = H^+ + I^- + HIO$, is responsible for the solution of 3.2×10^{-6} mole of iodine. Therefore the solubility of iodine as such (I_2) is 0.0006383 −0.0000032 or 0.000635. The figure 0.000638 given by Jones and Hartmann is incorrect owing to an arithmetical error made by them in this calculation.

potassium iodide solution used around the silver iodide electrode is not the same as the concentration of the iodide ion in the unsaturated iodine electrode. It is computed by the formula $E_o = (RT/F)$ ln $(C_2f_2/C_1f_1) = RT/F$ ln $\Sigma K/\Sigma I$, where C_2 (= ZK) is the concentration of the iodide in the original potassium iodide solution and C_1 represents the concentration of the iodide in the solution containing some free iodine (ZI). It is assumed that the conversion of a part of the iodide into tri-iodide does not change the activity coefficient ($f_2 = f_1$).

E_j is the correction for liquid junction potential because the liquid junction potentials in the two cells measured although nearly equal are not exactly so (Gerth makes an error in assuming them to be equal). The correction which must be applied is the potential between a pure potassium iodide solution and the same solution after a part of the iodide has been converted into the slower moving tri-iodide ion. It is computed by the

Table I

Experimental data, $N/10$ KI

	At 25°		At 0°			
Expt. no.	25	26	20	21	22	23
ΣK, g mol /l.	0 10000	0 10000	0.10017	0 10017	0 10017	0 10017
M, g mol./l.	.008246	.0048655	,003673	,003562	006964	.01139
12, **g. mol./l.**	.00012413	.000070864	.000027008	.00002624	.00005241	.00009328
ΣI_3, g. mol /l.	.0081219	.0047946	.0036460	.0035358	0069116	.011297
ΣI, g. mol./l.	,091878	,095205	.096524	.096634	.093258	.088873
k = $(\Sigma I \times I_2)/\Sigma I_3$	.001403	.001407	.000715	.000717	000707	.000734
% sat. with I_2	9 4	5.4	4 2	4.1	8 3	14.7
E_1 (J. and H), volts	+.7000	+.7000	+ 69360	+ 69360	+.69360	+ 69360
E_2, volts	− ,0424	− 0503	−.04780	− 04833	− 03905	− 03170
E_c, volts	+ ,03037	+.03757	+ 03716	+ ,03750	+ 02936	+.02258
E_o, volts	−.00218	− 00126	− 00087	−.00085	− 00168	− 00282
E_j, volts	+.00050	+ 00029	+ 00021	+.00021	+ 00040	+ 00066
E, **volts**	.68629	.68630	.68230	+ ,68213	.68263	+ 68231
k, average	= 0 001405			.000718		
E, average	= 0 6863			6823		
A, calories	= 15,835			15.744		

dE/dT = 0.000160. dA/dT = 3.64 **calories per degree.**

Table IIa

Experimental data, $N/20$ KI at 25°

Expt. no.	I	2	3	6	10	13
ΣK, g. mol./l.	0.05019	0 04994	0.04994	0.04977	0 04998	0.05000
M, g. mol /l.	.012687	.012496	.012078	.002670	.0011534	.001364
I_2, g. mol./l.	.000452	.000441	.000419	.00007647	.000031518	.000031105
ΣI_3, g. mol./l.	.012235	.012055	.011659	.0025935	.0011219	.0011053
ΣI, g. mol /l.	.037955	.037885	.038281	.047176	,048858	,048895
$k = (\Sigma I \times I_2)/\Sigma I_3$	.001403	,001387	.001375	,001391	.001372	001376
% sat. with I_2	34 2	33 4	31 7	5.8	2 4	2.35
E_1, volts		+ .69920		+ .69920	+ ,69920	+ .69920
E_2, volts		− .02250		− .0495	− 06160	− .06180
E_c, volts		+ .01407		+ .03659	+ ,04798	+ .04814
E_o, volts		− .00710		− ,00137	− ,00058	− ,00057
Ej, **volts**		+ 00150		+ 00031	+ .00014	+ .00014
E, volts		+ .68517		.68523	.68514	.68511

k, average = 0 001386 **E, average** = 0.68516. **A, calories** = 16,809.

TABLE IIB

EXPERIMENTAL DATA, $N/20$ KI at 0°

Expt. no.	16	17	18
ΣK, g. mol./l.	.05000	0.05000	0.05000
M, g. mol./l.	.001824	,001984	.002004
I_2, g. mol./l.	.00002712	.000030255	.00002935
XIs, g. mol./l.	.0017969	,0019537	.00197465
ΣI, g. mol./l.	.048203	,048046	.048025
$k = (ZI \times I_2)/\Sigma I_3$	.0007275	,000744	.000714
% sat. with I_2	4.3	4 8	4 6
E_1, volts	+ .6920	+ .6920	+ .6920
E_2, volts	− .04890	− ,04740	− .04750
E_c, volts	+ .03711	+ 03582	+ .03618
E_o, volts	− .00086	− .00094	− .00095
E_j, volts	+ 00021	+ ,00023	+ .00023
E, volts	.67956	+ ,67971	.67996

k, average = 0.000729. E, average = 0.67974. ***A*****,** calories = 15,684.
$dE/dT = 0.000217$. $dA/dT = 5.0$.

TABLE III

EXPERIMENTAL DATA, $N/50$ KI

	At 25°		At 0°
Expt. no.	28	29	39
ΣK, g. mol./l.	0.02000	0.02000	0.02000
M, g. mol./l.	.0023668	,001194	.0016505
I_2, g. mol./l.	.0001745	.00008353	.000062015
ΣI_3, g. mol./l.	.0021923	.0011105	.0015885
ZI, g. mol./l.	.017808	.0188895	.0184115
$k = (\Sigma I \times I_2)/\Sigma I_3$	.001417	.001421	.000719
% sat. with I_2	13.2	6.3	9.8
E_u, volts	+ .66110	+ .65040	.6537
E_c, volts	+ .02599	+ ,03546	+ .02738
E_o, volts	− .00298	− .00147	− .00194
E_j, volts	+ .00067	+ ,00034	+ .00047
E, volts	.68478	.68473	.67961
k, average, 0.00142			.000719
E**,** average = 0.6847_5			6796
A**,** calories = 15,800			15681

$dE/dT = 0.000206$. $dA/dT = 4.74$ cal. per degree.

formula $E_j = RT/F \ln \Sigma C_A\Lambda_A/\Sigma C_B\Lambda_B$ where $\Sigma C_A\Lambda_A$ is the sum of the product of the concentration and the mobility of each of the ions in the pure potassium iodide solution and $\Sigma C_B\Lambda_B$ is the corresponding value for the solution containing free iodine. The addition of all of these potentials gives the effective electromotive force, E, of the cell Ag, AgI, I_2.

The results obtained with the tenth normal solution were still different from the results obtained with the twentieth normal solution. Therefore it seemed desirable to work with still more dilute solutions. Jones and Hartmann had made an attempt to do this but had abandoned it owing to the

TABLE IV

EXPERIMENTAL DATA, N/100 KI

	At 25'		At 0°	
Expt. no.	33	34	35	36
ΣK, g. mol./l.	0.010274	0.010274	0.010300	0.010300
M, g. mol./l.	.00065807	.0006422	.0005672	.0007245
I_2, g. mol./l.	.00008283	.00008168	.00003832	.00005006
ΣI_3, g. mol./l.	.00057524	.00056058	.00052888	.00067444
ΣI, g. mol./l.	.0096988	.0097134	.0097711	.0096256
$k = (\Sigma I \times I_2)/\Sigma I_3$	.001397	.001415	.000708	.000714
% sat. with I_2	6.3	6.2	6.0	7.9
E_u, volts	+ .65010	+ .65010	+ .64740	+ .65060
E_c, volts	+ .03556	+ .03574	+ .03304	+ .02990
E_o, volts	− .00148	− .00144	− .00124	− .00159
E_j, volts	+ .00034	+ .00033	+ .00030	+ .00036
E, volts	.6845$_2$	.6847$_3$	+ .6795$_0$	.6792$_7$
k, average,	0.00141		.000711	
E, average =	0.6846$_2$		0.67939	
A, calories =	15,797		15,676	

$dE/dT = 0.000209$. $dA/dT = 4.83$ cal. per degree.

fact that their cells containing dilute solutions had such a high resistance that their galvanometer was not sufficiently sensitive. This difficulty we have overcome by the invention of an improvement to the potentiometer system described above. In this work with more dilute solutions the iodine solutions containing dilute solutions from the equilibrator were measured directly against the silver–silver iodide electrode prepared by the method of Jones and Hartmann without using saturated iodine electrodes. The electromotive force, E_u, thus obtained is equivalent to $E_1 - E_2$ shown in the table above.

These experiments using unsaturated iodine solutions show a reduction in the osmotic work correction and liquid junction correction as compared with all previous work in this field. With saturated solutions the osmotic work correction is about 18 millivolts at 25° and 15 millivolts at 0°, whereas in some of the above experiments the osmotic work correction was reduced to 0.6 millivolt while the average of all at 25° was 2.04 millivolts and at 0°, 1.3 millivolts. These averages include some experiments in which the solutions were purposely made stronger in iodine than is necessary in order to detect a possible trend, but there is no evidence of such a trend. In Gerth's experiments the osmotic work correction was of about the same magnitude at 25° and from 5.1 to 5.6 millivolts at 11.5'. Gerth does not give data as to tri-iodide formation, so that it is impossible to check his calculations. The liquid junction potential has been reduced from about 3.0 millivolts with saturated solutions to less than one-tenth of this value in our unsaturated solutions but it is not negligible as is assumed by Gerth. A comparison of the results for the equilibrium constant, k, the electromotive force, *E*, and free energy, A, and its temperature coefficient, d*A*/d*T*, indicates that there is no systematic variation with the concentration in the range 0.05 to 0.01 N, but the data obtained with 0.1 N appear significantly different, thus indicating that higher polyiodides are present in sufficient amount to invalidate the results with the more concentrated solutions. In order to test this hypothesis and check still further the work of Fischer it was decided to work with *N*/3 KI also.

Cells of the type Ag, AgI, *N*/3 KI, *N*/3 KI + I_2 sat., Pt were prepared and the potential measured at 25 and 0°. Some of the *N*/3 solution was also used in the equilibrator with less iodine than required for saturation and the distribution constant determined at 25°. Unfortunately, the electromotive force measurements on these dilute solutions were lost owing to an accident and there was no time available to repeat them. The results are shown in Table V.

TABLE V

EXPERIMENTAL DATA, *N*/3 KI

	At 25°		At 0°
Expt. no.	30	31	40
ZK, g. mol./l.	0.32975	0.33333	0.32386
M, g. mol./l.	.18016	,0034913	.16253
I_2, g. mol./l.	.00132	.00001471	.000635
ΣI_3, g. mol./l.	.17884	.0034766	.161895
ZI, g. mol./l.	.15091	,32985	.161965
k = (ZI × I_2)/ΣI_3	.001113	.001396	.000635
% sat. with I_2	100	1.11	100
E_1, volts	+ ,70150		.6960
E_o, volts	− .02036		− .01656
E_j, volts	+ .00349		+ .00309
E, volts	.68463		.68253

A, calories = 15,797 15,748 calories

d*E*/d*T* = 0.000084. d*A*/d*T* = 1.94 calories per degree.

The data on the equilibrium constant of the reaction KI + I_2 KI_3 are summarized in Table VI. The figures are computed on the assumption that higher polyiodides are absent and that the activities of the iodine

TABLE VI

SUMMARY OP EQUILIBRIUM CONSTANTS OP THE IODIDE–IODINE–TRI-IODIDE REACTION

	At 25°		At 0°	
Concn. of *K I*	Solns. satd. with I_2	Solns. unsatd. with I_2	Solns. satd. with I_2	Solns. unsatd. with *Iz*
N/3	0.00111	0.00140	0.000635	.....
0.1 *N*	,00131	.00141	.000693	.000718
.05 *N*	.00137	.00139	.000707	.000729
.02 N	.00137	.00142	.000712	.000719
.Ol N	.00139	,00141	.000710	.000711
.005 N	.00142	....	.000711	.....
.002 N	,00147	....	.000706	.....
.001 N	.00150	....	.000694	.....

and tri-iodide ions in their common solution are identical. The data for the saturated solutions (except $N/3$ KI, which are from Table V) are taken from Bray and MacKay at 25° and Jones and Hartmann at 0°, recomputed on the above basis.

The solutions unsaturated with iodine show no evidence of a systematic trend in spite of a variation in iodine content from 2 to 34% of saturation and in KI concentration from 0.01 N to $N/3$; in view of the low concentration of free iodine in some of the solutions the concordance is satisfactory. It is more difficult to secure concordant results at 0° than at 25°, owing to the smaller vapor pressure of iodine, the weaker solutions used and the greater difficulty of maintaining temperature constancy over the longer periods required for the experiments. The equilibrium constant may be taken as 0.00140 at 25° and 0.00072 at 0°, but the solutions which are saturated with iodine show clearly a systematic decrease of the constant with increasing concentration which is clearly evident with the $N/3$ solution. The variation is greater at 25° than it is at 0°. These data emphasize the importance of working with dilute solutions of potassium iodide unsaturated with iodine when using iodine electrodes. The fact that there appears to be a greater tendency to form the more complex polyiodides at 25° than at 0° shows that when working with strong solutions saturated with iodine as Fischer did the error will have a temperature coefficient. The experimentally determined values for E, dE/dT, A, dA/dT and U for the reaction Ag + $^1/_2$ I_2 = AgI are summarized in Table VII.

TABLE VII

SUMMARY OF DATA FOR THE REACTION AG + $^1/_2$ I = AGI

	$N/3$	0.1 N	0.05 N	0.02 N	0.01 N
E at 25°	(0.68463)	0.6863	0.6851_6	0.6847_5	0.6846_2
E at 0°	($.6825_3$)	.6823	$.6797_4$	.6796	$.6793_9$
dE/dT	(.000084)	.000160	.000216	.000206	.000209
A at 25°	(15797)	15835	15809	15800	15797
A at 0°	(15748)	15744	15684	15681	15676
dA/dT	(1.94) cal. *per degree*	3 64	5.00	4.74	4.83
U at 25°	(15219)	14750	14318	14386	14358

The results with the $N/3$ solutions are not directly comparable with those obtained with the more dilute solutions because no experiments using the equilibrator and dilute solutions were completed with $N/3$ KI, but these data are comparable with Fischer's measurements. These data indicate that the results are unreliable in solutions 0.1 N or stronger, probably owing to the formation of polyiodides more complex than the tri-iodide or possibly a complex formed by action of potassium iodide on silver iodide, but that in solutions as dilute as 0.05 N and below no such disturbing effect is observed. We therefore believe that the new results obtained with dilute solutions unsaturated with iodine are the most reliable.

The results of the different experimenters on the entropy of the reaction $Ag + \frac{1}{2} I_2 = AgI$, are summarized in the following table, arranged in chronological order and also arranged to show the influence of the concentration of the potassium iodide on the results, except in the case of Gerke, who did not use potassium iodide at all.

TABLE VIII

SUMMARY OF THE VALUES OF dA/dT OR THE ENTROPY OF THE REACTION $Ag + \frac{1}{2} I_2 = AgI$, BY VARIOUS OBSERVERS, IN CALORIES PER DEGREE

Concn. of KI used	Fischer	Jones and Hartmann	Gerth	Cerke	Webb	Jones and Kaplan
$N/2$	2.419	..	..	..	..	
$N/3$	1 267	..	..	..	..	1.96
$N/10$	1 66	3.68	..	..	2.6	3.64
$N/20$	..	4.52	2 22	..	..	5.00
$N/40$	..	..	2 37	..	..	
$N/50$	..	..	..	..	..	4.74
$N/100$	..	..	..	3 4	..	4.83

If the specific heat measurements on silver, iodine and silver iodide determined by Nernst are reliable and the Nernst-Lindemann formula is used to extrapolate the data down to absolute zero, the value 2.19 calories per degree would be a confirmation of the Third Law.

It will be noticed that Fischer's temperature coefficients of the free energy vary greatly with the concentration but in no systematic manner. For the purpose of testing the Third Law, Fischer averages the results obtained with the $N/2$ and $N/3$ solutions and rejects the results obtained with the $N/10$—an objectionable procedure. Moreover, inadequate allowance for the influence of tri-iodides and higher polyiodides in these strong solutions saturated with iodine vitiates the results. Gerth's results come close to the figure 2.19 which, assuming the accuracy of the specific data obtained in the Nernst laboratory, would support the validity of the Third Law; but as has been pointed out in more detail above, Gerth's new method of surmounting the difficulties due to the formation of tri-iodides fails completely at 0°, and at other temperatures the manner of applying the correction varies considerably with the temperature, thus introducing an error into the temperature coefficient, dA/dT. Moreover, the vapor pressure of iodine is not known as a function of the temperature with sufficient accuracy for the purpose. Our new method of using the equilibrator is a considerable improvement over Gerth's method in principle and radically different in technique. It is equally usable at 0° and at 25° and permits working with solutions more dilute in iodine than Gerth's method. The work of Jones and Hartmann, although improved upon, is confirmed and the opinion that they expressed as to the greater reliability of the data obtained with dilute solution is confirmed.

Since the papers of Fischer and of Jones and Hartmann were published, new determinations of the specific heat of iodine at low temperatures have been published by Günther[18] and by Lange.[19] Günther's results agree substantially with the earlier results obtained by Nernst at temperatures above 30° absolute but differ considerably between 20 and 30° absolute. Günther has proved that there is a transition between two allotropic forms of iodine which occurs at some temperature between 20 and 30° absolute but this transition is a slow one and his data do not make it possible to determine the heat of transition, the specific heat of the form stable at the lower temperature, or the exact temperature of transition. Recently, the heat capacity of iodine has been redetermined by Lange within the range 10 to 52° absolute. He obtained lower results than Nernst, and Gunther.

Lange obtained no indication of the existence of a transition temperature between allotropic forms within this range but of course that does not disprove the existence of another form more stable at low temperatures. Lange combines his data at low temperatures with Nernst's at temperatures above 52° and gives a table from which the entropy of iodine at 25° may readily be computed to be 13.95 entropy units. If this is correct and if Nernst's data on silver and silver iodide are correct, then the value of the entropy change during the formation of silver iodide which would be predicted from the heat capacities by the Third Law is $26.6 - 13.95 - 10.25 = 2.6$ instead of 2.19 based on the measurements of Nernst. If Gunther's observations are correct, Lange was probably working with an unstable modification of iodine at the lower temperatures and unstable forms commonly have a higher heat capacity than the stable form. Moreover, Lange's work shows that the data of Nernst are too high in the lower range of temperature and makes it probable that they are too high in the upper range also. If this is correct the value 13.95 for the entropy of iodine may be too high and this would make the value 2.6 for the entropy of formation of silver iodide too low.

Therefore the value of 2.19 for the entropy of formation of silver iodide based on the specific heat of measurements of Nernst can no longer be regarded as having a sound experimental basis, and the fact that the electromotive force measurements of Fischer and Gerth, which are shown above to be faulty, agree with this figure cannot furnish proof of the validity of the Third Law of Thermodynamics. But a conclusion that the theorem is not valid cannot be drawn from the available evidence of this case because of the uncertainty as to the entropy of iodine. The essence of the theorem is that at absolute zero temperature the entropy of chemical reactions is zero and therefore the entropy at any other temperature is a

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[18] Günther, *Ann. Physik,* [4] **51,** 839 (1916).

[19] F. Lange, *Z. physik. Chem.,* 110,352 (1924).

function of the specific heats alone. In the past decade evidence supporting the validity of the Third Law of Thermodynamics has accumulated, especially by the work of G. N. Lewis and his associates at the University of California and by the work of H. S. Taylor and his students at Princeton, but more extensive and reliable data on the heat capacities from absolute zero to room temperatures and on the heat effect of any changes of crystalline form that occur within this range of temperature are urgently needed to test this very important theoretical principle.

Summary

1. The earlier work on the free energy of formation of silver iodide is reviewed.

2. The equilibrium constant, $(I^- \times I_2)/I_3 = k$, of the reaction $I^- + I_2 \rightleftharpoons I_3$ was found to be 0.00140 at 25° and 0.00072 at 0°. The results show no systematic variation with the concentration of the iodine between the limits of 2 and 33% of saturation and no systematic variation with the concentration of the iodide between the limits 0.01 and 0.1 N. Solutions saturated with iodine give a lower value for the constant especially in the more concentrated solutions of iodide. This indicates that in the stronger solutions some higher polyiodides are formed.

3. A modification of the potentiometer by replacing the usual dead-beat galvanometer with a ballistic galvanometer and shunting an electrostatic condenser of high capacity across the galvanometer and its tapping key has made it possible to determine the potential of a cell having an internal resistance of 1,600,000 ohms within 0.02 millivolt. This invention overcomes the principal difficulty in the measurement of the potential of cells having the liquid junction within a ground glass joint.

4. Measurements have been made of the potential of iodide concentration cells with one electrode consisting of a platinum electrode dipping in a solution of potassium iodide saturated with iodine and the other electrode being similar except that it is unsaturated but with the free iodine activity fixed by the equilibrator.

5. Determinations were made of the solubility of iodine in $N/3$ potassium iodide solution at both 25 and 0°.

6. The free energy of formation of silver iodide has been determined by the aid of the equilibrator, using solutions containing much less iodine than is necessary to produce saturation so that disturbances due to the formation of polyiodides are minimized and can be allowed for by the use of the data supplied by the equilibrator. The results show no systematic variation with the concentration within the range 0.01 to 0.05 N, but do show a slight variation at the higher concentration.

7. The average results obtained with the most dilute solutions (0.01 to 0.05 N) are: free energy at 25°, 15,802 calories; free energy at 0°

15,680 calories; change in free energy per degree, or entropy change, 4.8; heat of formation at 25°, 14,354 calories.

8. The bearing of these data on some earlier attempts to verify the Third Law of Thermodynamics is discussed.

CAMBRIDGE 38, MASSACHUSETTS AND MORGANTOWN, WEST VIRGINIA

[CONTRIBUTION FROM THE PITTSBURGH EXPERIMENT STATION, U. S. BUREAU OR MINES]

NOTE ON MEASUREMENTS OF THE RATE OF DECOMPOSITION OF NITROGEN PENTOXIDE AT VERY LOW PRESSURES[1]

BY ALBERT G. LOOMIS[2] AND DAVID F. SMITH[2]

RECEIVED MARCH 7, 1928 PUBLISHED JULY 6, 1928

Introduction

The decomposition of nitrogen pentoxide is one of the most interesting and most extensively studied of the few known unimolecular reactions. Data on the rate of its decomposition are of great importance to the advancement of our knowledge of the mechanism of chemical reaction.

Although the decomposition of nitrogen pentoxide has finally been shown to be strictly unimolecular over a considerable pressure range,[3] the measurements of Hirst and Rideal[4] would seem to indicate a quite unexpected increase in the specific rate of decomposition at very low pressures. These authors state that, after a critical consideration of their data, they are of the opinion that the increase is real and outside of the experimental uncertainty. Just preceding the presentation of our data, Hibben,[5] by a method similar to Hirst and Rideal's, the details of which are not given, fails to agree with Hirst and Rideal and concludes that the normal rate obtains down to very low pressures.

Since Hirst and Rideal's result is totally unexpected and requires a unique theoretical treatment,[6] it was thought advisable to repeat these measurements by the method which would avoid or at least detect the presence or absence of what seemed to us some objectionable features in Hirst and Rideal's experiments. Especially does this seem desirable since another investigator, using a method similar to Hirst and Rideal's, has obtained a totally different result.

The possible objections to Hirst and Rideal's method that occurred to us were the following. First, unless the apparatus were of proper design,

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[1] Presented before the Division of Physical and Inorganic Chemistry at the 74th Meeting of the American Chemical Society, Detroit, Michigan, September 5 to 10, 1927.

[2] Physical Chemist, Pittsburgh Experiment Station, U. S. Bureau of Mines.

[3] Daniels and Johnston, THIS JOURNAL, 43, 53 (1921); Lueck, *ibid.*, 44, 757 (1922); Runt and Daniels, *ibid.*, 47, 1602 (1925); White and Johnson, *ibid.*, 47, 1240 (1925).

[4] Hirst and Rideal, *Proc. Roy. Soc. London*, **109A,** 526 (1925).

[5] Hibben, *Proc. Nat. Acad. Sci.,* 13 (8), 626 (1927).

[6] See Thomson, *Phil. Mag.,* 269, (7), *241* (1927).

the condensation of a heavy gas in the presence of a noncondensable gas might be a relatively slow and incomplete process even at low pressure. Second, condensation of the heavy gas might involve a considerable amount of occlusion of the lighter gas. Third, adsorption effects, which would be inappreciable at high pressures, might at low pressures be relatively large compared to the total amount of gas present.

Experimental Method

The authors' apparatus and experimental procedure may be understood by reference to Pig. 1. The nitrogen pentoxide prepared in the usual way by dehydrating pure nitric acid with phosphorus pentoxide, was first distilled into a receiver (not shown in the figure) cooled by ice and salt. A small part of this, as needed, was distilled in a stream of dry ozone into the tube a, which was kept cold. The purified crystals in *a* were then pumped off at 0 and -20° by means of an oil pump connected through a liquid-air trap. They were then pumped off at -100° with a mercury diffusion pump. After the whole apparatus had been thoroughly baked and pumped out with the diffusion pump until a spark discharge gap showed perfectly dark (pressure $< 10^{-5}$ mm.), the tube a was brought to 0° and the pipet c kept at about 1° while the latter was filled with nitrogen pentoxide at its vapor pressure at 0" (50 mm.). The volume of the pipet c was such as to give the required pressure when its contents were admitted to the 5-liter flask g. The nitrogen pentoxide from the pipet was allowed to pass over and condense in the U-tube f, which was cooled by liquid air. After sufficient time had elapsed to allow complete condensation in the U-tube, the apparatus was evacuated again through the stopcock d while the tube was sealed off at e. At no time did the spark gap show the presence of any oxygen at this point.

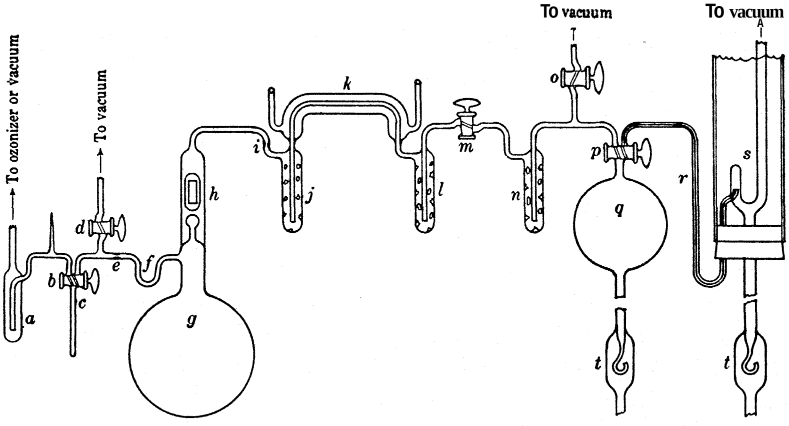

Fig. 1.—Diagram of apparatus.

The 5-liter flask g was provided with a thin glass bulb by means of which communication could be established with the rest of the apparatus by applying a magnet to raise and lower the piece of iron enclosed in a glass tube at *h*, thus breaking the thin bulb. The flask g, after removal of the liquid air from the U-tube, was placed in a thermostat at 30.00°, at which temperature nitrogen pentoxide decomposes at a convenient rate. During the time the decomposition of the nitrogen pentoxide was taking place, the flask was sealed onto the rest of the apparatus, and the connecting tubes were baked out and thoroughly evacuated with the diffusion pump. The small glass tubes *j*, *l* and *n* are filled with glass beads to serve as condensers; k is a jacket through which cold air could be passed to prevent decomposition of nitrogen pentoxide if it was desired to distil the nitrogen pentoxide back and forth between *j* and 1.

After an experiment the oxygen was pumped out of g by means of a large (2-liter) Toepler pump *q*, the heavy gases being retained in the liquid-air condensers *j* and *l*. The oxygen was delivered from the Toepler pump into the calibrated pipet *s* containing mercury and surrounded by a jacket filled with water at a uniform temperature. Pressures and volumes were measured in the pipet by means of a high-grade cathetometer. Air traps were provided, as at t, wherever there was danger that air might be carried into the apparatus by the mercury. Great care was taken to pump out thoroughly every part of the apparatus and to avoid subsequent entrance of traces of air. Points on the apparatus where seals were later to be made were always previously heated to the softening temperature and pumped off in order to avoid driving out gas from the glass during sealing.

After the flask g was pumped out, it could be sealed off at *i*. The total nitrogen pentoxide present was determined by closing the stopcock *m* and heating the condensers to decompose all the nitrogen pentoxide. The resulting oxygen was then pumped over into the pipet *s* as before, a third liquid-air trap at *n* assuring that no heavy gases escaped into the Toepler pump.

Adsorbed gas in g could be obtained by heating and further pumping. Occluded gas in the traps *j* and *l* could be obtained, after sealing off at *i*, by distilling the condensate back and forth between *j* and *l* and pumping off the gas so liberated.

Experimental Results

Experiment 1.—As a check on our method, an experiment was made first at moderate pressure. The oxygen from the decomposition that took place in seventy minutes at a temperature of 30.00° occupied a volume of 3.2909 cc. at a pressure of 104.22 mm and a temperature of 26.59°. The oxygen from complete decomposition had a pressure of 366.81 mm. at the same volume and temperature. The reaction rate constant for the decomposition of nitrogen pentoxide is thus calculated from these data to be $k = 4.7 \times 10^{-3}$. Calculated from the experiments of Daniels and Johnston, the constant at high pressures is 4.1×10^{-3}. We considered this agreement to be as close as could be expected. The original pressure of nitrogen pentoxide in the 5-liter flask in this experiment was thus about 0.25 mm.—the pressure below which Hirst and Rideal state that the constant begins to increase. The total oxygen obtained is roughly that which we expected from the amount of nitrogen pentoxide injected into the reaction flask.

Experiment 2.—An experiment was next made at a pressure which, judging from Hirst and Rideal's results, would be low enough to effect a marked increase in the rate of decomposition. Approximately 1.4 cc. of nitrogen pentoxide at a pressure of about 50 mm. was put into the reaction flask. The results are as follows: time of reaction at 30°, 105 min.; oxygen from reaction, 0.7580 cc. at $p = 12.90$ mm. and $t =$ 24.50"; oxygen from complete decomposition, 0.7580 cc. at $p = 17.99$ mm. and $t =$ 24.50°. From the oxygen recovered, the pressure in the reaction flask is calculated to be 0.0055 mm. The rate constant from these data is 12 X 10^{-3}, which would seem to confirm Hirst and Rideal's results. However, the amount of nitrogen pentoxide calculated from the oxygen recovered is but about 40% of that actually put into the apparatus. This fact suggested the existence of adsorption or occlusion effects.

Experiment 3.—Experiment 3 was designed to determine the extent to which the heavy gases condensed in the two liquid-air traps had occluded oxygen. Approximately 1.0 cc. of nitrogen pentoxide at 50 mm. was injected into the 5-liter reaction flask: time of reaction at 30°, 102 min.; oxygen from the decomposition taking place in this time, 0.4908 cc. at $p = 11.13$ mm. and $t =$ 26.33"; oxygen from complete decomposition of the nitrogen pentoxide, 0.4908 cc. at $p = 13.53$ mm. and $t =$ 26.33" (includes preceding amount of oxygen); oxygen after repeatedly redistilling and pumping condensate, 0.4908 cc. at $p = 16.73$ mm. and $t =$ 26.33" (includes both preceding amounts of oxygen). The oxygen occluded is thus about 24% of the oxygen which would otherwise be obtained. The total oxygen recovered would correspond to a pressure of nitrogen pentoxide in the 5-liter flask of 0.0033 mm. This is but 30% of the nitrogen pentoxide actually used.

Experiment 4.—An attempt was made to determine the amount of adsorption of nitrogen pentoxide in the 5-liter reaction flask. One cc. of nitrogen pentoxide at approximately 50 mm. was injected into the reaction flask. To show further that no nitrogen pentoxide had decomposed during its injection into the reaction flask, the apparatus was pumped out with the Toepler pump at this stage of the experiment, with the liquid air still in the U-tube f of Fig. 1. No oxygen was obtained. The liquid air was then removed from the U-tube, the apparatus having been provided with a stopcock at e in place of the seal at *h*. The flask was allowed to stand at room temperature for ten minutes. The stopcock was then opened to the liquid-air-cooled condensers *j* and *l* and the flask pumped out with the Toepler pump. The amount of oxygen obtained was 0.6100 cc. at $p = 6.00$ mm. and $t =$ 27.04'. (At this point the reaction flask was heated with a flame and pumped out several times.) The oxygen obtained, including the previous amount, was 0.6100 cc. at $p = 10.64$ mm. and $t =$ 27.04°. The stopcock at e was then closed and the remaining nitrogen pentoxide decomposed. The oxygen obtained, including both previous amounts, was 0.6100 cc. at $p = 16.41$ mm. and $t =$ 27.04'. The nitrogen pentoxide adsorbed in the 5-liter reaction flask was thus 25% of the total accounted for nitrogen pentoxide.

Experiment 5.—Although it was not thought that oxygen would be appreciably adsorbed on the glass in the presence of the heavier gases, an experiment was made to determine the magnitude of adsorption effects with pure oxygen. Accordingly about 1.5 cc. of oxygen at 40 mm. was injected into the 5-liter flask, provided with a stopcock as before. After a few minutes' standing at room temperature, the oxygen was pumped out with the Toepler pump. The amount of oxygen obtained was 0.7300 cc. at $p =$ 71.63 mm. and $t = 26.41°$. The additional amount of oxygen obtained by heating the 5-liter flask was $v = 0.7300$ cc. at $p = 2.54$ mm. and $t = 26.41°$. The stopcock at e was then closed, the liquid air was removed from the condensers *j* and *l*, and the condensers were heated with a flame while the adsorbed oxygen was pumped out. An additional amount of oxygen was obtained from the condensers of 0.7300 cc. at $p = 6.71$ mm. and $t = 26.41°$. The oxygen adsorptions might be still smaller in the presence of the heavier gases.

Experiment 6.—In order to furnish a more conclusive demonstration that surface effects were causing the discrepancy, an experiment was made in the same reaction flask in which had been placed, after careful cleaning and drying, about 24 meters of tubing (of Pyrex glass the same as that of the reaction flask) of 3 mm. internal and 5 mm. external diameter, cut into 3.5-cm. lengths. This tubing increased the ratio of surface to volume in the reaction flask from 0.28 to 1.52 or about 5.4-fold.

The nitrogen pentoxide injected into the flask was 1.4 cc. at about 50 mm. The oxygen obtained after seventy-four minutes' decomposition at 30.00" was 0.5217 cc. at $p = 1.55$ mm. and $t = 25.72$". The oxygen from complete decomposition of the nitrogen pentoxide caught in the condensers *j* and 1 was 0.5217 cc. at $p = 3.19$ mm. and t = 25.72" (including the previous amount of oxygen). The reaction velocity constant calculated directly from these data is 9 X 10^{-3}. The total oxygen recovered, however, corresponds to but 4.6% of the amount of nitrogen pentoxide injected into the reaction flask.

Discussion of the Results

Our data show that adsorption and occlusion effects involve a large fraction of the gas present at low pressures. It is likely that surface conditions changed during the course of the experiments and, since they were not well defined, the quantitative reproducibility of surface effects could not be expected. Experiment 6, however, aside from any quantitative data, conclusively shows the large part played by surface effects. Thus, with an increase of roughly 5-fold in the ratio of surface to volume, the amount of nitrogen pentoxide accounted for in our ordinary procedure was at most only about 15% of the usual recovery. We believe that the effect in this experiment is entirely outside of any possible experimental uncertainty.

Because of the conditions mentioned, we considered it inadvisable to attempt further work by this method on the reaction in glass apparatus at very low pressures. Some of the complications involved are the following: the reproduction of surface conditions and the necessary uniform treatment of the surfaces involved, in regard to heating and pumping off adsorbed gases, would be troublesome if not impossible; the measurement of oxygen adsorptions in the presence of nitrogen pentoxide at these temperatures could not well be accomplished; the amount of occlusion doubtless depends not only upon the quantities of gases present, but also on the rate of condensation of the heavy gas; the rate of decomposition of the nitrogen pentoxide which is attached to the walls of the apparatus is not known; and during the time taken to pump out the reaction flask the adsorbed nitrogen pentoxide would be decomposing and contributing an indeterminate amount of oxygen. We have therefore been content to demonstrate the existence of these effects without attempting to estimate quantitatively the true homogeneous rate of the reaction. However, although the application of corrections to the rate on the basis of our data is somewhat arbitrary, it seems likely that a reasonable account of these effects would tend toward giving about the normal rate of decomposition.

Although we do not know how different, if at all, these adsorption and occlusion effects were in the apparatus used by Hirst and Rideal and by Hibben, the presumption is that these effects were present to some degree in their experiments also. Results at these low pressures which do not take account of adsorption and occlusion effects when present we feel are fictitious, and we believe that the information previously obtained on the rate of decomposition of nitrogen pentoxide at very low pressures is open to serious question. Without knowing more of the details of the apparatus and procedure used by the other investigators, we are, of course unable to say in what way, if in any, their results may have been influenced by effects such as we found.

In the light of previous knowledge of adsorption phenomena, it is readily seen why adsorption does not appreciably affect experiments in which comparatively large quantities of gas are used. The nitrogen pentoxide adsorption is evidently that type which, at very low pressures, increases with increasing pressure only up to the point at which the surface becomes completely covered with adsorbed gas. Occlusion effects in any method involving condensation of the heavier gases might be appreciable, even at higher pressures; in fact, our first experiment seems to indicate this.

Summary

1. Objectionable features in previous methods for the study of the decomposition of nitrogen pentoxide at very low pressures have been painted out and the reaction has been studied by a new method.

2. At very low pressures the adsorption of nitrogen pentoxide on the walls of our Pyrex glass apparatus and the occlusion of oxygen as the heavier gases are condensed have been shown to involve a large fraction of the total amount of gas present.

3. It is believed that experiments formerly thought to indicate an increased rate of decomposition of nitrogen pentoxide at low pressures are open to serious question, and that any experiments by the method hitherto used would yield fictitious results when adsorption and occlusion effects are present and not taken into account.

PITTSBURGH, PA.

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 179]

THE PRODUCTS OF THE PHOTOCHEMICAL DECOMPOSITION OF HYDROGEN AZIDE

BY ARNOLD O. BECKMAN AND ROSCOE G. DICKINSON

RECEIVED APRIL 11, 1928 PUBLISHED JULY 6, 1928

Introduction

Since the first preparation of hydrogen azide by Curtius[1] in 1890, this substance and its salts have been the subject of many investigations. The anhydrous material[2] is a moderately volatile (b. p. 37°), colorless liquid. Although the anhydrous liquid is violently explosive, the vapor may be handled at somewhat reduced pressure without difficulty. Since the gas is colorless, visible radiation may be anticipated to be without photochemical effect. However, we have found the gas to be decomposed by ultraviolet radiation of a sufficiently short wave length; the present paper is concerned chiefly with an examination of the products of this decomposition.

We are indebted to Dr. Don M. Yost for his interest in this work. Financial assistance has been received from a grant made to Professor A. A. Noyes by the Carnegie Institution of Washington.

Preparation of Hydrogen Azide

Sodium azide, NaN_3, was purified by acidifying and distilling an aqueous solution of the salt. The aqueous distillate was just neutralized with carbonate free sodium hydroxide and evaporated to dryness.

Gaseous HN_3 was obtained[3] by dropping sulfuric acid (2 vols. concd. H_2SO_4, 1 vol. H_2O) on solid NaN_3. The HN_3 evolved was swept by a current of air (previously passed through a liquid air trap) through a long calcium chloride tube into a trap immersed in liquid air. The generating flask was then sealed off and the trap and a 1-liter storage bulb attached to it were evacuated. The liquid air was then removed, allowing the HN_3 to volatilize into the storage bulb; the HN_3 pressure was about 13 cm. of mercury.

Apparatus and Procedure

A diagram of the apparatus is shown in Fig. 1. The HN_3 was stored in the flask, A. With the aid of two stopcocks, B, small amounts of HN_3 were admitted to the vacuum system; the mercury cut-offs C and D were kept closed when this occurred. The HN_3 was frozen out by applying liquid air at E, and traces of non-condensable gas pumped off. Then with the cut-offs and the McLeod gage closed, the liquid air was removed from E and the gas illuminated in the quartz tube, F, which was joined to the glass apparatus through a graded seal.

The source of radiation was a condensed, high frequency spark between aluminum electrodes, located about 30 cm. from the tube, F. The electrical energy was supplied through a step-up transformer, the primary current being 50–100 amperes[4] at 220 volts,

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[1] Curtius, *Ber.*, 23,3023 (1890).

[2] Curtius and Kadenhausen, *J. prakt. Chem.*, 43,207 (1891).

[3] Dennis and Isham, THIS JOURNAL, 29,216 (1907).

[4] Such an intense source was not essential to the present experiments but was used because it was at hand for other purposes.

50 cycles per second. The secondary voltage was 13,000 volts. A 0.1 mf. condenser was shunted across the spark. The spark was blown out by a blast of air.

At the close of the illumination, liquid air was applied at E or G. The cut-off D was opened and readings were made with the McLeod gage and quartz fiber gage,[5] H. This gage was of the bifilar type[6] and was arranged with the magnetic starting device already described by one of us.[7] Liquid *air* was maintained at the U-tube, J, throughout the experiment. In some cases the condensable constituents were frozen out in one of the bulbs, G, which was then sealed off for analysis.

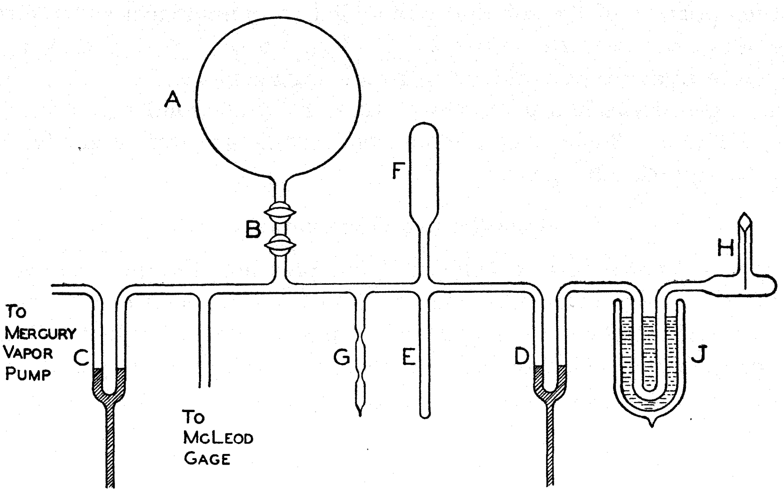

Fig. 1.

Qualitative Observations

It was found that brief illumination of gaseous HN_3 produced a gas non-condensable in liquid air. Somewhat longer illuminations, especially at higher HN_3 pressures (about 5 cm.), produced a white solid on the inside wall of the reaction bulb nearest the spark.

These effects were absent when the radiation was filtered through 5 mm. of 66% acetic acid in a quartz container. The acetic acid removed[8] radiation of wave lengths shorter than 2400 Å. Photographs of the absorption of gaseous HN_3 made with a quartz spectrograph showed that appreciable absorption set in at about 2200 Å. and increased toward shorter wave lengths. Accordingly, short wave length radiation was clearly necessary for the photochemical effects; the important radiation was probably the strong lines at 1854, 1862, 1935 and 1990 Å.

The white solid was volatile, subliming to a cooler portion of the tube when the tube was slightly warmed with a flame; when the tube was

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[5] Haber and Kerschbaum, *Z. Elektrochem.*, 20,296 (1914).

[6] Coolidge, THIS JOURNAL, 45, 1637 (1923).

[7] Beckman, *J. Opt. Soc. Am.*, 16,276 (1928).

[8] Henri, "Études de Photochimie," Paris, Gauthier-Villars, 1919, p. 90.

evacuated the solid quickly disappeared. In one experiment, after some of the solid had been formed, the quartz tube, F, was cut off from the apparatus and a little of the solid removed for examination. The polarizing microscope showed the solid to be composed of small optically anisotropic crystals. The remaining solid quickly dissolved in a small amount of water added to the tube. The solution gave with Nessler's reagent the heavy, yellowish-brown precipitate characteristic of ammonia. Another portion of the solution was added to ammoniacal silver nitrate; there was no trace of a mirror or a coloration on heating, showing the absence of hydrazine or other strong reducing agent.

These properties and tests showed that the white solid was ammonium azide, NH_4N_3. Analyses of the non-condensable gas were made with the aid of the quartz fiber gage.

Quantitative Observations

It is well known that at sufficiently low pressures the quartz fiber gage can be used to measure the value of $\Sigma(p\sqrt{M})$, the sum of the products of the partial pressures of the separate components of the gas into the square roots of their molecular weights. Indeed, if τ is the time required for the amplitude of the vibrations to decrease by some definite fraction of its value,[5]

$$\frac{1}{\tau} = a\,\Sigma(p\sqrt{M}) + b \tag{1}$$

where a and b are apparatus constants.

Since, in the present case, the non-condensable gas can contain only nitrogen and hydrogen, we may write

$$\Sigma(p\sqrt{M}) = x(\Sigma p)\,\sqrt{M_{H_2}} + (1 - x)\,(\Sigma p)\,\sqrt{M_{N_2}} \tag{2}$$

where x is the mole fraction of hydrogen and M_{H_2} and M_{N_2} are the molecular weights of hydrogen and nitrogen, respectively. Solution of this equation for x gives[9]

$$x = \frac{\sqrt{M_{N_2}} - \dfrac{\Sigma(p\sqrt{M})}{\Sigma p}}{\sqrt{M_{N_2}} - \sqrt{M_{H_2}}}$$

Measurement of $\Sigma(p\sqrt{M})$ with the fiber gage, and of Σp with the McLeod gage then permits the calculation of x.

The gage was calibrated with air, nitrogen and hydrogen. The calibration plot of $1/\tau$ *vs.* $\Sigma(p\sqrt{M})$ was a straight line at pressures below 2×10^{-2} mm. When the products had higher pressures, a portion was confined (for example in the McLeod gage) and was expanded after the remainder had been pumped off. The gage was tested as an analytical instrument by making measurements of the mole fraction of hydrogen in

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[9] Dickinson and Mitchell, Proc. Nat. *Acad.*, *12*, 694 (1926).

hydrogen–nitrogen mixtures made up to a known composition. The results of these tests are given in Table I.

TABLE I

ANALYSIS OF KNOWN MIXTURES OF HYDROGEN AND NITROGEN

Σp, mm.	$\Sigma(p\sqrt{M})$	x_{H_2}, by analysis	x_{H_2}, by synthesis	A
0.935×10^{-2}	4.60×10^{-2}	0.098	0.093	+0.005
.987	4.69	.139	.142	− .003
.625	2.82	.219	.218	+ .001
1.371	3.30	.746	.760	− .014

Analyses of the non-condensable gas resulting from illumination of HN_3 showed 10 to 15 mole per cent. of H_2. There are several possible ways in which H_2 and N_2 as well as NH_4N_3 might result: (1) decomposition of HN_3 into NH_4N_3 and N_2, and subsequent decomposition of NH_4N_3 (or NH_3) into N_2 and H_2; (2) decomposition of HN_3, giving simultaneously NH_4N_3, N_2 and H_2; (3) decomposition of HN_3 into N_2 and H_2 and subsequent formation of NH_3 (as, for example, by $H_2 + HN_3$ (activated) $= NH_3 + N_2$). Experiments in which sufficiently little decomposition is allowed to take place should in case (1) lead to $x_{H_2} \cong 0$, in case (3) to $x_{H_2} \cong 0.25$ and to intermediate values in case (2).

A series of exposures was made in which the time of illumination and the pressure of HN_3 were chosen to give amounts of products covering a wide range. The results are given in Table II.

TABLE II

DEPENDENCE OF COMPOSITION OF PRODUCTS ON EXTENT OF DECOMPOSITION

p_{HN_3}, mm.	Time, sec.	$p_{H_2+N_2}$, mm.	x_{H_2}
1.5	25	3.21×10^{-2}	0.091
12	7	5.37	.098
12	10	6.42	.091
29	56	32.1	.112
16	90	54.6	.147
7.5	240	62.0	.136
18	90	64.9	.153

Although the amount of non-condensable products was varied 20-fold, there appears to be no tendency for x_{H_2} to approach either 0 or 0.25 at zero decomposition. It is concluded, therefore, that the formation of N_2 and H_2 and of NH_4N_3 occurs simultaneously (case (2)). Since the mole fraction of H_2 is increased somewhat by prolongation of exposure, it appears that subsequent decomposition of NH_4N_3 or NH_3 occurs. NH_3 is known[10] to be photochemically decomposed by radiations of the wave lengths 2025–2139 Å.

Since, in the decomposition products, the total number of gram atoms of nitrogen must be three times the total number of gram atoms of hy-

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[10] Warburg, *Sitzb. preuss. Akad. Wiss.*, **1912**, p. 216.

drogen, the amount of ammonia in the products can be predicted from the amounts of nitrogen and hydrogen if no other products are formed. The number of moles of ammonia expected to be finally present can be easily shown to be given by

$$N_{NH_3} = \frac{pv}{4\,RT}(1 - 4x_{H_2})$$

where p, v and T are the total pressure, volume and temperature of the nitrogen–hydrogen mixture. A determination of the amount of ammonia formed was made at the end of each of three illuminations. For this purpose the liquid air was applied, not at E but at the end of the chain of bulbs, G, the last of which was then sealed off. This bulb was dipped in liquid air and its tip then broken under ammonia free water, the water rushing in and filling the bulb. By then breaking the tip at the other end of the bulb, the contents were transferred to a 2cc. colorimeter tube containing 1 cc. of Nessler's reagent. The same amount of Nessler's reagent was added to each of two other colorimeter tubes and these were made up with measured amounts of **0.000474** M NH_4Cl solution to colors which approximated and bracketed the color of the unknown. The results are given in Table III.

TABLE III

COMPARISON OF AMOUNTS OF NH_3 EXPECTED AND FOUND

$p_{H_2} + p_{N_2}$ (mm. Hg)	v, cc.	x_{H_2}	NH_4Cl soln., cc.	N_{NH_3} calcd. micromoles	N_{NH_3} found, micromoles
0.0617	476.5	0.1122	0.511	0.219	0.242
.1054	478	.1532	.666	.317	.315
.1214	480	.1365	.740	.358	.351

The number of moles of NH3 calculated from the composition of the non-condensable gas and the number found by colorimetric analysis agree well within the error of the latter determination; hence it appears unlikely that any products other than H_2, N_2 and NH_3 are iormed in considerable amount. The mole fraction of hydrogen, 0.09, in the non-condensable gas initially produced (Table II) corresponds stoichiometrically to **73%** decomposition of the HN_3 into NH_3 and N_2 and 27% into H_2 and N_2.

The Molecular Weight of Hydrogen Azide

In the literature, the conclusion that hydrogen azide vapor consists of unassociated HN_3 molecules appears to be based upon a single vapor density determination by the Victor Meyer method at the boiling point of chloroform.[3] In extension of this result, we have made several molecular weight determinations by means of the quartz fiber[11] and McLeod gages.

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[11] **A new fiber gage was used in these measurements. It differed from the first only in having a** *single* **flat fiber** *4* **cm. long and was found entirely satisfactory. A single fiber with elliptical cross section has been used by Coehn and Jung,** *Z. physik. Chem., 110,* **709 (1924).**

The hydrogen azide was admitted in the usual manner. It was then pumped down to a pressure of about 0.02 mm. The trap, J, was packed in ice and readings of the two gages were made. From the value $\Sigma(p\sqrt{M})$ obtained from the fiber gage was subtracted 0.0030 mm. corresponding to the $p\sqrt{M}$ of the mercury vapor present. The remainder, divided by the pressure, as read on the McLeod gage, gave $\sqrt{M}$. The results are given in Table IV.

TABLE IV

MOLECULAR WEIGHT OB GASEOUS HN_3

p (mm. X 10^2) (McLeod)	$\Sigma(p\sqrt{M}) \times 10^2$ (Quartz fiber)	M	Dev. from av.
2.26	15.46	44.9	1.3
2.00	12.90	39.7	3.9
1.47	9.96	43.3	0.3
1.24	8.75	46.5	2.9
		Av. 43 6	2.1

Summary

Gaseous hydrogen azide has been found to be decomposed by ultraviolet radiation from an aluminum spark, giving hydrogen, nitrogen and ammonia (ammonium azide). These products are formed by concurrent reactions; on brief illumination 27% of the decomposition gives H_2 and N_2 and 73% gives NH3 and N_2.

By means of the quartz fiber and McLeod gages, the molecular weight of hydrogen azide has been determined as 43.6 ± 2.1.

PASADENA, CALIBORNIA

THE SPECIFIC HEATS AT LOW TEMPERATURES OF MANGANOUS OXIDE, MANGANOUS-MANGANIC OXIDE AND MANGANESE DIOXIDE[1]

BY RUSSELL W. MILLAR[2]

RECEIVED APRIL 13, 1928 PUBLISHED JULY 6, 1928

The present article is one of a series from this Laboratory dealing with the thermodynamic properties of the oxides of metals which are important in metallurgical processes. Preceding articles have dealt with zinc oxide,[3] but it is now proposed to extend the investigations to many other oxides, as well as to several sulfides.

The specific heats of the oxides of manganese so far determined have been confined, with the exception of those of Russell[4] at low temperatures,

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[1] Published by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.)

[2] Associate Chemist, Pacific Experiment Station, Bureau of Mines.

[3] (a) Maier, THIS JOURNAL, 48, 356 (1926); (b) Maier and Ralston, *ibid.*, 48, 364 (1926); (c) Maier, Parks and Anderson, *ibid.*, 48,2564 (1926).

[4] Russell, *Physik. Z.*, 13, 59 (1912).

to the measurements of Regnault[5] and Kopp[6] at slightly above room temperature. The previous results are summarized in Table I.

TABLE I

THE MOLAL HEAT CAPACITY OF MnO AND MnO_2

Substance	t, °C.	C_p	Investigator
MnO	13–98	11.14	Regnault
MnO_2	−187–78.0	8.50	Russell
MnO_2	−78.2–0	12.23	Russell
MnO_2	2 448.3	14.27	Russell
MnO_2	1748	13.8	Kopp

The method of the present investigation was that originally used by Eucken[7] in Nernst's laboratory, and has since been adopted by almost all investigators in this field.

The apparatus differed but little from that of Gibson and Giauque,[8] who improved considerably on the original design. Changes, however, were made, some of which have been described by Giauque, Buffington and Schulze.[9] The vacuum jacket, 10 by 25 cm. in size, was of brass tubing with walls 3 mm. thick. The cover, which was of brass 13 mm. thick, was soldered onto the jacket. The heavy protecting shield was of lead poured between concentric copper tubes. The wall of the outer tube was made 6 mm. thick, in order to distribute rapidly the heat generated in a coil of constantan wire wound in grooves on the outer surface. A copper sheath protected the shield from radiation. The protecting shield, with its cover, weighed 8 kilograms.

The cover of the shield, of 2.5cm. copper sheet, was secured by machine screws. In it were Bakelite conduits through which passed the wires leading to the calorimeter. Each wire, before passing through the cover, was soldered to one end of a strip of thin copper clamped by a screw to the cover but insulated from it by very thin mica. Beat passing down the wire thus found its way to the shield of high heat capacity instead of to the calorimeter.

The calorimeter, of copper tubing 3.7 by 13 cm., was wound with about 260 feet of No. 40 B. & S. gage double silk covered copper wire, which served as both thermometer and heating coil. Additional insulation and thermal contact were obtained with Bakelite varnish. The calorimeter was protected from radiation by a sheath of copper, 0.025 mm. in thickness, which was stuck on by Bakelite varnish. Rapid distribution of heat was obtained by means of sheets of 0.13mm. copper, parallel to each other and to the axis of the calorimeter, which were soldered at their edges to the inner wall. Since these sheets were spaced at 3 mm. and the voids between the particles of the sample were filled with hydrogen, the distribution of heat was so rapid that thermal equilibrium was obtained in three to ten minutes. The volume of the calorimeter was 130 cc., the weight, 115g.

With respect to the vacuum system and the electrical wiring, the apparatus was similar to that of Gibson and Giauque. Electrical measurements were made with a White double potentiometer and time measurements with an accurately calibrated stop watch.

The copper resistance thermometer was calibrated during the specific heat determinations for each substance by means of a single junction copper–constantan thermocouple soldered to the bottom of the calorimeter. This thermocouple was made of wire

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[5] Regnault, Ann. *chim. phys.*, [3] 1,129 (1841).

[6] Kopp, *Phil.* Trans., [1] 155, 71 (1865).

[7] Eucken, *Physik. Z.*, 10, 586 (1909).

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

[9] Giauque, Buffington and Schulze, *ibid.*, **49**, **2343** (1927).

from the same spool as thermocouple No. 17 of Giauque, Buffington and Schulze.[9] This thermocouple was compared with No. 17 through a secondary standard, and No. 17 was itself compared by Giauque, Buffington and Schulze with the hydrogen gas thermometer, and with the hydrogen and oxygen vapor pressure thermometers by Giauque, Johnston and Kelley.[10]

The correction for the exchange of heat between the calorimeter and its surroundings was made by the assumption of Newton's law of cooling. The small correction for the difference in temperature between the thermometer wire and the average temperature of the calorimeter described by Giauque and Wiebe[11] was calculated and applied. At room temperature this correction often amounts to as much as 1% and occasionally 2%, but at liquid air temperatures only about 0.1% correction is necessary on this account. The effect of the correction is to lower the calculated value of the specific heat.

Materials.—Manganous–manganic oxide was prepared by igniting a good grade of C. P. manganous sulfate in platinum at 1100°. The sample was heated for a week, pulverized and heated again as before. It was then heated in a current of gaseous hydrochloric acid according to St. Clair-Deville;[12] nitrogen was passed over the hot crystals for three hours to displace the hydrochloric acid, and the product was cooled. The product was finely crystalline. The preparation showed 1.006 times the oxidizing power of pure manganous–manganic oxide toward oxalic acid. Although Meyer and Rötgers[13] state that oxidation of manganous–manganic oxide prepared by the ignition of manganese dioxide does not occur in air, possibly under the conditions of the present test this particular sample combined with the small amount of oxygen in the nitrogen.

Manganous oxide was prepared by reduction of amorphous manganous–manganic oxide by hydrogen and crystallization by gaseous hydrochloric acid. A finely crystalline, bright green product resulted. This product showed no oxidizing power toward oxalic acid but the total manganese determined by oxidation to manganese dioxide with standard potassium permanganate corresponded to only 99.0% manganous oxide. Correction was made in the specific heats for the impurity, which consisted of small flakes of silica from the wall of the preparation flask.

Manganese dioxide was prepared by heating the nitrate at 170° until the evolution of the oxides of nitrogen had ceased. The product was 99.6% manganese dioxide.

The results are given in Tables II–V.

TABLE II

THE HEAT CAPACITY PER GRAM MOLECULE OR MnO

Run no.	T, °K	C_p	Run no	T, °K.	C_p	Run no.	T, °K.	C_p	Run no.	T, °K	C_p	Run no.	T, °K.	C_p
1	70 4	4.426	9	116.5	17 65	17	111.0	10.53	25	116 2	23.96	33	203.3	9.173
2	74.3	4 869	10	118 9	7.530	18	112.0	10 98	26	117 1	7.837	34	217.5	9.462
3	82.1	5.650	11	92 1	6 797	19	113 0	11 71	27	...	....	35	229.7	9.592
4	88.5	6.348	12	96.5	7 362	20	113 9	12 50	28	128 6	7.482	36	247.1	9.728
5	109.1	9.829	13	98 9	7 757	21	114 8	13 78	29	143.3	7.793	37	272.9	9.992
6	118.5	7.564	14	104.8	8.769	22	1155	2370	30	155.6	8 124	38	289.1	10.16
7	126.8	7.470	15	108 8	9 664	23	115 7	67.68	31	178.0	8.625	39	293.7	10.26
8	134.5	7593	16	1099	10.13	24	1159	107.56	32	189.7	8927	40	300.2	10.30

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[10] Giauque, Johnston and Kelley, THIS JOURNAL, 49,2367 (1927). The author takes this occasion to express his gratitude to Professor Giauque for his kindness in furnishing him with the temperature scale and for many suggestions during the progress of the measurements.

[11] Giauque and Wiebe, THIS JOURNAL, 50,101 (1928).

[12] St. Clair-Deville, *Compt. rend.*, 53, 199 (1861).

[13] Meyer and Rotgers, *Z. anorg. allgem. Chem.*, 57, 104 (1908).

TABLE III

THE HEAT ABSORPTION PER MOLE, AH, BETWEEN T_1 AND T_2 FOR MnO

Run no.	T_1	T_2	AH	Run no.	T_1	T_2	AH
9	115 810	117.109	22.93	22	115.152	115.647	11.73
17	110.488	111.533	11.01	23	115.644	115.830	12.61
18	111538	112.533	1093	24	115 823	115.942	12 80
19	112.544	113.476	10.91	25	115.943	116.429	11.64
20	113.485	114357	10.90	27	109.937	121.207	147.17
21	114.315	115161	10.97				

TABLE IV

THE HEAT CAPACITY PER GRAM MOLECULE OF Mn_3O_4

Run no.	T, °K.	C_p	Run no.	T, °K.	C_p
1	72.2	9.725	14	188.0	26.26
2	76.0	10.46	15	199.1	27.34
3	85.5	12.11	16	200.4	27.37
4	95.6	13.68	17	209.4	28.23
5	103 6	15.02	18	220.0	28.75
6	111.9	16.45	19	233.2	30.15
7	121.5	18.02	20	241.4	30.69
8	129.8	19.25	21	252.5	31.28
9	138.2	20.29	22	263.1	32.07
10	151.9	22.14	23	271.5	32.45
11	160.0	23.08	24	283.4	32.76
12	167.4	23.97	25	295.3	33.35
13	177.6	25.11	26	305.2	33 46

TABLE V

THE HEAT CAPACITY PER GRAM MOLECULE, C_p, OF MnO_2

Run no.	T, °K.	C_p	Run no.	T, °K.	C_p	Run no.	T, °K.	C_p
1	956	6.406	14	72.8	3.901	26[a]	...	...
2	97.4	6.193	15	748	4.151	27	2219	1124
3	107.2	5.847	16	767	4.372	28	2366	11.70
4	90 2	7 262	17	78 8	4.619	29	249.8	12.19
5	1154	6.285	18	81.1	4.994	30	72.5	3.875
6	119.7	6 514	19	83.4	5.370	31	74.6	4.114
7	130.2	7.006	20	86.0	5849	32	91.8	8.510
8	139.6	7.494	21	883	6.450	33	92.5	9.034
9	148 8	7.996	22	90.3	7.343	34	93.2	8.667
10	166.9	8869	23	92.9	8 658	35	93.9	7.810
11	179 3	9 453	24	93.7	8.140	36	292.6	13.60
12	188.7	9.872	25	95.4	6.549	37	293.8	13.53
13	199.5	10.35						

[a] **Run No.** 26. **Heat absorption between** 87.743°K. **and** 98.437°K. = 76.35 **cal./mole.**

The figure accompanying this text displays the results for all three oxides. Table III shows the heat input for the points which fall on the steep slopes of the specific heat curve for manganous oxide, and the initial and final temperatures. Obviously the curve rises so rapidly that the recorded heat capacities at the average temperatures are not valid and cannot be plotted; in the figure they are used only to indicate the course of the curve.

No reason can be given for the discontinuities in the curves for manganous oxide and manganese dioxide. Although it might be suspected that the maximum in the curve for manganese dioxide was due to an impurity of the manganous oxide, this could not have been true, since Meyer and Rötgers[13] found that manganese dioxide was stable in air at 530°, and the sample used here was heated only to 170°. Furthermore, manganous–manganic oxide is certainly stable at 1100°, and the curve for this substance showed no discontinuity in the temperature range of the experiments.

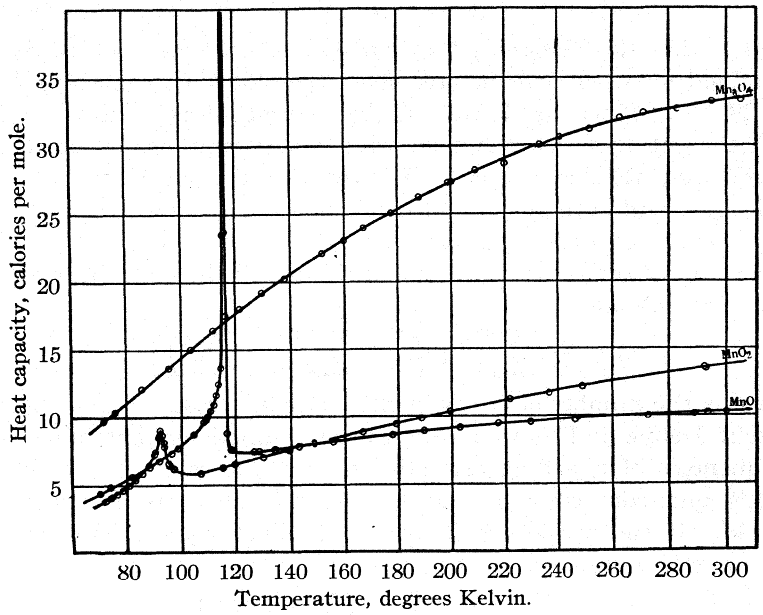

Fig. 1.—The molal heat capacities of MnO, Mn_3O_4 and MnO_2.

Attention should be called to the fact that points on the steep portions of the curves for manganous oxide and manganese dioxide are perfectly reproducible and that the specific heats in the regions of the discontinuities are independent of the history of the substance. Thus, in Table II we note that a continuous series of runs extended from 70.4°K. to 134.5°K., and that the sample was cooled to about 116°K., where two runs were made. The sample was then allowed to come to room temperature, cooled to 92°K. and a continuous series of runs was made from that temperature to room temperature. An examination of Table V shows that the sample was cooled to liquid air temperatures three times—for runs 1, 14 and 30—but that the points obtained near 97°K. fall on the same smooth curve independently of the history of the substance.

Ewald[14] found that ammonium chloride had a higher specific heat between −80 and 0° than between 0 and 50°, but dilatometric measurements in the lower range failed to reveal a volume change. Simon[15] has measured the true specific heat of this salt and found at 242.6°K. a change greatly resembling that of manganous oxide. Parks and Kelley[16] measured the heat effect for a similar change in magnetite at 115°K. Measurements in this Laboratory, soon to be published, show the curve for magnetite to be similar to that of manganous oxide.

In order to calculate the entropy at 298°K., it is necessary to integrate graphically the equation

$$\int \mathrm{d}S = \int C_p \, \mathrm{d} \ln T$$

from 0 to 298°K. Assuming the third law of thermodynamics, $S_0 = 0$, it remained for us to find the area under the plot of C_p against ln T from 0 to 298°K. Since the lowest of the present measurements is about 70°K., the extrapolation was made with the assumption that at very low temperatures, that is, about 30°K., the equation of Debye gives the specific heat and entropy. In all that follows, the teferences are to plots of log T as abscissa and C_p as ordinate.

According to the theory of Born and Kármán,[17] the molal heat capacity at constant volume

$$C_v = \frac{1}{3P}\left[\sum_1^3 D\left(\frac{\beta v_i}{T}\right) + \sum_{j=1}^{3(p-1)} E\left(\frac{\beta v_j}{T}\right)\right] \qquad (1)$$

where p is the number of atoms in the molecule, $D(\beta v_i/T)$ and $E(\beta v_j/T)$ represent Debye and Einstein heat capacity functions containing values of frequencies of v_i and v_j, respectively; β is the ratio h/k, where h is Planck's quantum constant and k is Boltzmann's gas constant for 1 molecule. If the frequencies in the three directions are assumed to be the same, the equation reduces to

$$C_v = \frac{1}{p}\left[D\left(\frac{\beta v}{T}\right) + \sum_{j=1}^{p-1} E\left(\frac{\beta v_j}{T}\right)\right] \qquad (2)$$

These equations may be expected to hold only at low temperatures; for the substances for which data are shown here, Equation 2 holds only to about 150°K., and it is not expected that Equation 1 will hold at temperatures much higher. No attempts were made to use Equation 1. At very low temperatures the Einstein terms disappear and the heat capacity is represented solely by the Debye terms.

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[14] Ewald, Ann. *Physik,* [4] 44, 1213 (1914).

[15] Simon, *ibid.,* [4] 68, 241 (1922).

[16] Parks and Kelley, *J. Phys. Chem.,* 30, 47 (1926).

[17] Born and Kármán, *Physik. Z.,* 13, 297 (1912); 14, 15, 65 (1913); Born, "Dynamik der Kristallgitter," Teubner, Leipzig and Berlin, 1915.

According to Equation 2 the heat capacity per mole of manganous oxide should be represented by the sum of one Debye and one Einstein function. It was found that the experimental curve (C_p – log T coördinates), extending down to only 70.4°K., could be extrapolated to meet, without an abrupt change of direction, the Debye function of frequency $\beta v = 231$. A curve was then drawn representing the probable course of the curve without discontinuity, and the differences between this curve and the Debye function were plotted. As high as 178°K. these differences could be represented, within the accuracy of the experimental data, by an Einstein function of frequency $\beta v = 502$. Above 178°K. the differences fell below the Einstein curve, instead of above it, as we should expect, since C_p and not C_v was measured. In reality, the values of C_v, if the necessary data for the calculation from C_p were available, would probably not fit the theoretical curves above 150°K.

The entropy at 35.48°K., as given by the Debye function, is 0.514. The area under the curve and its extrapolation to 35.48°K. between this temperature and 298°K. amounts to 14.406. We have, for MnO, $S_{298} = 14.92$ cal./deg.

For manganous–manganic oxide we should have $C_v = D(\beta v_i/T) + 6E(\beta v_j/T)$, where v_j may have the same or different values for the six terms. It was found convenient, however, to represent the data by three Debye and four Einstein functions, using values of $\beta v = 278$ and 611, respectively. The agreement with the data was excellent up to 158°K., and with true values of C_v probably up to 140°K. The Debye entropy below 31.62°K. is 0.704, and the remainder below 298°K. is 35.022. We have for Mn_3O_4, $S_{298} = 35.73$ cal./deg.

For manganese dioxide one Debye function with $\beta v = 268$ and two Einstein functions with $\beta v = 653$ fit the data to 140°K. The Debye entropy below 31.62°K. is 0.257 and the remainder below 298°K. is 13.677. For MnO_2, $S_{298} = 13.93$ cal./deg.

In each extrapolation it was found that even though the Debye curve were shifted along the axis of abscissas to positions so unreasonable that sharp breaks were necessary to join it with the experimental curve, such shifting of the Debye curve did not change the entropy at 298°K. more than 0.1 unit. Simon[15] has shown that it is possible, in fitting theoretical curves to the experimental data on complicated substances, to obtain satisfactory combinations other than those demanded by the Born-Kármán theory, and even to fit the values of C_p rather than those of C_v.

The free energies were calculated from the equation

$$AF = AH - TAS$$

where AF is the change in free energy in forming the oxide from its elements, AH the heat of formation and AS the change in entropy, all at the temperature T.

In order to calculate the entropy of formation, the entropy of oxygen at 298°K. must be known. The calculations of Lewis, Gibson and Latimer[18] give for O_2, $S_{298} = 48.0$ as the weighted mean of 3 values—namely, from Eucken's[19] specific heats and heats of transition of the several forms of oxygen and the third law of thermodynamics, they give Lewis and Gibson's[20] calculation of O_2, $S_{298} = 48.23$; from the data for the reaction $C_G + {}^1/_2O_2 = CO$, they give for O_2, $S_{298} = 45.6$; from the entropy of mercuric oxide and mercury and the entropy change in the formation of mercuric oxide from its elements, they give for O_2, $S_{298} = 49.2$.

Giauque and Johnston,[21] who have recently repeated very accurately the work of Eucken on oxygen, have given 40.8 as a preliminary value of the entropy per mole of oxygen at its boiling point. Millar and Sullivan[22] have calculated, from the data of Scheel and Heuse,[23] the increase in entropy of gaseous oxygen at 1 atm., when heated from the boiling point to 298°K., to be 8.36. The sum, 49.16, agrees almost exactly with the result of Lewis, Gibson and Latimer obtained from the entropy change of the reaction $Hg + {}^1/_2O_2 = HgO$. The value chosen for O_2 is $S_{298} = 49.2$.

The entropy of manganese, $S_{298} = 7.3$, is taken from Lewis and Gibson.[20]

The heats of formation of these oxides have been determined by both Berthelot[24] and LeChatelier[25] with much better agreement than is usual with data of this kind. For manganous oxide Berthelot gives 90,900 cal.; LeChatelier, 90,800. For manganous–manganic oxide both give 328,000, while Ruff and Gersten[26] give 329,000 ± 740. For manganese dioxide Berthelot gives 125,300 and LeChatelier 126,000, while Mixter[27] gives 119,600 cal., but he states that this value is only an approximation, and that LeChatelier, who used pure natural pyrolusite, probably gives a more accurate value for crystalline manganese dioxide. Although the manganese dioxide used in the present investigation was similar to that used by Mixter, Berthelot's value will be used because of errors in Mixter's work which he himself points out.

Table VI exhibits the data used and the resulting values of the free energy of formation of the oxides.

It is hoped that the specific heats necessary to extend these calculations of the free energies of formation to high temperatures will some day be available.

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[18] Lewis, Gibson and Latimer, THIS JOURNAL, 44, 1008 (1922).

[19] Eucken, *Ber. deut. physik. Ges.*, 18, 4 (1916).

[20] Lewis and Gibson, THIS JOURNAL, 39, 2554 (1917).

[21] Giauque and Johnston, personal communication.

[22] Millar and Sullivan, *Bur. of Mines Tech. Paper, No. 424*, 1928.

[23] Scheel and Heuse, *Ann. Physik*, [4] 37, 79 (1912).

[24] Berthelot, "Thermochimie," Vol. II, Gauthier-Villars et Fils, Paris, 1897.

[25] LeChatelier, *Compt. rend.*, 122, 80 (1896).

[26] Ruff and Gersten, *Ber.*, 46, 400 (1913).

[27] Mixter, *Am. J. Sci.*, [4] 30, 193 (1910).

TABLE VI

DATA AND VALUES

Substance	Mn	O_2	MnO	Mn_3O_4	MnO_2
S_{298}	7.3	49.2	14.92	35.73	13.93

Reaction	ΔH	AS	ΔF
$Mn + {}^1/_2O_2 = MnO$	−90,900	−17 0	− 85,830
$3Mn + 202 = Mn_3O_4$	−328,000	−84.6	−302,800
$Mn + O_2 = MnO_2$	−125,300	−42 6	−112,600

Summary

The specific heats of manganous and manganous–manganic oxides and of manganese dioxide have been measured from 70 to 300°K.

With the aid of the third law of thermodynamics, the free energies of these substances at 298° K. have been calculated.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PRINCETON UNIVERSITY]

THE DIELECTRIC POLARIZATION OF LIQUIDS. III. THE POLARIZATION OF THE ISOMERS OF HEPTANE

BY C. P. SMYTH AND W. N. STOOPS

RECEIVED APRIL 14, 1928 PUBLISHED JULY 6, 1928

Accurate measurements of the dielectric constants of methane, ethane and hexane over a wide range of temperature[1] have made it possible to calculate that the molecules of these substances have no electric moments and calculations made by an approximate method have also indicated the, absence of an electric doublet in the molecules of octane and decane.[2] This is in accord with the fact that, according to calculations from molecular structure,[2] it should be possible to replace a hydrogen atom attached to a carbon atom by a methyl group without altering the electric symmetry of the molecule unless the bulk of the methyl group causes distortion of the structure or unless the methyl group itself is distorted due to small shifts of electrons in the field of a doublet already present. Since, with the exception of methane which, as the first member of the series, might be expected to be abnormal, all of the hydrocarbons studied had contained an even number of carbon atoms, it seemed desirable to investigate an odd member of the series, which, of course, would contain an even number of C–C bonds. Measurements made upon pure samples of all of the isomers of heptane very kindly loaned to us by Dr. Graham Edgar of the Ethyl Gasoline Corporation have made it possible to determine the electric symmetry of nine different arrangements of six C–C bonds. An octane, 2,2,4-trimethylpentane, loaned by Dr. Edgar, has also been studied.

[1] (a) Sanger, *Physik. Z.*, 27, 556 (1926); (b) Smyth and Zahn, THIS JOURNAL, 47,2501 (1925); (c) Smyth and Morgan, *ibid.*, 50,1547 (1928).

[2] Smyth, THIS JOURNAL, 46,2151 (1924).

In the first of this series of papers[3] the method of obtaining the electric moment of the molecule of a substance has been discussed. The molar polarization of a substance, $P = (\epsilon-1)/(\epsilon + 2) \times M/d = P_E + P_A + P_M$, in which ϵ = the dielectric constant, M = the molecular weight, d = the density, $P_E + P_A$ = the polarization due to shifts of charges in the molecule inducible by an external field and P_M = the polarization due to the orientation of the permanent electric doublets of the molecules. When P_M is 0, the moment of the molecule must be 0. P_E may be calculated as the molar refraction for light of infinite wave length, MR, = $(1-\lambda_0^2/\lambda^2)[(n^2-1)/(n^2 + 2) \times M/d]$, where n is the index of refraction for light of wave length λ and λ_0 is the wave length corresponding to a characteristic vibration frequency in the ultraviolet region. P_A, the difference between P_E, the polarization due to electronic shifts, and the total induced polarization, is commonly attributed to induced shifts of atoms or radicals.

The refractive indices were measured by Mr. E. W. Engel with the assistance of one of the writers. A Pulfrich refractometer was used and accurate temperature control was obtained by a flow of water from carefully regulated thermostats. A complete series of measurements was made for the sodium D line. A month later, after readjustment of the instrument and installation of a new prism, measurements were made again for the D line and also for the α, β and γ hydrogen lines. The new values for the D line showed an average difference from the old values of only 0.00009, the sign of the difference being disregarded. The molar refractions for the different wave lengths are given in Table I, with the refractive[4] indices. These molar refractions were used to calculate the values of MR_∞, given in Table IV as P_E, by the substitution of the corresponding values of MR and X. As four equations were thus obtained for each substance and only two were necessary in order to solve for MR,, a test of the equation and the data was made by calculating MR, first from MR, and MR, and then from MR_β and MR_D. Although this method of combining the values is the one best calculated to make any error apparent, the greatest difference found between the values obtained from the two pairs of refractions was 0.02. The dispersions calculated from these data are given in Table IV.

The densities and dielectric constants were measured with the apparatus described in the first two papers of this series,[1c,3] the dielectric constant of the benzene used in calibrating the condenser being taken as 2.279 at 25°. Measurements were made upon three heptanes of markedly different structure and upon the octane, 2,2,4-trimethylpentane, over the entire range of temperature within which they were liquid. The dielectric constants were measured at intervals of about 15° and the densities at intervals of about 20°. As the temperatures were not the same for different

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[3] Smyth, Morgan and Boyce, THIS JOURNAL, 50, 1536 (1928).

Table I

Refractive Indices and Molar Refractions at 20°

	n_γ	n_β		n_α	MR_γ	MR_β	MR_D	MR_α
2'2-Dimethylpentane	1.39106	1.38710	1.38233	1.38038	35.32	35.00	34.61	34.46
2,4-Dimethylpentane	1.39097	1.38702	1.38233	1.38042	35.27	34 95	34.57	34.42
2-Methylhexane	1.39377	1.38983	138509	1.38311	35 26	34.95	34.57	34 41
n-Heptane	1.39646	1.39248	1 38777	1.38579	35.23	34 91	34.54	34.39
3-Methylhexane	1.39744	1.39343	1.38873	138677	35.13	34.82	34.45	34.30
2,2,3-Trimethylbutane	1.39817	1.39419	1.38940	1.38744	35.08	34.77	34.39	34.24
3,3-Dimethylpentane	1.39987	1.39589	1.39114	1.38918	35.00	34.69	34.32	34.17
2,3-Dimethylpentane	1.40071	1.39675	1.39201	1.39005	34.98	34.67	34.31	34.15
3-Ethylpentane	1.40232	1.39839	1.39366	1.39169	34.92	34.61	34.25	34.10
2,2,4-Trimethylpentane	1.40074	1,39649	1.39163	1,38962	40.07	39.69	39.25	39.08

measurements and as the values varied uniformly with temperature, the data were interpolated at 10° temperature intervals. These results for the dielectric constant and density, together with the values of the molar po-

Table II

Dielectric Constants, Densities and Polarizations of Three Heptanes

	n-Heptane			2,2-Dimethylpentane			3-Ethylpentane		
t, °C.	ϵ	d	P	ϵ	d	P	ϵ	d	P
−120	...	...	...	2.120	0.7926	34.32	...	...	...
110	...	...	...	2.106	.7841	34.40	2.132	0.8079	33.95
100	...	...	...	2.091	.7757	34.42	2.118	.7995	34.00
90	2.083	0.7752	34.25	2.076	.7670	34.48	2.102	.7912	34.00
80	2.069	.7670	34.27	2.062	.7588	34.51	2.089	.7831	34.05
70	2.055	.7587	34.31	2.047	.7502	34.53	2.075	.7749	34.08
60	2.041	.7501	34.38	2.033	.7418	34.57	2.060	.7666	34.10
50	2.027	.7420	34.41	2.018	.7333	34.59	2.045	.7582	34.11
40	2.013	.7337	34.44	2.004	.7249	34.62	2.029	.7499	34.10
30	1.999	.7252	34.48	1.989	.7162	34.64	2.014	.7419	34.09
20	1.986	.7170	34.53	1.975	.7077	34.68	2.000	.7335	34.12
−10	1.972	.7088	34.55	1.960	.6993	34.70	1.985	.7251	34.13
0	1.958	.7004	34.60	1.945	.6908	34.72	1.971	.7160	34.19
+10	1.944	.6921	34.62	1.930	.6823	34.73	1.956	.7075	34.20
20	1.930	.6838	34.64	1.915	.6738	34.73	1.942	.6988	34.24
30	1.916	.6755	34.65	1.901	.6652	34.76	1.927	.6900	34.26
40	1.903	.6667	34.72	1.887	.6564	34.79	1.913	.6812	34.30
50	1.888	.6575	34.78	1.872	.6477	34.81	1.899	.6724	34.34
60	1.873	.6483	34.80	1.857	.6390	34.82	1.885	.6634	34.38
70	1.858	.6392	34.84	1.843	.6301	34.86	1.870	.6540	34.42
80	1.842	.6300	34.83	1.828	.6215	34.85	1.855	.6442	34.47
+90	1.825	.6208	34.79	...	...	...	1.840	.6340	34.55

TABLE III

DIELECTRIC CONSTANTS, DENSITIES, AND POLARIZATIONS OF 2,2,4-TRIMETHYLPENTANE

t, °C.	ϵ	d	P	t, °C.	ϵ	d	P
−100	2 114	0 7897	39.14	0	1.971	0 7078	39 42
90	2.100	.7814	39.19	+10	1.957	,6998	39.43
80	2 086	.7733	39 23	20	1 943	6918	39 44
70	2.072	,7652	39 27	30	1.928	.6837	39 44
60	2.058	.7569	39.31	40	1.914	6756	39.45
50	2.043	.7488	39.32	50	1.900	.6676	39.46
40	2.029	.7407	39.34	60	1.886	,6587	39.53
30	2.015	.7326	39.37	70	1.872	.6498	39.58
20	2.000	.7242	39.41	80	1.858	.6402	39.66
−10	1.985	.7160	39.40	90	1.844	.6303	39.76
				100	1 830	.6206	39.86

TABLE IV

PHYSICAL CONSTANTS OF THE HEPTANES AND OF 2,2,4-TRIMETHYLPENTANE AT 20°

		$\frac{d\epsilon}{dT} \times 10^4$(20–30°)	d	P	P_E	P_A	$MR_\gamma - MR_\alpha$	$n_\lambda - n_\alpha$	η
2,2-Dimethylpentane	1.915	14	0.6737	34.73	33 82	0 91	0.86	0.01068	0.00385
2,4-Dimethylpentane	1.917	15	.6745[a]	34.75	33.79	.96	.85	.01055	,00361
2-Methylhexane	1.922	14	.6789[a]	34.70	33.78	.92	.85	,01066	,00378
n-Heptane	1.930	14	.6836	34.65	33.77	.88	.84	,01067	.00409
3-Methylhexane	1.930	14	.6870[a]	34.49	33.68	.83	.83	.01067	,00372
2,2,3-Trimethylbutane	1.930	13	.6892	34.38	33.61	.78	84	01073	.00585
3,3-Dimethylpentane	1.940	15	.6934	34.45	33 55	90	.83	01069	00454
2,3-Dimethylpentane	1 942	15	6951"	34 42	33 54	.88	.83	01066	,00406
3-Ethylpentane	1.942	15	.6988	34.24	33.48	.76	.82	,01063	.00377
2,2,4-Trimethylpentane	1.943	15	,6918	39.44	38.35	1 09	.99	.01112	.00503

[a] Determined by Dr. Graham Edgar.

larization calculated from them, are given in Tables II and III. Since the three heptanes and the octane showed similarity of behavior in their slight variation of the polarization with temperature as represented in Fig. 1, the other heptanes were measured only at 20 and 30". For the sake of comparison, Table IV gives for each of the heptanes and for the 2,2,4-trimethylpentane at 20°, the dielectric constant, the temperature coefficient of the dielectric constant calculated from the values at 20° and 30°, the density, the molar polarization, P, and the molar refraction for light of infinite wave length = P_E. The values of P_A are calculated as $P-P_E$, which will be discussed later. The densities of all the heptanes at 20 and 30° have been determined by Dr. Graham Edgar. As the values which we have obtained at these temperatures are in excellent agreement with those of Dr. Edgar, we have used his values for four of the substances as indicated. The viscosities in c.g.s. units at 20°, measured by Mr. H. E. Rogers with a Bingham viscometer, as well as the dispersions calculated from the data in Table I, are included.

In Fig. 1 the scale on which the polarization is plotted against temperature is so large that many of the points appear to lie some distance from the straight lines which best represent them. Actually, the polarization of these substances varies little with temperature, but the variation, such as it is, is an approximately linear increase with increasing temperature, while, if the molecules possessed electric moments, the polarization would normally decrease with rising temperature. The increase, less than 2% for a 200° change of temperature, is not predicted by the theory of dielectric constants. As a small increase in refraction with rising temperature has been observed for a number of liquids, while vaporization also appears to bring about a slight increase in refraction,[4] it seems possible that the force fields of adjacent molecules reduce the mobilities of the bound electrons to a small extent, thereby reducing the refraction. As the molecular separation and motion increase with rising temperature, the effect of the force fields upon the electrons is decreased, the refraction, and hence the

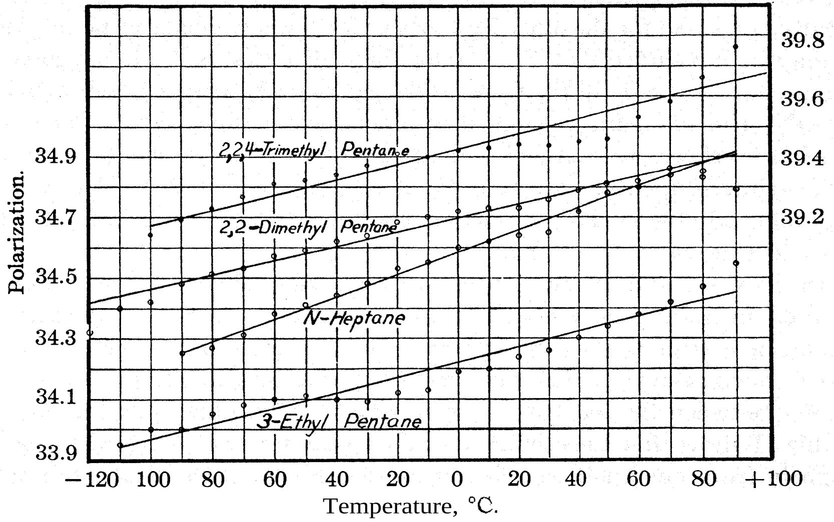

Fig. 1.—Variation of polarization with temperature. The values for the polarization of 2,2,4-trimethylpentane are shown at the right.

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[4] (a) Eisenlohr, "Spektrochemie organischer Verbindungen," F. Enke, Stuttgart, 1912, p. 19; (b) Lorenz, *Ann. Physik*, 11, 70 (1880); (c) Brühl, *Z. physik. Chem.*, 7, 1 (1891).

polarization, thus being increased. Another and perhaps more important factor is the increase in the number of degrees of freedom with increasing temperature, which should facilitate the displacement of charges in the molecules and, hence, increase the polarization. As change of temperature alters the degree of molecular association or orientation, which has a great effect upon the polarization, the small effects just described may often be so masked as not to be apparent. Hexane, benzene and a few other substances which have electrically symmetrical molecules also show a slight increase in polarization with rising temperature.[1c,5]

The curves in Fig. 1 may be regarded as establishing the absence of any measurable electric moment in the molecules of the four substances represented. Consequently, $P_M = 0$ and $P_A = P-P_E$. As $P-P_E$ is practically the same for the other heptanes as for these which have no moment, it may be concluded that $P_M = 0$ for them also, that is, that they have no moments. Indeed, if P_A were neglected entirely and P_M set equal to $P-P_E$, the moments calculated would be exceedingly small. The conclusion is, therefore, justified that the moments of all the heptanes and of 2,2,4-trimethylpentane are zero or, at least, too small to be detected by any method now available, which, of course, is all that can be said as to the electric symmetry of any molecule.

In Tables I and IV the isomers are arranged in the order in which many of their properties have been found by Edgar and Calingaert[6] to fall. As would be expected, the dielectric constants, densities and refractive indices vary concomitantly. The temperature coefficients of the dielectric constants between 20 and 30° are approximately the same, but the data of Table II show that the coefficients over a wide range of temperature differ slightly from one another. The viscosities show a much greater variation in values than do any of the other properties listed and the first five in the list depart markedly from the regular order observed, at least approximately, for the other properties. The values of the dispersion, $n_\gamma - n_\alpha$, are approximately the same for all the heptanes, a marked rise being apparent on passing to the octane. The values of the molar dispersion, $MR_\gamma - MR_\alpha$, vary little, if any, more than might be caused by experimental error, but there appears to be a slight decrease in going down the list. A slight and irregular decrease is also apparent in going down the column of P_A values for the heptanes. The absolute variation in the values of P_A is much less than that in the values of P and P_E, which fall approximately in the usual order and vary concomitantly. As the refraction and polarization depend upon the mobility of the outer electrons of the molecule, the small but concomitant variations of P and P_E show that variation in the positions of the atoms in the molecules has a detectable effect

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[5] Isnardi, *Z. Physik*, 9, 153 (1922); Sanger, *Physik. Z.*, 27, 165 (1926).

[6] Private communication to the authors.

upon the mobilities of the binding electrons, the average mobility decreasing slightly in the order indicated by the decreasing values of P and P_E.

The conclusion to be drawn from these results, taken in conjunction with the work on other hydrocarbons, is that the atoms in a saturated hydrocarbon molecule may be joined together in every possible configuration without giving rise to any measurable lack of electric symmetry. This has a very definite bearing upon the electronic theories of valence in organic compounds, for the heptane molecules may be resolved into the various alkyl radicals to which it is customary to assign varying degrees of electronegativity, the formulas of the radicals being represented with a pair of bonding electrons at varying distances from their carbon atom.[7] If such a variation is an inherent property of the radicals, it should exist when the radicals occur in the heptane molecules and give rise to electric moments of varying sizes and, hence, to different values of P_M. It has been concluded that P_M differs from zero by a negligible amount. If it is not actually zero, any variation in its value must be included in that of P_A as calculated. The largest difference observed between the values of P_A for any two isomers, namely, that of 0.20 between 2,4-dimethylpentane and 3-ethylpentane, would, if due to but one pair of electrons, correspond to a displacement of the effective position of the charges of less than 3×10^{-11} cm. from a symmetrical location. It seems improbable that such a displacement and the very small change in forces which it must cause would have an appreciable effect upon the properties of the molecule. It must be further remembered that the possible displacement which has been estimated is the greatest that could occur and is probably much larger than any actually existing in these molecules. This does not preclude the possibility that the bonding electron pairs of different alkyl groups may be differently affected when they hold more polar groups in combination, but the relatively small variation in the electric moment of the molecule among the different alcohols and among the members of other series provides strong evidence[8] against the assumption of any considerable variation in the position of the bonding electron pair. The hypothesis of a bonding electron pair located in positions of varying unsymmetry thus receives no support from the physical evidence here considered.

Summary

The dielectric constants, densities, refractive indices, dispersions and viscosities of the isomers of heptane and of 2,2,4-trimethylpentane have been measured. The polarizations of three of the heptanes and of the octane calculated from dielectric constant and density measurements over

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[7] See Kharasch and Grafflin, THIS JOURNAL, 47, 1948 (1925); Kharasch and Marker, *ibid.*, 48, 3130 (1926); Kharasch, J. Chem. Education, **5**, 404 **(1928).**

[8] Smyth, THIS JOURNAL, 46, 2151 (1924); Krchma and Williams, *ibid.*, 49,2408 (1927).

the entire range of temperature within which the substances are liquid increase very slightly with temperature, indicating that the molecules contain no electric moments. The very small differences between the polarizations and the molar refractions extrapolated to infinite wave length for all of the substances show the absence of a measurable moment in their molecules. It is concluded that the atoms in a saturated hydrocarbon molecule may be joined together in every possible configuration without giving rise to any measurable lack of electric symmetry, although very small differences in the rigidity of binding of the electrons are detected. The electrical symmetry of the molecules gives no evidence of a difference in the electronegativities of the various constituent radicals.

PRINCETON, NEW JERSEY

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

SOLUTIONS OF SALTS IN PURE ACETIC ACID. I. PRELIMINARY PAPER[1]

BY ARTHUR W. DAVIDSON

RECEIVED APRIL 14, 1928 PUBLISHED JULY 6, 1928

Introduction

The study of the solubilities and chemical reactions of salts in non-aqueous solvents reveals certain analogies between these solutions and the more familiar solutions in water. These analogies have been most extensively developed, by the well-known researches of Franklin and his co-workers, for solutions in liquid ammonia. Despite the large amount of work that has been done with other non-aqueous solvents, our knowledge of such solutions is still so fragmentary that the accumulation and organization of much additional information would seem to be desirable.

In a previous paper,[2] the writer described an attempt to study the solubilities and reactions of salts in anhydrous sulfuric acid, a liquid of very different nature from those non-aqueous solvents which have been most widely examined. It was found that the range of investigation in this solvent was severely limited by the fact that, due to the large self-ionization of sulfuric acid, reactions of a solvolytic nature were of such general occurrence as greatly to interfere with the study of other reactions. It was decided to investigate, from the same point of view, solutions of salts in anhydrous acetic acid, this liquid being sufficiently polar in nature to be a fairly good solvent for many salts, while its self-ionization is apparently very small, since its specific conductivity is of the order of 2×10^{-8} reciprocal ohm.

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[1] Presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society at the St. Louis meeting, April, 1928.

[2] Davidson, THIS JOURNAL, 47, 968 (1925).

The information that; has hitherto been gathered concerning the solubilities and reactions of salts in acetic acid is decidedly meager. It was thought until rather recently that this liquid was a very poor solvent for inorganic salts.[3] Such data as have been obtained are very widely scattered. Many of the results of investigations previous to 1924 have been collected by Walden, in his "Elektrochemie Nichtwassriger Lösungen,"[4] although even here the data must be sought under several different headings. Quantitative measurements of solubility at various temperatures have been reported for mercuric chloride, uranyl nitrate, magnesium bromide and iodide, calcium chloride, antimony chloride and bromide, and the acetates of sodium and silver.[5] In addition, several addition compounds between .salts and acetic acid have been isolated, including compounds with the acetates of the alkali metals,[6] and compounds with aluminum chloride, magnesium bromide and iodide, calcium chloride, antimony chloride and sodium iodide.? Conductivity measurements have been made on solutions of the alkali acetates and of several other salts.[8]

There have been a few scattered observations concerning reactions of metallic oxides with acetic acid, limited for the most part to the formation of acetates in which the metals exhibit unusually high valences.[9] The best known example of this is the formation of lead tetra-acetate from red lead.

Since the publication of Walden's text there have appeared, so far as the writer has been able to ascertain, three articles bearing on this subject. Webb[10] studied the activities of several salts in acetic acid solution, using the freezing-point method, and discussed the results on the basis of the assumption of practically complete ionization and the Debye-Hückel theory. Stranathan and Strong,[11] from the viscosities and conductivities of acetic acid–stannic chloride solutions, deduced the existence of an addition compound which, however, was not isolated. Still more recently, Hall and Conant,[12] in a study of hydrogen ion activities in what they

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[3] See, for instance, Beckmann, Z. *physik. Chem.*, 57, 129 (1907).

[4] Bredig's "Handbuch der angewandten physikalischen Chemie," Vol. XIII, J. A. Barth, Leipzig, 1924.

[5] (a) Étard, *Ann. chim. phys.* (7) 2, 555 (1894); (b) Oechsner de Coninck, *Compt. rend.*, **132,** 90 (1901); (c) Menschutkin, *Z. anorg. Chem.*, **54,** 89 (1907); (d) Menschutkin, J. *Russ. Phys.-Chem. Soc.*, 43, 1785 (1911); *C.* A., 6, 1280 (1912); (e) Kendall and Adler, THIS JOURNAL, 43, 1470 (1921).

[6] For references on this subject see ref. 5 (e), p. 1479.

[7] (a) Walker and Spencer, J. *Chem. Soc.*, 85, 1106 (1904); (b) Turner and Bissett, *ibid.*, 105, 1777 (1914); also refs. **5** c, d.

[8] **A** summary of these measurements is given by Walden in "Das Leitvermögen der Msungen," Leipzig, 1924.

[9] See ref. 4, p. 378.

[10] Webb, THIS JOURNAL, 48, 2263 (1926).

[11] Stranathan and Strong, J. *Phys. Chem.*, 31, 1420 (1927).

[12] Hall and Conant, THIS JOURNAL, 49,3047,3062 (1927).

propose to call "superacid" solutions, have described the neutralization of various organic bases by acids in glacial acetic acid, and have given some interesting speculations on the results, in terms of Bronsted's theory of acids and bases.

Object of the Present Work

In the investigation which is now in progress in this Laboratory, it is the writer's intention to extend the solubility data for salts in acetic acid by the determination of a large number of solubilities qualitatively, and a few typical ones quantitatively, and to make a study of reactions which take place between ionized salts in this medium, this being a field which has scarcely been touched. Only salts of inorganic bases will be considered.

The present paper reports the results of some preliminary experiments of a qualitative nature, which appear to the writer to be of interest. Quantitative experiments are in progress.

Experimental Part

The solvent used in these experiments was a special grade of C. P. glacial acetic acid, which had a melting point of 16.4°. The salts were of a reliable C. P. grade and were dried under suitable conditions. The anhydrous sulfuric acid used was prepared as described by Kendall and Carpenter,[13] and had a melting point of 10.4°.

1. Solubilities of Salts in Acetic Acid.—The number of salts which were found to be appreciably soluble was considerably larger than might be supposed from the meager data in the literature. The results of qualitative tests of solubility are given below.

The following salts were found to be readily soluble at room temperature: $LiNO_3$, $Ca(NO_3)_2$, NH_4NO_3, $Cu(NO_3)_2$, $CaCl_2$, $ZnCl_2$, $FeCl_3$, $SbCl_3$, BaI_2, ZnI_2, NH_4SCN, KCN, $LiC_2H_3O_2$, $KC_2H_3O_2$, $NH_4C_2H_3O_2$, $Pb(C_2H_3O_2)_2$, $Cd(C_2H_3O_2)_2$.

The following were found to be somewhat less soluble than the above: $AgNO_3$, $AlCl_3$, $HgCl_2$, HgI_2, $CoCl_2$.

The following were appreciably, though slightly, soluble (apparently less than one part in one hundred of solvent at ordinary temperature): NaCl, KCl, KBr, KI, NH_4Cl, NH_4Br, NH_4I, $NaNO_3$, KNO_3, $BaCl_2$, $KClO_3$, Na_2SO_4, $(NH_4)_2SO_4$, $Cu(C_2H_3O_2)_2$.

The following salts were found to be practically insoluble: AgCl, AgBr, AgI, AgCN, AgSCN, $PbCl_2$, PbI_2, HgCl, CdI_2, $Ba(NO_3)_2$, $Ca_3(PO_4)_2$, $Cu_3(PO_4)_2$, $CaCO_3$; also the sulfates of Li, K, Cu, Ag, Ca, Ba, Mg, Zn, Cd, Hg(-ous and -ic), Al, Pb, Mn, Ni, Co and Fe(-ous and -ic).

2. Double Decomposition Reactions in Acetic Acid.—Double decomposition reactions were found to take place in this solvent as readily

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[13] Kendall and Carpenter, THIS JOURNAL, 36, 2498 (1914).

as in water, the course of such reactions being determined largely by the solubilities of the several salts in question. In many cases these reactions were similar to familiar phenomena in aqueous solution. Thus silver chloride, bromide, iodide, cyanide and thiocyanate were each precipitated upon the addition of a solution of a salt containing the corresponding anion to a solution of silver nitrate. The silver cyanide precipitate, however, failed to dissolve in an excess of potassium cyanide solution. Lead chloride and lead iodide were precipitated from lead acetate solutions by sodium chloride and potassium iodide solutions, respectively. Solutions of cadmium acetate, lead acetate, zinc chloride, antimony chloride and silver nitrate all readily gave precipitates of the corresponding sulfides upon the introduction of hydrogen sulfide gas.

A solution of ferric chloride[14] gave, with ammonium thiocyanate solution, a deep red color, but no precipitate, just as in aqueous solution.

In many other cases, however, the reactions followed a less familiar course. A few examples of this will be described. When a solution of copper nitrate was treated with sodium acetate, a finely-divided, green crystalline precipitate of copper acetate was formed. A barium iodide solution, upon the addition of sodium nitrate, gave a finely-divided, white crystalline precipitate, which was shown to be barium nitrate. Any of the sulfates could be precipitated by the addition of a drop of anhydrous sulfuric acid, or a small amount of a solution of sulfuric acid in acetic acid, to a solution of a soluble salt of the metal in question. These came down as amorphous, flocculent precipitates from dilute solutions, or as gelatinous masses from concentrated ones. Even the sulfates of the alkali metals were readily precipitated in this way, although very dilute solutions of sodium and ammonium salts gave no precipitate. In connection with the general insolubility of sulfates in acetic acid, it is an interesting fact that sulfates which normally form hydrates can be precipitated in the anhydrous condition even when the solution contains some water. Thus, when *hydrated* cupric nitrate was dissolved in acetic acid and a little concentrated sulfuric acid added, a white precipitate of anhydrous cupric sulfate was obtained. Similarly, hydrated nickel nitrate gave yellow anhydrous nickel sulfate, and hydrated cobalt nitrate, pale pink anhydrous cobalt sulfate. It is worthy of notice that sulfates are insoluble in liquid ammonia, also.[15]

The only salt that was found to be noticeably solvolyzed by acetic acid was sodium carbonate with which, even at ordinary temperature, the solvent reacted fairly vigorously, with the evolution of CO_2. The reaction

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[14] According to Weinland, a solution of ferric chloride in 96% acetic acid contains the cation $Fe_3(C_2H_3O_2)_6^{+++}$. See, for instance, Weinland, Kessler and Bayerl, *Z. anorg. allgem. Chem.*, 132, 209, 225 (1924).

[15] Franklin and Kraus, *Am. Chem. J.*, 21, 8 (1899).

was, of course, not nearly so vigorous as in the case of aqueous acetic acid. Sodium bicarbonate was solvolyzed only very slowly, and calcium carbonate not at all.[16]

3. Effect of Sodium and Ammonium Acetates upon Solubilities of Certain Other Salts.—The acetates of the metals may be regarded as bases in acetic acid, since they presumably have the same negative ion as the solvent.[17] This being the case, it might be expected that in this solvent they would exhibit properties analogous to those of the hydroxides in water. The following observations support this hypothesis.

Zinc acetate is practically insoluble in acetic acid,[18] even at the boiling point. It was found, however, to dissolve quite readily in a sodium acetate solution (about 5 mole per cent. of sodium acetate). This is analogous to the solubility of zinc hydroxide in aqueous sodium hydroxide solution, and would appear to be due to the amphoteric nature of zinc. The solubility of copper acetate in acetic acid was not increased by the presence of sodium acetate.

Ammonium acetate, in acetic acid, may be regarded as the analog of ammonium hydroxide in water. That this analogy is far from being merely a formal one is indicated in a rather striking manner by the following facts. Zinc acetate was found to dissolve readily in ammonium acetate solution (about 5 mole per cent. of ammonium acetate), as does zinc hydroxide in water. Copper acetate, which was found to be only slightly soluble in acetic acid to give a greenish solution, and which could, in fact, be precipitated from a solution of a soluble copper salt by the addition of a small amount of ammonium acetate solution, not only dissolved readily in excess of this solution, but gave a dark blue color when so dissolved. When this solution was heated, its color gradually deepened, until at the boiling point it became a very intense purplish-blue, which was practically identical with the characteristic color attributed to the copper–ammonia ion in aqueous solution. On cooling this characteristic purplish tinge disappeared. It seems reasonable to suppose that ammonium acetate reversibly dissociates to some extent into free ammonia and acetic acid as the solution is heated, and that the purplish-blue color is due to an ion of similar nature to that which gives rise to it in aqueous solutions. Ammonium acetate was also found to dissolve other difficultly soluble salts, notably silver chloride, cupric sulfate, cobalt sulfate and nickel sulfate. All these phenomena are being investigated further, and will be discussed in a subsequent paper.

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[16] In connection with solvolysis by acetic acid, it should be mentioned that Rosenheim and Miiller, *Z. anorg. Chem.*, 39, **175** (1904), found that ferric chloride and ferric bromide crystallized from anhydrous acetic acid as $Fe(C_2H_3O_2)_2Cl$ and $Fe(C_2H_3O_2)_2Br$, respectively.

[17] Compare ref. **2,** p. 969.

[18] See ref. 5e, p. 1478.

Summary

1. A fairly large number of salts, especially halides and nitrates, have been found to be soluble in acetic acid. All sulfates are very slightly soluble.

2. Double decomposition reactions have been found to take place quite readily in this solvent, A number of such reactions have been described.

3. Solvolysis does not occur in acetic acid solutions to any marked extent.

4. Analogies have been pointed out between the behavior of certain acetates in acetic acid and that of the corresponding hydroxides in water.

LAWRENCE, KANSAS

[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICS, UNIVERSITY OF PITTSBURGH]

THE MOLECULAR HEAT AND ENTROPY OF HYDROGEN CHLORIDE CALCULATED FROM BAND SPECTRA DATA

BY ELMER HUTCHISSON

RECEIVED APRIL 14, 1928 PUBLISHED JULY 6, 1928

I. Introduction

It is well known that the heat capacity of gases decreases with temperature in the neighborhood of absolute zero. The temperature variation of the molecular heat of gaseous hydrogen chloride is especially interesting because it may be used to confirm the interpretation which the new quantum mechanics places upon band spectra. The computation of molecular heats, by means of the energy levels derived from band spectra, was first carried through by Hicks and Mitchell.[1] They made use of the spectral measurements of Imes and of Colby, Meyer and Bronk and assumed the "*a priori* probabilities" or weights of the quantum states to be 2, 4, 6, 8, etc., corresponding to those states characterized by the rotational quantum numbers $^1/_2$, $^3/_2$, $^5/_2$, $^7/_2$, etc. Van Vleck[2] and others have pointed out that according to the new quantum mechanics the *a priori* probabilities must be 1, 3, 5, 7 for the states $^1/_2$, $^3/_2$, $^5/_2$, $^7/_2$ for simple polar molecules like HCl. Experimental proof that these probabilities are correct is furnished by Bourgin's[3] measurements of the absorption intensities of hydrogen chloride.

The band spectra measurements of Colby, Meyer and Bronk have been recalculated by Kemble,[4] who has obtained equations expressing the energy levels as a function of the vibrational and rotational quantum numbers.

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[1] Hicks and Mitchell, THIS JOURNAL, 48, 1520 (1926).

[2] Van Vleck, Phys. *Rev.*, 28, 986 (1926); see also Hutchisson, ibid., 29, 360A (1927).

[3] Bourgin, *ibid.*, 29, 794 (1927).

[4] Kemble, J. Opt. *Soc. Am.*, 12, 1 (1926).

The calculations made in this paper are based on Kemble's values for the energy levels and the a *priori* probabilities assigned by the new mechanics. Besides the molecular heats, the entropy values of hydrogen chloride at the various temperatures are calculated in accordance with the method given by Giauque and Wiebe.[5] The calculated results are then compared with experiment.

II. Calculations

The molecular heat of a gas is obtained by differentiating the energy of a mole of the gas with respect to the temperature. The translational energy of the gas remains constant and may therefore be left out of consideration. The rotational and vibrational energy may be obtained by summing up the different energy levels obtained from band spectra data. The expression for the molecular heat is well known and has been used by several investigators. It may be written as

$$C = \frac{N}{J}\frac{d}{dT}\frac{\Sigma_n \Sigma_m\, p^n_m\, W^n_m\, e^{-\frac{W^n_m}{kT}}}{\Sigma_n \Sigma_m\, p^n_m\, e^{-\frac{W^n_m}{kT}}}$$

where p^n_m is the *a priori* probability of the m^{th} rotational state and the n^{th} vibrational state, J is the mechanical equivalent of heat and N is Avogadro's number. For purposes of computation a more convenient form is as follows

$$C = \frac{Nk}{J}\left[\frac{P_3}{P_1} - \left(\frac{P_2}{P_1}\right)^2\right]$$

in which

$$P_j = \Sigma_n \Sigma_m\, p^n_m\, (\sigma^n_m)^{(j-1)}\, e^{-\sigma^n_m} \text{ and } \sigma^n_m = \frac{\epsilon^n_m\, ch}{kT}$$

where e^n_m are the band spectra wave numbers expressed in cm.$^{-1}$.

Kemble's equations for the spectral energy levels may be written[6] (expressed in cm.$^{-1}$)

$$F_m(m) = A_n + 2\delta\, m + B_n\, m^2 + D_n\, m^4$$

where

$A_0 = 0$ $B_0 = 10.4469 \pm 0.0050$ $D_0 = -0.000529$
$A_1 = 2887.19 \pm 0.053$ $B_1 = 10.1417 \pm 0.0050$ $D_1 = -0.000522$
$A_2 = 5667.23 \pm 0.17$ $B_2 = 9\ 8624 \pm 0\ 0023$ $D_2 = -0.000514$

and $\delta = 0.078 \pm 0.012$. In the 600° K. calculation 28 terms for $n = {}^1/_2$, 24 terms for $n = {}^3/_2$, and 12 terms for $n = {}^5/_2$, are needed. In these calculations m takes the value ${}^1/_2$, ${}^3/_2$, ${}^5/_2$, ${}^7/_2$, etc.

The results of the computations are given in Table I. The constants used in all the results are those found in the "International Critical Tables."

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[5] Giauque and Wiebe, THIS JOURNAL, *50*, 101 (1928).

[6] In this equation our m is the same as Kemble's $(j - {}^1/_2)$.

The probable error in the value of molecular heat may be indicated by making use of the probable errors assigned to the band spectra constants by Kemble. For instance, in the computation for 0° (273.1°K.) the B_0 term is the major portion of important energy levels so that the percentage probable error remains constant for all terms. A change may therefore be made in the temperature which will balance the change in ϵ_m^n and still keep σ constant. The required change in temperature is ± 0.13°K. This change in temperature would produce a change of only a few units in the fifth decimal place. Kemble's constants and therefore the molecular heats are given for the lighter isotope of HCl. The change produced by the other isotope would be very small.

TABLE I

RESULTS OF COMPUTATIONS

T, °K.	C(Rot. + Vib.) cal. deg.$^{-1}$ mole^{-1}	C_v cal. deg.$^{-1}$ mole^{-1}	$\int_0^T C/T\,dT$ Entropy units per mole	T, °K.	C(Rot. + Vib.) cal. deg.$^{-1}$ mole^{-1}	C_v cal. deg.$^{-1}$ mole^{-1}	$\int_0^T C/T\,dT$ Entropy units per mole
600	2.1010	5.0814	9.354	13	2.1782	5.1586	1.619
450	2.0182	4.9986	8.761	11	2.1630	5.1434	1.255
373.1	2.0023	4.9827	8.385	8	1.7235	4.7039	
273.1	1.9962	4.9766	7.761	6	0.9517	3.9321	
200	1.9945	4.9749	7.140	5	.5140	3.4944	
120	1.9933	4.9737	6.121	4	.1799	3.1603	
60	1.9954	4.9758	4.739	3	.0259	3.0063	
30	2.0110	4.9914	3.352	1	.0000	2.9804	
15	2.1386	5.1190	1.928				

In Fig. 1 the molecular heats are plotted against the temperature.[7] This graph shows the sharp maximum which occurs at about 12.5°K. The shape of this curve is markedly different from the experimental molecular heat–temperature curve for hydrogen, which has a gradual monotonic increase in C_v from $^3/_2$ R at 60°, to approximately $^5/_2$ R at room temperature. The explanation[8] of the absence of a maximum on the basis of the quantum theory in the case of hydrogen, is that the gas is made up of a mixture of molecules of different types (those having symmetrical and those having antisymmetrical "eigenfunctions"). The molecular heat of this mixture gives a curve which agrees well with experiment at low temperatures[9]

There are not many accurate determinations of the molecular heat of gaseous hydrogen chloride. Observations have been made by Masson,[10]

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[7] It should perhaps be noted that these calculations take no account of the Van der Waals forces. However, the experimental values have been reduced to the ideal state so that the calculated values should agree with experiment. The possible existence of $(HCl)_2$ molecules has been neglected.

[8] Dennison, *Proc. Roy. Soc. (London),* **115A,** 463 (1927).

[9] Cornish and Eastman, THIS JOURNAL, 50, 627 (1928).

[10] Masson, *Phil.* Mag., 13, 533 (1857).

Regnault,[11] Strecker[12] and Muller,[13] but their values disagree among themselves so much that it is difficult to have much faith in any of them. Pier[14] measured the molecular heat of HCl from 0 to 1600°, using the bomb method, and obtained the equation $C_v = 4.90 + 0.0009\,\Theta$, where Θ is the centigrade temperature. The values obtained from his equations are included in Fig. 1. Pier's data for hydrogen appear to be too low at room temperature, so it is possible that the same is true for hydrogen chloride.

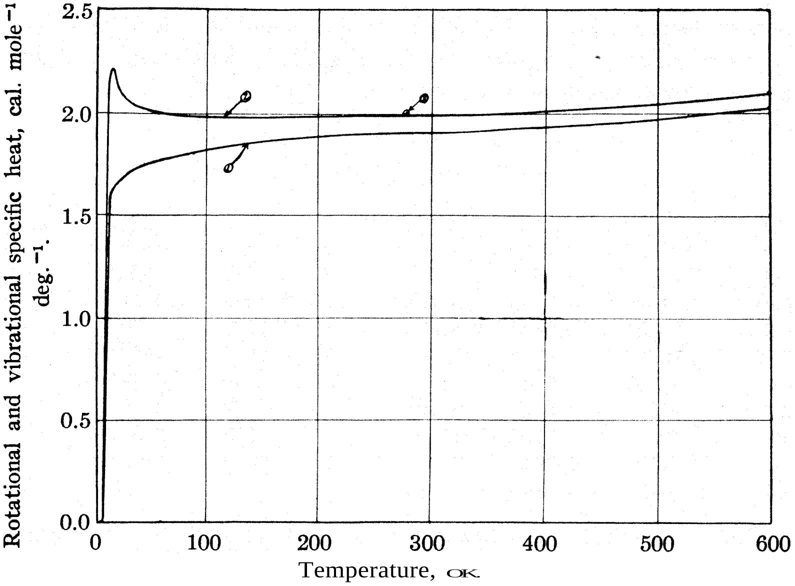

Fig. 1.—Graph showing the variation of the specific heat of hydrogen chloride with temperature calculated from band spectra data. Curve **1** is taken from Hicks and Mitchell's data. Curve **2** shows the values calculated in this paper based upon the a *priori* probabilities indicated by experiment and the new quantum mechanics. The single reliable experimental point is shown at **(3)**.

The most accurate measurements are, without doubt, those of Schweikert,[15] using the velocity of sound method. His values have been slightly corrected by Partington and Schilling.[16] His value for C_v at 0° is 4.995 cal. mole^{-1} deg.$^{-1}$, which agrees well with the calculated value ($C_v = 4.977$) given, and certainly confirms this result rather than the calculated value of $C_v = 4.879$ on the basis of the older quantum mechanics.

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[11] Regnault, *Mem. Acad.*, **26**, 1 (1862).

[12] Strecker, *Wied. Ann.*, **13**, 20 (1881); **17**, 85 (1882).

[13] Muller, *ibid.*, **18**, 94 (1883).

[14] Pier, *Z. physik. Chem.*, **66**, 759 (1909); Nernst, *Z. Electrochem.*, **17**, 272 (1911).

[15] Schweikert, *Ann. Physik*, **48**, 593 (1915).

[16] Partington and Schilling, "Specific Heat of Gases," Ernst Benn, Ltd., London, 1925.

Giauque and Wiebe have shown that the same terms used for specific heats may be used to evaluate $\int_0^T C/TdT$ for entropy calculations. In our notation their equation may be written

$$S_2 = \int_0^T CT/dT = R\left[\ln P_1 - \frac{P_2}{P_1}\right]$$

The values of this integral for the various temperatures are included in Table I. The total entropy may then be obtained by using the Sackur equation for the entropy due to the translational energy

$$S_1 = \frac{3}{2} R \ln M + \frac{3}{2} R \ln T + R \ln V + S_0$$

where S_0 has the values -11.06 (Tetrode) or -11.38 (Lewis) entropy units per mole. Giauque and Wiebe have given, as the experimental value of the entropy per mole, 41.2 Entropy Units at the boiling point (188.07°K.). Extrapolating between the values given in Table I, we obtain $S_2 = 7.02$ at 188.07°K. Using the values given in the "International Critical Tables," S_1 is found to be 34.35 or 34.03, depending upon the value of S_0. Our value for the total entropy per mole at the boiling point is therefore 41.45 or 41.13 E. U., while the experimental value given by Giauque and Wiebe is 41.3 when corrected to the ideal state. At 298.1°K. our calculated value of the entropy is 44.65 or 44.33, while the experimental value is given as 44.5. The calculated values at 298.1°K. are 0.01 E. U. higher than those given by Giauque and Wiebe. At 0° the total entropy per mole amounts to 44.04 or 43.72 E. U.

If we make use of the value of S_2 taken from Hicks and Mitchell's data, which is given as 6.75 at 298.1°, we may compare the entropy results of the older quantum theory with those of the new mechanics. It was noted by Giauque and Wiebe that Hicks and Mitchell neglected the zero point entropy. It may also be noted that Hicks and Mitchell have an error in summing up the components of the entropy, S_1 and S_2, to obtain their final entropy value in the case that uses the Tetrode constant. Using S_2 as given, the entropy per mole at 298.1°K. is 44.85 or 44.53 E. U. as compared with the experimental value of 44.5 E. U. In this case, also, the present calculations give slightly better agreement than those based on the older quantum theory, although the agreement is not decisive because of the large probable error in the experimental result.

Summary

The molecular heat of gaseous hydrogen chloride is computed from band spectra data for temperatures from 1°K. to 600°K. It is shown that the curve obtained by plotting the molecular heat against temperature rises to a maximum at 12.5°K. At 0° the calculated molecular heat agrees very well with the single reliable experimental value, while the earlier calculations of Hicks and Mitchell give a value about 0.1 cal. mole–' deg.$^{-1}$ too low.

The values of $\int_0^T C/TdT$, which may be used to calculate the entropy

for the various temperatures, are calculated by the method suggested by Giauque and Wiebe. The entropy at 0° is found to be 44.04 or 43.72 Entropy Units per mole, depending upon whether the Tetrode or Lewis value of the chemical constant is used.

PITTSBURGH, PENNSYLVANIA

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

A RAPID METHOD FOR THE SEPARATION OF ALUMINUM AND BERYLLIUM

BY I. M. KOLTHOFF AND ERNEST B. SANDELL

RECEIVED APRIL 23, 1928 PUBLISHED JULY 6, 1928

From the voluminous literature on the subject of the separation of aluminum and beryllium it may be concluded that the estimation of these elements in the presence of each other is of great difficulty, and that there is no simple, satisfactory method for their accurate determination. An excellent summary of the older methods for the separation of aluminum and beryllium will be found in C. L. Parsons' "The Chemistry and Literature of Beryllium." H. T. S. Britton[1] concluded from an experimental study of the more important methods proposed that the only four which were capable of giving satisfactory results, if the details of the respective procedures were carefully adhered to, were the following. 1. Decomposition by boiling of sodium hydroxide solutions of aluminum and beryllium.[2] Sodium beryllate is hydrolytically decomposed, giving a precipitate of beryllium oxide; sodium aluminate remains in solution. 2. Parsons and Barnes" method.[3] Beryllium hydroxide is dissolved by hot sodium bicarbonate solution; aluminum hydroxide is not dissolved. 3. Method of Wunder and Wenger.[4] The oxides are fused with sodium carbonate and the residue is extracted with water. Aluminum goes into solution. 4. F. S. Havens'[5] ether–hydrochloric acid method. Beryllium chloride alone is soluble in a mixture of hydrochloric acid and ether saturated with hydrogen chloride. Of these methods, Britton considered 1 and 4 to be the most satisfactory. For discussion and criticism of these methods, see Hellmut Fischer[6] and also L. Moser and M. Niessner.[7] A method which appears to be superior to any hitherto proposed has recently

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[1] Britton, *Analyst*, 46, 359, 437 (1921); 47, 50 (1922).

[2] R. Gmelin and Schaffgotsch, *Pogg. Ann.*, 83, 175 (1843); Penfield and Harper, *Am. J. Sci.*, (iii), 32, 110 (1886); Zimmermann, *Z. anal. Chem.*, **27**, 61 (1888).

[3] Parsons and Barnes, THIS JOURNAL, 28, 1589 (1906).

[4] Wunder and Wenger, *Z. anal. Chem.*, *51*, *470* (1912).

[5] Havens, *Z. anorg. Chem.*, *16*, 15 (1898).

[6] Fischer, "Wissentschaftliche Veroffentlichungen aus dem Siemens–Konzern," 1926, Band V, Heft 2, p. 99.

[7] Moser and Niessner, *Monatsh.*, 48, 113 (1927).

been described by L. Moser and M. Niessner,[7] in which aluminum alone is precipitated by a saturated solution of ammonium acetate containing 3% of tannin. The tannin must be destroyed in the filtrate before the beryllium can be precipitated. The method which is described below is simpler and more rapid.

R. Berg[8] has recently introduced the use of o-hydroxyquinoline (called "oxine" by F. L. Hahn)[9] for the separation and determination of various metals. According to our own experience, this new reagent is very useful in many different analytical procedures.

In a solution weakly acid with acetic acid and containing ammonium acetate, aluminum is precipitated quantitatively by a solution of oxine as $(C_9H_6ON)_3Al$. Beryllium is not precipitated under these conditions. On the addition of ammonium hydroxide to the filtrate from the aluminum precipitation, beryllium gives a precipitate of indefinite composition which appears to be beryllium hydroxide containing adsorbed oxine. Addition of oxine and ammonium hydroxide to a solution of a beryllium salt containing sufficient sodium potassium tartrate to prevent precipitation of beryllium hydroxide gives a yellow precipitate, somewhat difficult to filter, which unfortunately cannot be used in the estimation of the element, both on account of its solubility and its variable composition.

The procedure adopted is based on the following facts. (a) From a weakly acid solution containing aluminum and beryllium, aluminum is quantitatively precipitated by the addition of an acetic acid solution of oxine and an excess of ammonium acetate. The precipitate of $(C_9H_6ON)_3Al$ is weighed after drying at 120–140°.

(b) In the filtrate from the aluminum precipitation beryllium hydroxide is precipitated by the addition of ammonia and ignited to the oxide.

Procedure

Reagent.—R. Berg,[8] F. L. Hahn[9] and I. M. Kolthoff[10] all worked with a 5% solution of oxine in 95% alcohol when precipitating aluminum. Kolthoff found the results with aluminum to be about 0.4% too low when thus precipitated. We confirmed these results and found the low values obtained to be due to the solubility of aluminum *o*-hydroxyquinoline in the warm dilute alcoholic solution from which it is precipitated. We therefore recommend that an acetic acid solution of oxine be used in the precipitation of aluminum and possibly also with other metals. Moreover, the acetic acid solution of the reagent has the added advantage over the alcoholic solution that it is more stable and may be kept for many weeks without change. The reagent is prepared by dissolving a

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[8] Berg, *J. prakt. Chem.*, **115, 178 (1927)**; *Z. anal. Chem.*, **70,** *341* **(1927); 71, 23 (1927).**

[9] Hahn, *Z. anal. Chem., 71,* **122 (1927).**

[10] *I. M.* Kolthaff, *Chem. Weekblad., 24,606* **(1927).**

sufficient amount of finely powdered o-hydroxyquinoline in 2 *N* acetic acid to form a 5% solution. Ten cubic centimeters of reagent thus prepared are sufficient to precipitate one millimole of aluminum.[11]

Determination of Aluminum.—The solution of aluminum and beryllium salts (containing not more than 100 mg. of either oxide per 100 cc.) which should be only slightly acid is warmed to 50–60° and treated with an excess of the acetic acid solution of oxine. A solution of 2 N ammonium acetate is slowly added until a permanent precipitate is obtained and then 20–25 cc. more of ammonium acetate is added to insure the complete precipitation of aluminum. When the aluminum o-hydroxyquinoline has settled, the liquid is poured through a Jena glass or porcelain filter crucible (more convenient to use in this case than a Gooch crucible). The precipitate is washed with cold water and dried at 120–140°. It then has the composition $(C_9H_6ON)_3Al$ and contains 11.10% of Al_2O_3.

Determination of Beryllium.—The filtrate from the aluminum precipitation is heated nearly to boiling and ammonium hydroxide is cautiously added to the liquid until it smells faintly of ammonia. The beryllium hydroxide thus precipitated is colored yellow or brown by adsorbed oxine. It is filtered off and washed thoroughly with a hot dilute solution of ammonium acetate containing a few drops of ammonium hydroxide. The precipitate may be dried directly over a low flame and ignited (without the addition of oxalic acid) in a platinum crucible over a blast lamp. The beryllium oxide thus obtained is somewhat more hygroscopic than the form ordinarily obtained by ignition of beryllium hydroxide precipitated in the absence of oxine and it must therefore be weighed quickly. The single deflection method of weighing, as described by P. H. M.-P. Brinton[12] may be advantageously used.

Analytical Results

The standard solution of aluminum used was prepared by weighing out potassium alum obtained by recrystallization of *a* very pure product. The beryllium nitrate solution employed was standardized by careful gravimetric analyses according to the method of Parsons, the platinum crucibles used being reweighed after ignition.

In solutions containing only aluminum, or aluminum in the presence of alkali salts, results of a high degree of accuracy are obtained by the use of an acetic acid solution of o-hydroxyquinoline, as the following table shows.

TABLE I

RESULTS OF ANALYSES

Al_2O_3 taken, g.	Weight of oxine ppt., g.	Al_2O_3 found, g.	Error, g.
0.02691	0.2420	0.02686	−0.00005
.02691	.2424	.02691	.00000
.02691	.2422	.02688	− .00003
.02691	.2424	.02691	.00000
.02691	.2416	.02682	− .00009
.02691	.2431	.02698	+ .00007

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[11] Most of the determinations were made with o-hydroxyquinoline obtained from the Amsterdamsche Superphosphaatfabrieken. A good product—though rather expensive—is put on the market by the Eastman Kodak Company.

[12] Brinton, THIS JOURNAL, 41, 1151 (1919).

The separation of aluminum and beryllium was carried out in volumes of about 200 cc. of original solution according to the directions given above.

TABLE II

SEPARATION OF ALUMINUM AND BERYLLIUM

Aluminum			Beryllium		
Al_2O_3 taken, *g*.	Al_2O_3 found, *g*.	Error, g.	BeO taken, *g*	BeO found, g.	Error, *g*
0 00834	**0.00844**	+0.00010	**0.1854**	**0.1863**	+0 0009
.02083	.02090	+ .00007	.1854	.1856	+ .0002
.02691	.02695	+ .00004	.2	...	
.02691	.02700	+ .00009	.1	...	. .
.02691	.02704	+ .00013	.1	...	...
.02691	.02688	− .00003	.0927	.0924	− .0003
.02691	.02706	+ .00015	.0927	.0924	− .0003
.1086	.1082	− .0004	.0927	.0929	+ .0002
.1086	.1084	− .0002	.0927	.0922	− .0005
.1086	.1084	− .0002	.0464	.0483	+ .0019
.1086	.1086	.0000	.0232	.0236	+ .0004
.1086	.1083	− .0003	.0464	.0469	+ .0005
.1628	.1620	− .0008	.0927	.0934	+ .0007

If ferric iron is present it will be precipitated with the aluminum. Two separations of beryllium from ferric iron were made. A solution containing 1 g. of ferric alum and 0.0927 g. of BeO in about 100 cc. was treated with an excess of oxine, as described in the aluminum precipitation, and the black ferric o-hydroxyquinoline was filtered off and beryllium determined in the filtrate in the usual way. The weights of beryllium oxide obtained were 0.0931 and 0.0937 g. The separation is therefore satisfactory.

Prom the table of results given above it will be seen that the weight of beryllium oxide found is a little high in most cases. This is partially to be ascribed to a slight solubility of aluminum o-hydroxyquinoline in water, which was found to be increased to some extent by beryllium salts. An excess of oxine will, however, reduce the solubility of the aluminum compound. Therefore in those cases where there is much beryllium and little aluminum present, it is advisable to add at least 50% of oxine in excess. In ordinary cases where aluminum, and not beryllium, preponderates, an excess of 10–20% of oxine is sufficient.

If the amount of beryllium is quite small, it is best to convert the oxide to the sulfate and weigh the latter. Anhydrous beryllium sulfate has already been proposed as a weighing form for beryllium by Taboury.[13] A few drops of sulfuric acid (1:1) are added to the oxide, and then the water and most of the excess sulfuric acid are evaporated off. The residue may be safely heated to constant weight at temperatures from 350 to 400°. Satisfactory results with known amounts of beryllium oxide have been obtained.

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[13] Taboury, *Compt. rend.*, 159, 180 (1913).

Summary

A simple and rapid method has been described for the separation of aluminum and beryllium by the use of an acetic acid solution of *o*-hydroxyquinoline. Beryllium is also separated from ferric iron by means of this reagent.

MINNEAPOLIS, MINNESOTA

A NEW DESIGN OF APPARATUS FOR THE MOVING BOUNDARY METHOD OF DETERMINING TRANSFERENCE NUMBERS[1]

BY EDGAR REYNOLDS SMITH[2]

RECEIVED APRIL 26, 1928 PUBLISHED JULY 6, 1928

During the past few years several designs of cells for the determination of transference numbers by the moving boundary method have been described.[3] In each of these, the boundary moves through a calibrated tube and the number of coulombs which pass through the circuit, while the boundary moves through a predetermined volume, is measured. The purpose of this article is to describe an apparatus which has two unique features. (a) A calibration of the measuring tube is not required. (b) After the boundary has traversed the length of the measuring tube, it can be returned to the starting point for a fresh determination. This operation can be repeated any number of times without changing the solutions.

Apparatus and Manipulation

The cell is shown in the figure. The boundary tube B (of approximately 0.3 cm. inside diameter), the electrode tube C and their connecting tube are filled with the solution to be measured. The tube H contains mercury and the remainder of the cell is filled completely with the indicator solution to a point well above the stopcock D. The method of forming the boundary, except for a slight modification, is the one described by MacInnes and Smith.[3a] In this modified cell the boundary tube B projects about 0.3 cm. into the indicator reservoir I and its opening is ground flat, thus presenting a true surface for contact with the plunger F. The latter is fitted with a rubber cap to which two small hooks are attached. Rubber bands stretched between these hooks and the glass projections J serve to hold the plunger firmly against the top of B before beginning the measurement. For precise work it would be safer to sub-

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[1] Publication approved by the Director of the Bureau of Standards of the U. S. Department of Commerce.

[2] Associate Chemist, Bureau of Standards.

[3] (a) MacInnes and Smith, THIS JOURNAL, 45, 2246 (1923); (b) Smith and MacInnes, *ibid.*, 46, 1398 (1924); (c) MacInnes and Brighton, *ibid.*, 47, 994 (1925); (d) Smith and MacInnes, *ibid.*, 47, 1009 (1925); (e) MacInnes, Cowperthwaite and Huang, *ibid.*, 49, 1710 (1927).

stitute ground glass stoppers in place of the rubber stoppers on the closed side of the apparatus.

As soon as the electrical circuit is closed, the rubber bands are removed and, with stopcock E closed and D open, F is gently loosened. When the boundary appears in B, F is carefully raised to about a centimeter above the top of B. Stopcock D is then closed and E is opened. Just as the boundary reaches a mark m, a coulometer is connected into the circuit. After the boundary has moved through a suitable volume, depending on the deposit desired in the coulometer, mercury is slowly withdrawn from H into a weighing flask until the boundary has been raised slightly above m. When the boundary again crosses m, the coulometer is disconnected and at the same time a second coulometer can be connected into the circuit for a second measurement.

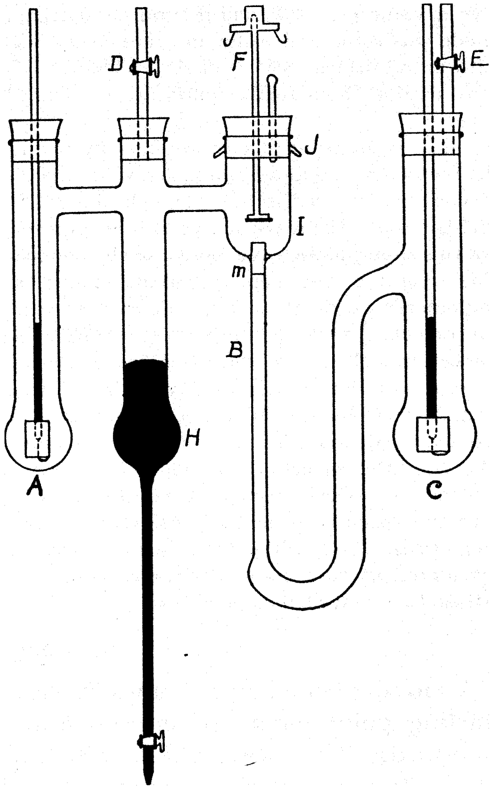


Fig. 1

From the weight of mercury and of the deposit in the coulometer, the transference number is calculated by means of the equation[3d]

$$T = \frac{VF}{\phi Q} \pm \frac{\Delta v}{4} \qquad (1)$$

where V is the volume through which the boundary has moved (the observed weight of mercury divided by its density), ϕ is the equivalent volume of the measured solution, F is the faraday, Q is the number of coulombs passed and Δv is the correction[4] for the volume change per faraday due to the electrode reaction and to transference in the closed side of the cell.

Experimental Test

A preliminary experiment showed that the boundary could be raised any desired number of times without distortion provided the rate of withdrawal of the mercury was not fast enough to produce turbulence. An

[4] Lewis, This Journal, 32, 862(1910).

attempt to hold the boundary stationary at a definite position by withdrawing the mercury at exactly the rate of motion of the boundary was abandoned because of the constant attention required.

Since the object of this investigation was to test the practicability of the apparatus, a measurement of the cation transference number of **0.1** weight normal potassium chloride was performed with **0.065** weight normal lithium chloride for the indicator solution, This combination has been well investigated by other methods[3,ab,c,d] which give a value of **0.492,** and it furnishes a reliable check on the present method. The anode was a piece of platinum gauze coated with silver and the cathode was the same with an additional coating of silver chloride. Dried salts of analytical reagent quality were used without further purification. The silver coulometer was of the porous cup type.

The coulometer was thrown into the circuit when the boundary reached m. After the boundary had moved through a volume of about 1 cc. it was raised and then allowed to continue down the tube through about **1.7** cc. It was then raised to a position slightly above the mark and when it again reached m the coulometer was disconnected. By this manipulation the motion of the boundary after having been raised is included. The weight of the mercury withdrawn was **36.65** g. and the silver deposited in the coulometer weighed **0.0588** g. From these weights the values of V/ϕ, F/Q and of T_K (uncorrected) were, respectively, **0.0002688, 1835** and **0.493.** Since the anode side of the cell was closed, the correction ($\Delta v/\phi$ in equation **1)** to be applied in this case is calculated as follows. Per faraday at the anode, **1** molecular weight of silver chloride is formed. 1 atomic weight of silver disappears and T_{Li} equivalents of lithium chloride are lost by migration. The accompanying volume change is an increase of approximately **14** cc. and the correction, which in this case is appreciable, amounts to **0.001** and must be subtracted. The corrected value of the transference number is therefore **0.492.** identical with the value by other methods. However, the experiment was carried out at room temperature **(22°)** without the use of a thermostat, and the result obtained is not to be considered as an accurate determination of the transference number but merely as a satisfactory test of the apparatus.

Summary

A moving boundary cell in which the boundary may be returned to the starting point for a new measurement any number of times has been described. The measurements with this apparatus are independent of any tube calibration. The method consists in closing one side of the cell and withdrawing mercury from the closed side so as to oppose the motion of the boundary. The mercury withdrawn is weighed to obtain the volume through which the boundary has passed.

WASHINGTON, D. C.

[151st Contribution from the Color and Farm Waste Division, Jointly with Soil Fertility Investigations, Bureau of Chemistry and Soils, United States Department of Agriculture]

SPECTROPHOTOMETRIC DETERMINATION OF HYDROGEN ION CONCENTRATIONS AND OF THE APPARENT DISSOCIATION CONSTANTS OF INDICATORS.

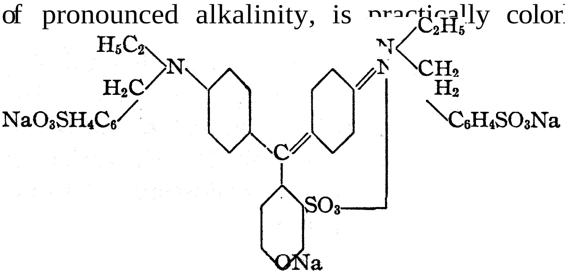
V. FAST GREEN F C F

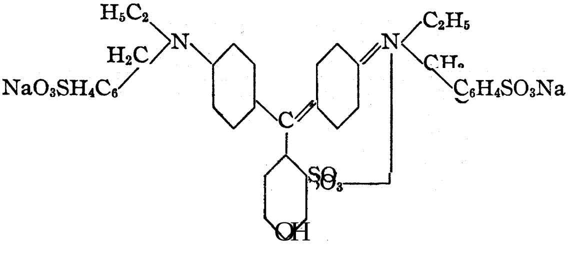
By W. C. Holmes and E. F. Snyder

Received April 30, 1928 Published July 6, 1928

Fast green F C F, or p-hydroxyerioglucine A (C. I. No. 671), is the most recent addition to the group of artificial coloring matters, the use of which is sanctioned in coloring foods.[1] It appears probable, also, that it will prove to be a very valuable biological stain.[2] The dye undergoes several color transformations with variation in hydrogen ion concentration. Since these phenomena might, in some measure, affect its utility in the application referred to and might, on the other hand, render it of use in indicator practice, their investigation was undertaken.

The tetrasodium salt of the dye, which is formed under conditions of pronounced alkalinity, is practically colorless. The trisodium salt is blue, having an absorption band with a maximum at approximately 611 $m\mu$. In passing from about P_H 10 to about P_H 6, the dye is transformed to the disodium salt which is green and has an absorption band with a maximum at approximately 628 $m\mu$. A further decided modification in color is formed in the region of pronounced acidity, consequent upon acid salt formation at the unsaturated amino group of the





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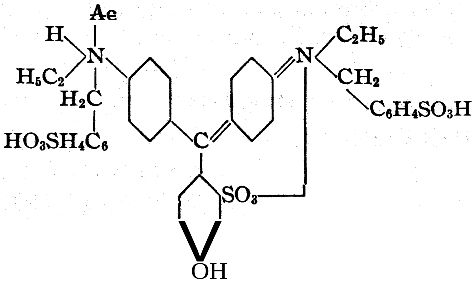
[1] H. Johnson and P. Staub, *Ind. Eng. Chem.*, 19, 497 (1927).

[2] R. Haynes, *Stain Technology*, 3, 40 (1928).

dye. The polyacidic salt formed is yellow and is doubtless to be considered as a yellow of the second order.



The two dissociation ranges of possible indicator utility are those of **the** polyacidic salt and of the phenolic salt.

The acid indicator range of the dye was investigated only in a preliminary manner. It was found that the conversion to the polyacidic dye salt was very nearly but not quite complete at P_H^{-1}. Spectrophotometric measurements carried out with buffered solutions of the dye over the range between P_H 0.87 and P_H 2.00 gave calculated values for apparent dissociation constants which increased with each step in the reduction of the acidity of the solution. Two intermediate products are formed in passing from the polyacidic salt of the dye to its disodium salt; the color acid and the monosodium salt. It was evident that the dissociation ranges of these various products overlapped and that their dissociation constants could not be determined by the methods at hand. It would have been possible to carry out an arbitrary calibration of a spectrophotometric ratio against hydrogen ion concentration in this region, but this was not undertaken, since the preliminary data indicated that the color of the dye was distinctly less sensitive to minor variation in acidity than is that of sulfonephthaleins available for employment in the same region.

The alkaline indicator range was investigated more thoroughly. The equipment and technique employed were those outlined in previous papers.[3] The ratio of the extinction coefficients of the solutions at 600 mμ to their extinction coefficients at 640 mμ was selected as the standard spectrophotometric ratio. Since a ratio of this type (R_2) is unaffected by variation in indicator concentration, no effort was made to avoid minor variation in that particular. All solutions, however, contained approximately 17.3 parts of dye per million parts of solvent. The temperature at which the spectrophotometric measurements were made was approximately 29°, and the Sørensen values of solutions recorded below have been corrected, when necessary, to conform to that temperature.

The dissociation of the indicator with increasing alkalinity appears normal until approximately P_H 9.8 is reached, at which point the forma-

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[3] Holmes and Snyder, This Journal, 47, 221 (1925).

TABLE I

STANDARDIZATION OF FAST GREEN F C F AGAINST SØRENSEN VALUES

PH	E at 600 mμ (Av.)	E at 640 mμ (Av.)	R_2	PH	E at 600 mp (Av)	E at 640 mμ (Av.)	R_2
6.14	1.18	1.50	0.79	8.55	1.425	1.02	1.40
6.68	1.21	1.46	.83	8.81	1.47	.97	1.52
7.12	1.26	1.43	.88	9.02	1.51	.95	1.59
7.62	1.29	1.31	.98	9.53	1.53	.90	1.69
7.82	1.30	1.25	1.04	9.80	1.54	.88	1.74
8.03	1.33	1.18	1.12	10.06	1.52	.85	1.77
8.22	1.37	1.12	1.23	10.41	1.50	.83	1.80
8.41	1.40	1.05	1.34	10.91	1.46	.805	1.81

tion of the trisodium salt is about 98% complete. Beyond that point it is evident that the further formation of the trisodium salt is accompanied by conversion of trisodium salt into the colorless tetrasodium salt. That circumstance is without effect upon spectrophotometric: application but renders suitable precautions advisable if the indicator is used in conjunction with drop ratio colorimetric practice. In drop ratio technique it is recommended that the color standards be prepared with buffer solutions of *PH* **9.8** and *PH* 6.5, whereby the indicator will be obtained in approximately 98% of its respective forms. Error will result if the alkalinity specified is exceeded.

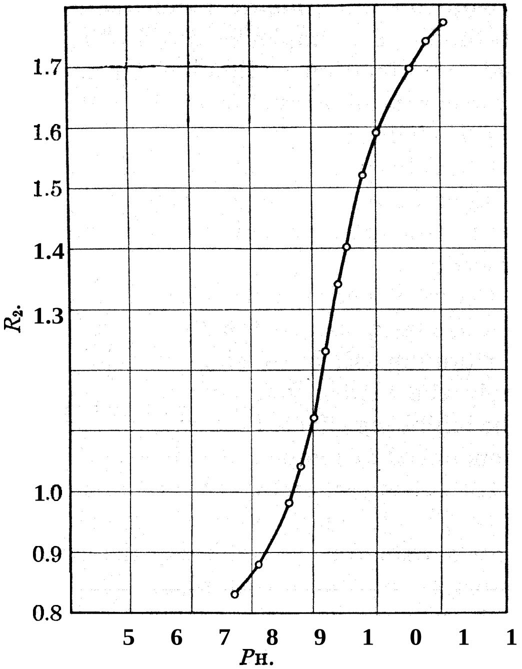

Fig. 1.—Fast green F C P. $R_2 = E$ at 600 mμ/E at 640 mμ. Temperature, 29° alkaline range.

The apparent dissociation constant of the indicator in this range is approximately 8.1(5). This calculated value was checked by measuring the combined absorptions of two solutions at *PH* 9.8 and *PH* 6.5, respectively, contained in cells of equal thickness.

Spectrophotometric technique in the alkaline range of Fast Green F C F is slightly less accurate than with such other indicators as have been investigated previously. Minor discrepancies were noted in duplicate determinations, which arose, apparently, from readjustments in physical equilibria, and the spectral interval between the bands of the dye forms is smaller than is desirable. Whereas, however, the sulfonephthaleins are to be preferred in general indicator application, Fast Green F C F may well prove useful under some circumstances.

Summary

Spectrophotometric data are supplied for the determination of hydrogen ion concentrations over the PH range between 6.7 and 10.0 with Fast Green F C F.

The apparent dissociation constant of the dye in this range is approximately 8.1(5) at 29°.

WASHINGTON, D. C.

NOTE

Note on Colorimetric Estimation of Titanium by Hydrogen Dioxide Method.—The employment of hydrogen dioxide as reagent in the colorimetric estimation of titanium compounds, in acid solution, constitutes an accurate and rapid method for the determination of small quantities of this element.

It has been ascertained[1] that the presence of phosphoric acid produces a slight fading of the yellow to orange coloration, even when present in small amounts, rendering corrections essential to the accuracy of the procedure.

During experimental work undertaken and carried out by the writer, the fact has been observed that the addition of uranium acetate to the solution of titanium salt in solutions containing free hydrogen ions eliminates entirely the tendency to fading, at temperatures ranging from 20 to 50°. The inhibiting effect of the uranium compound upon the $PO_4^{\equiv}$ ion is not so pronounced at temperatures in excess of the maximum figure furnished.

It has been found that the uranium compound, in the proportion of 1 cc. of 0.1% solution to each 0.1 mg. of the element under examination, is most satisfactory in stabilizing the coloration produced by the action of hydrogen dioxide on titanium salts in solutions containing phosphoric acid, thus counteracting the tendency of the acid in question to decrease the intensity of the original coloration obtained.

The effect of the uranium acetate solution is independent of the amount or quantity of phosphoric acid or its compounds present in the solution under investigation.

CONTRIBUTION FROM THE
CHEMICAL LABORATORY OF THE
BUREAU OF STANDARDS, DEPARTMENT OF PUBLIC WORKS
CITY OF BALTIMORE, MARYLAND

FREDERICK G. GERMUTH

RECEIVED APRIL 10, 1928
PUBLISHED JULY 6, 1928

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[1] P. Faber, *Z. anal. Chem.*, 46, 277 (1907).

[CONTRIBUTION FROM THE DIVISION OF CHEMISTRY, AGRICULTURAL EXPERIMENT STATION, STATE COLLEGE OF WASHINGTON]

AN INVESTIGATION OF THE HYPOTHETICAL COMBINED PENTOSE AND THE SO-CALLED FREE PENTOSE WITH INFERENCES ON THE COMPOSITION OF PECTIN

BY RONALD B. MCKINNIS

RECEIVED JANUARY 5, 1928 PUBLISHED JULY 6, 1928

Introduction

In connection with a study of the carbohydrate changes in apples, a question arose as to the pentose content. A study of the literature revealed the fact that very little had been done by other workers. The results obtained from this investigation point to some very significant and interesting facts concerning pectin and pentose.

Occurrence

Pentoses are commonly assumed to be components of leaves and other portions of plants. Spoehr[1] states that the existence of free pentoses in leaves is entirely uncertain. Colin and Franquet[2] question the findings of Davis and Sawyer and state that pentoses, if present at all, are there in very slight quantity.

The pentoses are widely distributed in a hypothetical combined form as components of complex substances such as glucosides, nucleinic acids and most commonly as anhydride-like condensation products of unknown molecular weight and structure.

On preliminary inspection it seems probable that the main source of pentose in apples would be the pectins and hemicelluloses. The existence of free pentoses would, then, be dependent upon the hydrolysis of the pectins.

Method of Determining Pentoses

Although many methods have been used for determining pentoses, none is entirely satisfactory. The method used in this work is similar to the Official Method,[3] with the exception that steam is slowly passed through the mixture to carry off the furfural, and at the same time maintain the volume of the mixture more constant. Distillation is stopped when the distillate fails to give a red color with freshly prepared aniline acetate test paper. Phloroglucinol is used to determine the furfural.

Free Pentoses

It is evident that before estimating free pentoses there must first be made a separation from pectin, pectic acids and galacturonic acids, be-

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[1] Spoehr, "Photosynthesis," A. C. S. Monograph, Chemical Catalog Co., New York, 1926, pp. 189–194.

[2] Colin and Franquet, Bull. *soc. chim. biol.*, 9, 114 (1927).

[3] "Official and Provisional Methods of Analysis," U. S. Dept. of Agr., Bur. of Chem., *Bull.* No. 107, 54–55 (1912).

cause these give a considerable yield of furfural. This separation can probably be best obtained by extraction with 95% alcohol, keeping the concentration of the alcohol on the apples at least 80%. The free pentoses will be found in the alcohol extract along with the hexoses. Such an extract, from Delicious apples, failed to give an estimable precipitate of furfuralphloroglucide. This is significant as it shows that free pentoses are absent, or are present in only small amounts.

Combined Pentoses. Pentoses in Pectin

In estimating the total, or combined pentoses, an error will result due to the furfural from the pectin. Various workers, but especially Ehrlich[4] and Dore,[5] have shown that pectin and the galacturonic acids yield considerable quantities of furfural. All pectic substances contain galacturonic acid as an essential constituent.

Due to the fact that pectin yields furfural on distillation with hydrochloric acid, it has generally been assumed that pectin contains a pentose, probably arabinose. Nanji, Paton and Ling[6] include one arabinose molecule in their hexa-ring formula for the structure of pectin.

Ahmann and Hooker[7] state that the pentose of pectin probably does not exist as such, but is a decomposition product of galacturonic acid, which in turn is derived from pectin.

According to Ehrlich,[4] even so mild an hydrolysis as boiling with water splits off the araban portion of the pectin complex in a form soluble in 70% alcohol. Since all ordinary pectin preparations are produced by a treatment at least as drastic as boiling with water, it would appear that the arabinose-containing fraction of pectin could be leached out by digesting in 70% alcohol. The furfural yield of the residue might then be a measure of the galacturonic acid content and the furfural yield of the extract a measure of the pentose. Dore,[5] however, found that the furfural yield of the residue varied and that after two successive digestions the yield was much less and constant.

According to Nanji, Paton and Ling,[6] in their hexa-ring formula for pectin, arabinose is within the ring. For this reason it does not seem probable that arabinose within could be split off with 70% alcohol. According to Dore,[5] an extraction with 70% alcohol might extract arabinose extraneous to the ring. His results show that this is possible, as his furfural yields vary accordingly.

If the furfural error due to galacturonic acid could be found, an estimation of pentose would be possible. One molecule of galacturonic acid will

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[4] Ehrlich, *Chem.-Ztg.*, **41,** 197 (1917).

[5] Dore, THIS JOURNAL, 48, 232 (1926).

[6] Nanji, Paton and Ling, *J. Soc. Chem. Ind.*, **44,** 253T (1925).

[7] Ahmann and Hooker, *Univ. of Missouri Agr. Expt. Sta. Res. Bull.*, 1925, p. 77.

theoretically yield either one molecule of mucic acid or one molecule of furfural.

$$\mathrm{COH(CHOH)_4COOH} \xrightarrow{\mathrm{HNO_3}} \underset{\text{mucic acid}}{\mathrm{COOH(CHOH)_4COOH}}$$

$$\mathrm{COH(CHOH)_4COOH} \xrightarrow{\mathrm{HCl}} \underset{\text{furfural}}{\mathrm{C_4H_3O.CHO}} + \mathrm{CO_2} + \mathrm{3H_2O}$$

The furfural yield of the galacturonic acid could be estimated from the yield of mucic acid if we knew what fraction of the theoretical yield would be obtained in practice and that no galactose would take part in the reaction. Interference is quite probable since galactose is included in the hexa-ring formula of the pectin molecule. The estimation of galacturonic acid by determining the mucic acid yield would, therefore, be unsatisfactory.

The amount of carbon dioxide evolved, however, is theoretical and provides an accurate estimation of the galacturonic acid. This method is specific for the glucuronic acids and it can be assumed that the other isomeric glucuronic acids are absent.

Method of Determining Galacturonic Acid

For the determination of galacturonic acid, a modification of the Lefevre-Tollens method for glucuronic acid was used. Briefly stated, the method consists of decomposing the substance by heating with 12% hydrochloric acid and absorbing the evolved carbon dioxide in scrubbing towers containing a known volume of standard barium hydroxide solution. A current of carbon dioxide free air drawn by suction carried the carbon dioxide away from the surface of the liquid through a reflux condenser, which returned the condensable matter. For precaution, an absorption tower filled with granulated zinc was placed between the condenser and the carbon dioxide scrubbing towers. After the scrubbing towers came a guard tube of soda lime and an expansion chamber which was connected with the vacuum supply through a release valve which served to regulate the current.

Correlation between Galacturonic Acid Content and Furfural Yield

The samples used in all determinations were from ripe Winesap apples, grated and thoroughly mixed to get comparable samples. These samples, of 25 g. each, were preserved in sufficient strong alcohol to keep the alcohol concentration above 75%. All determinations were made on the whole 25g. sample, the alcohol being slowly evaporated off just before use.

The following results were obtained with the furfural distillation method already mentioned, without alcohol extraction of the phloroglucide.

Sample	1	3	4	5	Avg.
Furfural, g.	0.1013	0.1163	0.1025	0.1132	0.1083

With alcohol extraction lower results were obtained.

Sample	6	7		
Furfural, g.	0.0950	0.0790	Av.	0.0870

The galacturonic acid determinations gave the following results

Sample	9	10		
Carbon dioxide, g.	0.1125	0.1200	**Av.**	0.1162

0.1162 g. of carbon dioxide would be derived from 0.4885 g. of digalacturonic acid.

To check the actual furfural yield, Ehrlich's digalacturonic acid was isolated as follows. A water extract of the apples was prepared by repeated digestion with hot water. The apple extract was saponified by the addition of sodium hydroxide and boiled with hydrochloric acid. This, according to Ehrlich,[4] gives digalacturonic acid. These processes were repeated and the precipitate was dried and weighed. The procedure was similar to that used by Rowell,[8] for the determination of pectin. To the 200 cc. of apple extract obtained from 25 g. of apples, was added 10 cc. of 10% sodium hydroxide and the mixture was allowed to stand for fifteen minutes. Twenty cc. of 10% hydrochloric acid was then added. The mixture was boiled for five minutes and filtered on a fluted filter paper; the precipitate, washed with a small amount of hot water, was returned to the beaker and made up to 100 cc. Treatment with base and acid, boiling and filtration was repeated. Two hundred cc. volume was used for the boiling with acid. The precipitate was washed with hot water until the filtrate showed only a slight acidity, transferred to a tared Gooch crucible, dried first at 55-60', then overnight at 95° and weighed. The average yield from the 25g. samples of apples was 0.0955 g.

The acid has been shown by Ehrlich to be free from pentoses. It is prepared in the same way as the pectic acid of Wichmann and Chernoff, which Nelson[9] has shown to be identical with the digalacturonic acid of Ehrlich and Sommerfeld.[10]

Furfural determinations on the digalacturonic acid gave results as follows.

Sample, g.	0.0942	0.0968	Av.	0.0955
Furfural, g.	0.0166	0.0164	**Av.**	0.0165

0.0955 g. of digalacturonic acid would give a theoretical furfural yield of 0.0495 g., which makes the actual yield of 0.0165 g., 33.3% of the theoretical yield. From the 0.4885 g. of digalacturonic acid found by the carbon dioxide determination, a theoretical furfural yield of 0.2534 g. would be obtained. Actually the yield would be 33.3% of the theoretical or 0.0844 g. This checks well with the actual yield of 0.0870 g. found.

This relation of digalacturonic acid to pentose is more clearly shown by calculating the ratio of the furfural and carbon dioxide yields for the whole apple and the digalacturonic acid. The ratio, furfural/carbon dioxide

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[8] Rowell, State College of Washington, Master's *Thesis*, 1926.

[9] Nelson, THIS JOURNAL, 48,2412 (1926).

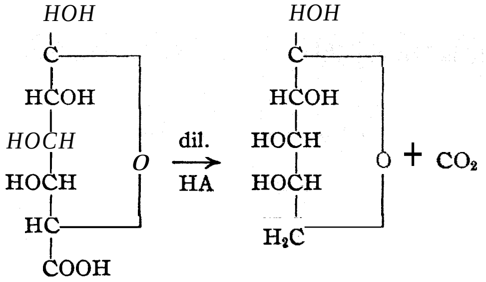
[10] Ehrlich and Sommerfeld, *Biochem. Z.*, 168,263 (1926).

for the apple sample was found to be 0.75, and for the digalacturonic acid, 0.74.

From this it seems evident that the apples contained no pentose whether free or combined and that the assumed pentose of pectin does not exist.

The Significance of Galacturonic Acid

It has been shown that pectin does not contain a pentose sugar. Ehrlich, however, has isolated by boiling with dilute organic acids, d-rotatory *l*-arabinose. This statement is not contradictory to what has just been found. With dilute weak acid hydrolysis, d-galacturonic acid very probably gives *l*-arabinose, as follows.



d-galacturonic acid *l*-arabinose

If stronger acid is used, furfural is formed from the arabinose. This accounts for the pentose confusion as being due to the fact that galacturonic acid with dilute acids gives 1-arabinose, while with more concentrated acid it gives furfural.

The digalacturonic acid of Ehrlich is probably a compound formed from d-galacturonic acid, as follows.

$$2COH(CHOH)_4COOH \longrightarrow [COH(CHOH)_4COOH]_2-H_2O$$

d-Galacturonic acid Digalacturonic acid

Pectin is probably composed of a number of these groups, with part or all of the carboxyl groups occupied by methoxyl or other esterifying or salt-forming groups, though it is not certain. The work is being extended to other fruits and the isolation and properties of digalacturonic acid are being investigated.

Summary

It has been shown that apples and apple pectin contain no pentose, either free or combined. The furfural comes from arabinose, which in turn is derived from the galacturonic acid. Arabinose is only an intermediate product in the formation of furfural from galacturonic acid. With weak acids some arabinose can be obtained before it is decomposed. The digalacturonic acid is probably the nucleus unit of the pectin molecule.

UNIVERSITY OF PITTSBURGH, PITTSBURGH, PENNSYLVANIA

[CONTRIBUTION FROM THE SCHOOL OF MINES AND METALLURGY, UNIVERSITY OF MISSOURI]

THE CATALYTIC ACTION OF NEUTRAL SALTS. THE EFFECT OF NORMAL ALKALI SULFATES ON ALKALI ACID SULFATES IN THE KETONIC SPLITTING OF ETHYL ACETOACETATE

BY E. A. GOODHUE AND H. L. DUNLAP

RECEIVED FEBRUARY 2, 1928 PUBLISHED JULY 6, 1928

In this work the action of normal potassium and sodium sulfates has been investigated with two concentrations of their corresponding acid salts. The compound used for studying this effect is ethyl acetoacetate, which gives carbon dioxide upon its ketonic splitting in an acid solution, thus serving as a means for carefully following the course of the reaction. Also, this reaction is irreversible, as one of the products of the reaction is removed as a gas.

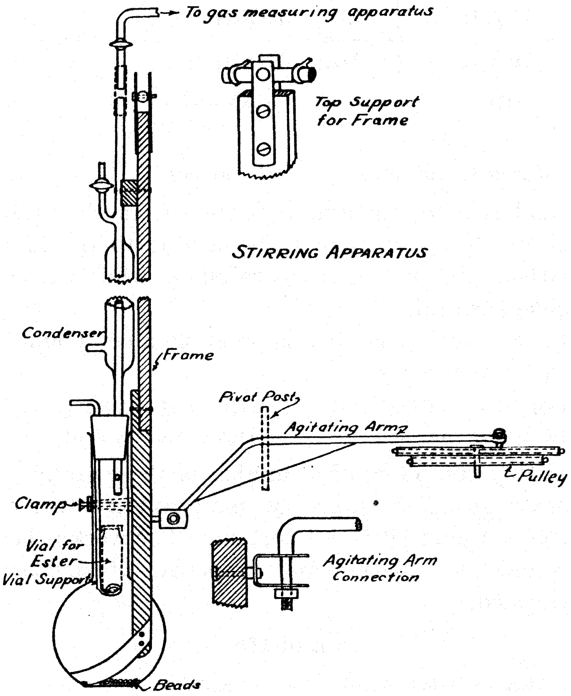


Fig. 1.

Bürki[1] used ethyl acetoacetate in his study of the hydrolysis reactions with sulfuric, hydrochloric and nitric acids and found that this ester was completely decomposed above 40°. The advantage in using this ester

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[1] Bürki, *Helv. Chim. Acta*, 1, 231 (1918).

is that the carbon dioxide evolved can be easily measured to follow the course of the reaction over a long period of time. The classical method[2] of halting the reaction, if this is possible, and determining by titration the amount of ester hydrolyzed at intervals, is subject to considerable error.

Experimental Part

Materials.—The best grade of ethyl acetoacetate was redistilled under reduced pressure and the middle half of the distillate used. This was stored in amber colored bottles, each containing enough for a few determinations, in order not to expose the ester to air over too long a period. The ethyl alcohol was dehydrated over lime and anhydrous copper sulfate in the usual manner.

The best grades of sodium and potassium sulfates and acid sulfates were each recrystallized from water several times, dried to constant weight and analyzed for their sulfate content. The various stock solutions of these salts were analyzed for their sulfate content to make sure that all solutions were of known concentrations. Aliquot parts of these stock solutions were taken for dilution to their required normalities.

Apparatus.—The apparatus used in the work was developed by Dr. C. E. Boord and H. L. Dunlap in an unpublished work on the study of alkali and alkaline earth chlorides with hydrochloric acid on the hydrolysis of this same ester. The thermostat was electrically heated and the temperature controlled to a tenth of a degree. The flasks were made specially for this work, having a capacity of two hundred cc. and with necks five inches in length. These were connected to a condenser (Fig. 1) by means of a two-holed rubber stopper, one for the condenser and the other for the stiff platinum wire which held the vial containing the ester. The flask and condenser were firmly fastened to a frame which was suspended at the top, the lower part being connected to a pivoted arm from a pulley. In operation, this gave the flask a circular motion in the bath and thus agitated its contents. The neck of the flask extended three inches above the thermostat liquid and thus permitted the watching of the

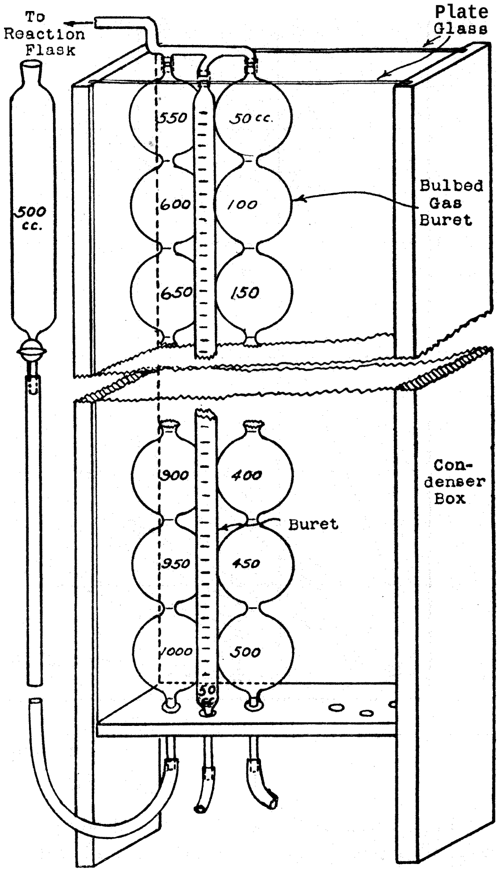

Fig. 2.—Gas measuring apparatus.

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[2] Ostwald, *J. prakt. Chem.*, **28**, 449 (1883).

vial before its release. The side arm at the top of the condenser permitted the adjusting of the pressure within the apparatus before tripping the ester into the solution for starting the reaction.

The gas measuring apparatus (Fig. 2) is a modified Blier-White chain of bulbs type. A three-way manifold connects all compartments of the condenser and leveling bulbs. These gas measuring compartments were all carefully calibrated and the volume of gas at any time could be read to one-tenth of a cc. The whole gas train was immersed in a water-filled box which had two opposite sides of glass. The temperature of the surrounding water was recorded with each reading for correcting the volume of the gas to standard conditions. Two sets of flasks were used in the thermostat, thus permitting of two determinations at the same time. Readings were taken at five-minute intervals.

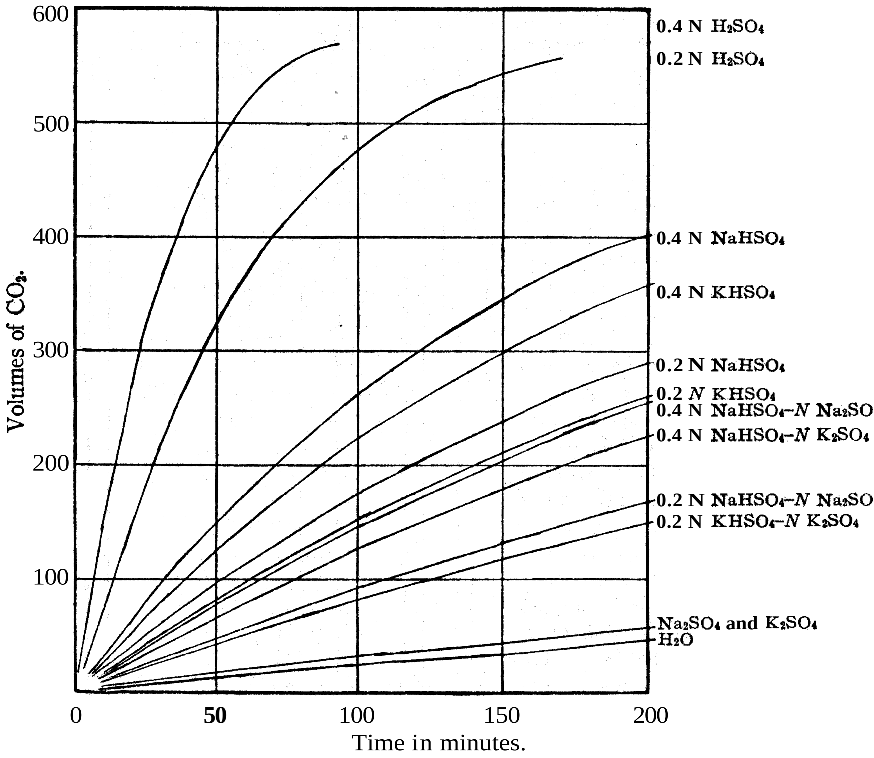

Fig. 3.—Hydrolysis of *N*/2 ester at 90°.

Experimental Procedure.—The desired concentration of salts was placed in the flasks along with one cc. of alcohol and water to make 46.8 cc. and when the ester (3.2527 g.) was introduced, this made 50 cc. of a half molar solution of ester. The capped vials containing the ester were held in place until the temperature of the flask and contents became that of the bath. After adjusting the measuring bulbs and starting agitation, the outside connection was closed, the vial dropped and the zero reading taken. As soon as 50 cc. of gas is collected in the burets, this is simply transferred to one of the 50-cc. bulbs. Checks were run in all cases with an allowable variation of three-fourths of one per cent. Vapor pressure corrections were made in all cases as that of pure water, which is in slight error but it is the same for all determinations.

The volume of carbon dioxide was reduced to standard conditions and graphs were plotted for the five minute intervals. The data are condensed in Tables I to VII. The reaction constant is calculated according to the formula

$$K = \frac{1}{t} \log_{10} \frac{560.3}{560.3 - V_t}$$

where V_t represents the corrected volume of carbon dioxide collected in time "t" and 560.3 is the volume of the gas which could be obtained by complete decomposition of the ester. The third column gives the various values for "k," the constant for a first order reaction.

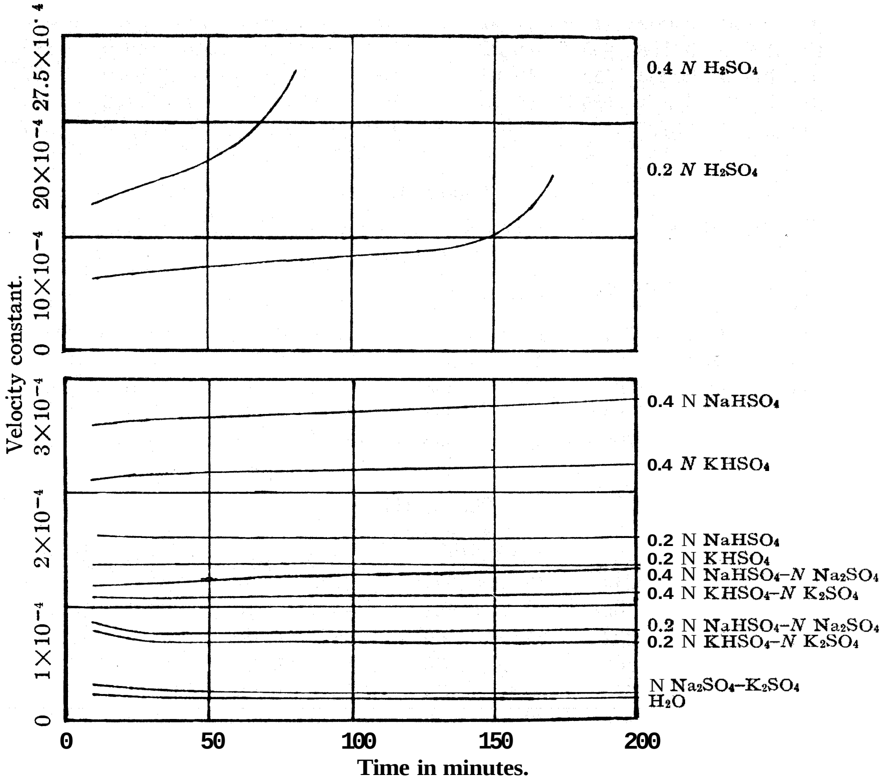

Fig. 4.—Reaction constants for hydrolysis of esters at 90°.

Data obtained with hydrolysis of the ester at 90° are shown graphically in Fig. 3 and the variation of the velocity constants with time is shown in Fig. 4. Similar curves are obtainable at other temperatures.

Discussion of Data.—It might be expected in the hydrolysis of the ester with pure acid that the reaction constant would increase with time as the more active hydrogen would be affected by the increasing concentration of the alcohol and acetone from the decomposition of the ester.

TABLE I

HYDROLYSIS OF N/2 ETHYL ACETOACETATE

	At 80° with					At 90° with			
	0.2 N H_2SO_4		0.4 N H_2SO_4			0.2 N H_2SO_4		0.4 N H_2SO_4	
Time, man.	CO_2	k X 10^3	CO_2	k X 10^3	Time, min.	CO_2	k X 10^3	CO_2	k X 10^3
25	94.0	31.90	173.6	64.42	10	75.7	6.304	142.1	12.70
50	179.1	33.45	309.0	69.65	30	213.2	6.932	358.1	14.75
100	311.0	35.17	466.7	77.71	50	316.6	7.231	478.8	16.74
150	401.9	36.56	530.8	85.24	70	395.9	7.607	540.3	20.68
200	461.0	37.57	561.0	...	90	454.7	8.053	...	...

	At 95° with					At 95° with			
	0.2 N H_2SO_4		0.4 N H_2SO_5			Water alone		N Na_2SO_4	
Time, min.	CO_2	k X 10^3	CO_2	k X 10^3	Time, min.	CO_2	k X 10^3	CO_2	k X 10'
20	191.3	9.069	310.1	17.51	50	20.9	0.333	24.4	0.387
40	318.4	9.119	455.7	18.22	100	39.2	.315	46.9	.380
60	404.5	9.264	522.5	19.52	200	72.2	.300	85.0	.357
80	460.6	9.371	555.8	26.19	300	100.6	.287	114.2	.330
100	496.2	9.417	...	...	400	125.9	.276	139.9	.314

TABLE II

NEUTRAL SALT EFFECT ON ACID SULFATE IN HYDROLYSIS OF N/2 ETHYL ACETOACETATE

	At 80° with							
	0.2 N $KHSO_4$		0.2 N $KHSO_4$ N K_2SO_4		0.2 N $NaHSO_4$		0.2 N $NaHSO_4$ N Na_2SO_4	
Time, min.	CO_2	k X 10^3	CO_2	k X 10^3	CO_2	k X 10^3	CO_2	k X 10^3
25	24.1	0.764	11.8	0.370	27.3	0.868	12.5	0.395
50	48.1	.780	23.0	.364	54.6	.890	25.4	.403
100	93.6	.794	44.3	.358	105.2	.903	51.0	.410
150	133.6	.796	66.3	.364	150.5	.906	75.6	.420
200	172.5	.798	86.5	.365	191.7	.909	98.9	.421

TABLE III

	At 80' with							
	0.4 N $KHSO_4$		0.4 N $KHSO_4$ N K_2SO_4		0 4 N $NaHSO_4$		0.4 N $NaHSO_4$ N Na_2SO_4	
Time, min.	CO_2	k X 10^3	CO_2	k X 10^3	CO_2	k X 10^3	CO_2	k X 10"
25	37.0	1.195	17.6	0.554	44.4	1.434	20.7	0.657
50	74.1	1.232	35.5	.569	88.1	1.485	41.7	.672
100	141.5	1.264	69.2	.573	165.6	1.521	82.7	.694
150	200.3	1.278	100.9	.574	230.8	1.538	121.6	.708
200	250.0	1.285	132.6	.586	286.5	1.555	158.4	.721

TABLE IV

	At 90° with							
	0.2 N $KHSO_4$		0.2 N $KHSO_4$ N K_2SO_4		0.2 N $NaHSO_4$		0.2 N $NaHSO_4$ N Na_2SO_4	
Time, min.	CO_2	k X 10^3	CO_2	k X 10^3	CO_2	k X 10^3	CO_2	k X 10^3
25	42.2	1.360	22.4	0.709	49.8	1.617	24.5	0.777
50	81.6	1.367	42.5	.685	94.6	1.606	47.0	.761
100	150.4	1.357	80.4	.673	171.9	1.591	90.4	.764
150	209.0	1.358	115.0	.665	237.3	1.595	130 5	.767
200	260.7	1.359	149.1	.667	(292.8)[a]	(1.605)[a]	(167.3)[a]	(.770)[a]

[a] Extrapolated from graphs.

TABLE V

NEUTRAL SALT EFFECT ON ACID SULFATE IN HYDROLYSIS OF $N/2$ ETHYL ACETOACETATE

At 90° with

Time, min.	0.4 *N* $KHSO_4$		0.4 *N* $KHSO_4$ *N* K_2SO_4		0.4 *N* $NaHSO_4$		0.4 *N* $NaHSO_4$ N Na_2SO_4	
	CO_2	$k \times 10^3$	CO_2	$k \times 10^3$	CO_2	$k \times 10^3$	CO_2	$k \times 10^3$
25	65.0	2.142	33.5	1.071	78.8	2.633	37.3	1.197
50	123.6	2.164	65.4	1.078	148.0	2.664	74.1	1.230
100	222.6	2.198	124.3	1.089	260.4	2.714	141.3	1.262
150	299.7	2.210	176.7	1.097	345.6	2.777	202.1	1.295
200	359.2	2.225	225.0	1.112	(405.3)[a]	(2.791)[a]	(256.8)[a]	(1.331)[a]

[a] Extrapolated from graphs.

TABLE VI

At 95° with

Time, min.	0.2 *N* $KHSO_4$		0.2 *N* $KHSO_4$ N K_2SO_4		0.2 N $NaHSO_4$		0.2 *N* $NaHSO_4$ N Na_2SO_4	
	CO_2	$k \times 10^3$	CO_2	$k \times 10^3$	CO_2	$k \times 10^3$	CO_2	$k \times 10^3$
25	55.8	1.822	32.8	1.048	62.9	2.068	34.9	1.117
50	103.0	1.764	52.8	0.963	116.1	2.017	63.5	1.045
100	181.3	1.698	101.9	.872	199.5	1.912	111.2	0.961
150	243.8	1.654	139.0	.826	264.9	1.853	152.5	.919
200	(296.4)[a]	(1.634)[a]	(173.0)[a]	(.809)[a]	316.0	1.803	(189.0)[a]	(.894)[a]

[a] Extrapolated from graphs.

TABLE VII

At 95° with

Time, min.	0.4 N $KHSO_4$		0.4 *N* $KHSO_4$ *N* K_2SO_4		0.4 N $NaHSO_4$		0.4 *N* $NaHSO_4$ N Na_2SO_4	
	CO_2	$k \times 10^3$	CO_2	$k \times 10^3$	CO_2	$k \times 10^3$	CO_2	$k \times 10^3$
25	82.7	2.774	46.5	1.505	95.5	3.250	48.3	1.566
50	148.2	2.668	83.1	1.394	171.6	3.176	89.5	1.512
100	250.6	2.575	147.5	1.328	284.5	3.078	161.6	1.478
150	322.8	2.485	202.2	1.295	359.3	2.968	220.3	1.446
200	(379.2)[a]	(2.455)[a]	248.1	1.270	(408.0)[a]	(2.829)[a]	(266.0)[a]	(1.399)[a]

[a] Extrapolated from graphs.

TABLE VIII

TIME RATIO DATA FOR POTASSIUM SALTS

Temp., °C.	Concn.	Time to produce 75 cc. of CO_2, min.	Ratio	Time to produce 150 cc. of CO_2, min.	Ratio
80	0.2 N $KHSO_4$	80	0.465	...	...
	0.2 N $KHSO_4$, N K_2SO_4	172		...	...
	0.4 N $KHSO_4$	50	.459	...	...
	0.4 N $KHSO_4$, N K_4SO_2	109		...	...
90	0.2 N $KHSO_4$	46	.495	99	0.490
	0.2 N $KHSO_4$, N K_2SO_4	93		202	
	0.4 N $KHSO_4$	28	.483	63	.508
	0.4 N $KHSO_4$, *N* K_2SO_4	58		124	
95	0.2 N $KHSO_4$	34	.500	79	.476
	0.2 N $KHSO_4$, N K_2SO_4	68		166	
	0.4 N $KHSO_4$	22	.489	50	.490
	0.4 N $KHSO_4$, *N* K_2SO_4	45		102	
		Average 0.2 *N*	.487		.483
		Average 0.4 *N*	.477		.499

The greater the concentration of the acid, the greater we should expect the variation of this reaction constant. Data in Table I show this to be true.

The effect of the neutral salt on the rate of hydrolysis may be shown by calculating the ratio of the time required with the acid sulfate plus the neutral salt for producing 75 and 150 cc. of carbon dioxide, to the time required with the acid salt alone for producing the same quantity of carbon dioxide. In this manner the constituents in the solution will be the same at the time of comparison. These calculations are given in Table VIII for potassium salts and calculations for sodium salts give very similar results.

Summary

An apparatus has been devised for accurately measuring the velocity of reactions at higher temperatures and over a long period of time with substances evolving a gas.

The effects of normal sodium and potassium sulfates on their corresponding acid sulfates in the hydrolysis of ethyl acetoacetate have been studied at the temperatures of 80°, 90° and 95°.

ROLLA, MISSOURI

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF STANFORD UNIVERSITY]

CARBONIC ACID AZIDES

BY CHARLES VINTON HART[1]

RECEIVED FEBRUARY 13, 1928 PUBLISHED JULY 6, 1928

Accepting the view of Franklin and his collaborators to the effect that guanidine, cyanamide, dicyandiamide and melamine are ammono carbonic acids,[2] then the compounds named and formulated as follows: (1) guanylazide, $HNC(NH_2)N_3$, (2) cyanazide, NCN_3, (3) dicyanamidazide, $NCNC(NH_2)N_3$, (4) dicyandiazide, $NCNC(N_3)_2$, (5) cyanuramiddiazide, $C_3N_3(N_3)_2NH_2$ and (6) cyanurtriazide, $C_3N_3(N_3)_3$, are to be looked upon as carbonic acid azides.

Dicyandiiide, $NCNC(N_3)_2$, and Dicyanamidazide, $NCNC(NH_2)N_3$.—By the action of cyanogen bromide on sodium azide in water solution, Darzens[3] obtained a crystalline product, formed as he believed in accordance with the equation, $NCBr + NaN_3 = NCN_3 + NaBr$, to which he gave the name carbon pernitride.

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[1] An abstract of a thesis submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy at Stanford University, 1927. Dr. Hart died at Berkeley, California, April 12, 1928. This paper, for the most part, is in the form mitten by the author. (E. C. Franklin.)

[2] Franklin, THIS JOURNAL, 44, 486 (1922); 46, 2137 (1924); Burdick, *ibid.*, 47, 1485 (1925); Blair, *ibid.*, 48, 87, 96 (1926). See also Pinck and Blair, *ibid.*, 49, 509 (1927).

[3] Darzens, *Compt.* rend., 154,1232 (1912).

Looking upon cyanogen bromide and sodium azide as a carbonic acid bromide and sodium ammono nitrate, respectively, then Darzens' compound, represented by the formula, $\mathrm{N}\overset{-}{\underset{-}{\equiv}}\overset{+}{\underset{+}{\ddagger}}\mathrm{C}+\,-\mathrm{N}=\,\ddagger\mathrm{N}\overset{+}{\underset{+}{\ddagger}}\overset{+}{\underset{-}{=}}\mathrm{N}$, would be a mixed carbonic-nitric anammonide.[4]

It was in an attempt to determine whether Darzens' compound would be converted into a mixture of cyanamide and hydrazoic acid by the action of ammonia that the investigation described in this paper had its origin.

When, accordingly, a current of dry ammonia gas was passed into an ether solution of Darzens' compound, ammonium azide was obtained as expected but instead of cyanamide the other product of the reaction proved to be a hitherto unknown compound of the formula, $NCN(NH_2)N_3$, to which the name dicyanamidazide has been given.

The formation of this carbonic acid azide is readily explained on the assumption that Darzens had the dimer of cyanazide in his hands, which under the action of ammonia is ammonolyzed as represented by the equation, $NCNC(N_3)_2 + NH_3 = NCNC(NH_2)N_3$, into dicyanamidazide and hydrazoic acid.

Hydrolysis of Dicyandiazide.—Darzens states that when his azide is hydrolyzed with boiling water, carbamic acid azide is first formed, which, being unstable, decomposes to give carbon dioxide and hydrazoic acid. The present investigation showed the hydrolysis to proceed in conformity with the equation

$$NCNC(N_3)_2 + H_2O = NCNC(OH)_2 + 2HN_3 = CO_2 + 2HN_3 + H_2NCN$$

The hydrazoic acid and cyanamide were not formed quantitatively for the reason that a certain portion of each disappeared to form 5-aminotetrazole.[5] When a sodium hydroxide solution was used in place of pure water for the hydrolysis, sodium azide and sodium cyanamide were formed almost quantitatively.

Reduction of Dicyandiazide and Dicyanamidazide.—Dicyandiazide is reduced to dicyandiamide in accordance with the equation, $NCNC(N_3)_2 + 2H_2S = NCNC(NH_2)_2 + 2S + 2N_2$, when treated with hydrogen sulfide. It is interesting to interpret the reactions involved as consisting in the reduction of a mixed carbonic-nitric anammonide to a mixed carbonic-nitrous acid which breaks down into a carbonic acid and nitrous anammonide, $\mathrm{NCNC}\ddagger(-\mathrm{N}=\,\ddagger\mathrm{N}\overset{+}{\underset{+}{\ddagger}}\overset{-}{\underset{-}{=}}\mathrm{N})_2 + 4\mathrm{H} = \mathrm{NCNC}\ddagger(-\mathrm{N}=\,\ddagger\mathrm{N}+\,-\mathrm{NH}_2)_2$ or $\mathrm{NCNC}\ddagger(-\mathrm{NH}-\,+\mathrm{N}\ddagger=\mathrm{NH})_2 = \mathrm{NCNC}(\mathrm{NH}_2)_2 + 2\mathrm{N}_2$.

Dicyanamidazide is reduced to dicyandiamide in a similar manner.

Tests for the Presence of Azide Groups.—During the early part of

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[4] An ammonia analog of a purely hypothetical carbonic-nitric anhydride, $OC(ONO_2)_2$.

[5] Hantzsch and Vagt, Ann., 314,362 (1900).

this investigation, some doubt was entertained as to whether or not we were dealing with azide groups in these compounds since azides tend to revert to the more stable isomeric tetrazoles. Although sodium azide is formed when dicyandiazide and dicyanamidazide, respectively, are warmed with sodium hydroxide solution, yet the literature concerning tetrazoles does not seem to exclude similarly acting substances from being ring compounds.[6] Tetrazoles are generally very resistant to the action of alkali or acid, so the formation of sodium azide by treating a compound with sodium hydroxide solution would strongly indicate the presence of a free azide group and not a stable ring compound. It is highly desirable that we have some other test to substantiate this one.

Turrentine[7] has shown that hydrogen sulfide reduces hydrazoic acid in the cold to nitrogen and ammonia. Thiele[8] in his investigation of guanylazide reduced this compound to guanidine with hydrogen sulfide, sulfur being precipitated and nitrogen evolved while in a similar manner Hantzsch and Vagt[9] reduced carbamic azide to urea.

These reactions together with experience to the effect that all the azides described in this paper readily undergo reduction when treated with hydrogen sulfide lead us to emphasize two tests for proving the presence of azide groups, (1) heating the substance with sodium hydroxide solution to form sodium azide and (2) the reduction of the azide group to the amino group by means of hydrogen sulfide with simultaneous evolution of nitrogen and the precipitation of sulfur.

Dicyanphenylamidazide and Phenyldicyandiamide.—When an alcoholic solution of dicyandiazide is treated with aniline, dicyanphenylamidazide is formed as represented by the equation, $NCNC(N_3)_2 + C_6H_5NH_2 = NCNC(N_3)NHC_6H_5 + HN_3$.

Dicyanphenylamidazide is a phenyl ester of a carbonic acid azide containing one unreplaced acid hydrogen atom in consequence of which it should show distinctly the properties of an acid. A sodium salt, stable in the presence of water, has been prepared.

When treated with hydrogen sulfide dicyanphenylamidazide is reduced to phenyldicyandiamide, $NCNC(NH_2)NHC_6H_5$, which is probably identical with phenylcyanguanidine.[10]

α-Naphthylamine, methylamine, ethylamine and phenylhydrazine were found to enter into reactions with dicyandiazide. With the exception of dicyan-α-naphthylamidazide the products formed were not purified and analyzed.

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[6] See, for example, (a) Thiele and Ingle, *Ann.*, 287, 233 (1895), and (b) Freund and Schander, *Ber.*, 29, 2500 (1896); (c) Ott and Ohse, *Ber.*, 54, 179 (1921).

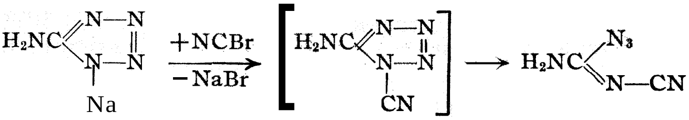
[7] Turrentine, THIS JOURNAL, 34, 285 (1912).

[8] Thiele, *Ann. Chem.*, 270, 48 (1892).

[9] Ref. 5, p. 355.

[10] Wheeler and Jamieson, THIS JOURNAL, 25, 721 (1903).

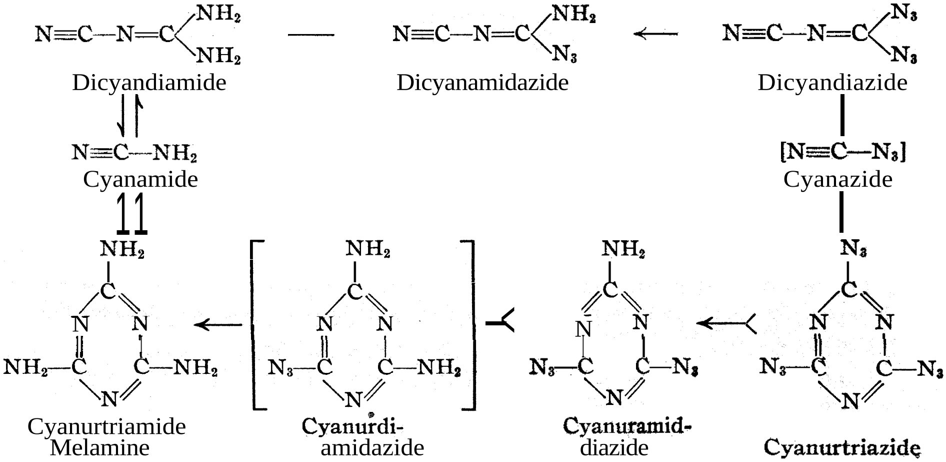
The Opening of a Tetrazole Ring.—An attempt was made to prepare 1-cyan-5-aminotetrazole, a tetrazole isomer of dicyanamidoazide (formula in bracket below) by treating the sodium salt of aminotetrazole with cyanogen bromide. Instead of the expected compound dicyanamidazide was obtained, the reaction taking the course represented by the scheme



Since aminotetrazole is formed from guanylazide by isomerization and the former is converted to dicyanamidazide by replacement of a hydrogen atom by a cyanogen group, the transformation of a compound possessing an azide group to a tetrazole, and from a tetrazole again to a compound having an azide group, has been effected.

Cyanurtriazide, $C_3N_3(H_3)_3$.—It will be recalled that cyanamide is capable of forming a trimolecular polymer known as melamine from which cyclic ammono carbonic acid three azides are theoretically derivable, depending upon whether it is considered as reacting with one, two or three molecules of hydrazoic acid.

Certain considerations led Ott, who first prepared this triazide, to assume that one or more tetrazole groupings might be present in the cyanurtriazide configuration. Referring to the two general tests already mentioned in this paper for the identification of azide groups, it is seen that the hydrolysis of cyanurtriazide into sodium azide and cyanuric acid by the action of hydroxide solution[6c] indicates the presence of three azide groups. In order to strengthen the evidence that cyanurtriazide contains three azide groups, it was subjected to the action of hydrogen sulfide, whereupon melamine was formed in accordance with the equation, $C_3H_3(N_3)_3 + 3H_2S =$



$C_3N_3(NH_2)_3 + 3S + 3N_2$. It must therefore be concluded that cyanurtriazide does not contain a single tetrazole group.

Cyanuramiddiazide, $C_3N_3(NH_2)(N_3)_2$ and Cyanurdichlorazide, $C_3N_3(Cl_2)N_3$.—The first compound was prepared by passing gaseous ammonia into an ether solution of cyanurtriazide; the second was obtained by treating one mole of cyanurtrichloride with one mole of sodium azide. Cyanuramiddiazide was reduced to melamine by the action of hydrogen sulfide.

Carbonic Acid Azides.—The scheme given above summarizes the relationships which have been established between three ammono carbonic acids and their azides.

Experimental Part

Preparation of **Dicyandiazide.**—To a solution of 25 g. of sodium azide in 100 cc. of water maintained at 0°, 45 g. of freshly prepared cyanogen bromide was added in small amounts with continuous stirring. After all of the cyanogen bromide was dissolved, the flask was removed from the ice-bath and allowed to stand three or four hours at room temperature, whereupon a colorless or slightly yellow oil separated at the bottom of the flask. The oil was extracted with alcohol free ether, washed once with a little water and then dried over anhydrous sodium sulfate. After one hour the ether solution was filtered into several evaporating dishes and the ether removed by a current of dry air. Some crystals usually formed on the sides of the dish and were carefully removed with a piece of filter paper and saved for future seeding. As a rule after the ether had disappeared, an oil remained to which a crystal of the substance had to be added in order to start the crystallization. After washing with a very small amount of anhydrous ether, the product was obtained in the form of needle-like crystals by recrystallization from pure, dry ether. The crystals were removed from the dish to a filter paper by the use of a horn spatula and dried in *vacuo* over phosphorus pentoxide. The yield was about 55%.

The purest reagents were used in this preparation since small amounts of impurities prevented crystallization even after seeding. If the crystals were not pure, or in case they were allowed to stand in contact with the mother liquor, a substance was formed after a time which was insoluble in ether and water, and was not exploded by shock. This fact was noted by Darzens, and believed by him to be evidence of the formation of a polymer of cyanogen azide. Furthermore, a well crystallized, explosive, water soluble compound showing no definite melting point was isolated from the reaction mixture. Unfortunately neither of these compounds was further investigated.

Dicyandiazide, especially when impure, is dangerously explosive. It is soluble in water, ether, chloroform and alcohol, but insoluble in petroleum ether. The purest crystals obtained in this investigation melted at 40.3° (corr.). Darzens gives the melting point, 35.5–36.0°. At a temperature of about 70°, it commences to decompose, and it explodes with extreme violence at about 170".

The analysis of this compound was made by mixing the powdered sample intimately with powdered cupric oxide and so regulating the combustion that the substance decomposed at a little above 100".

Anal. Calcd. for C_2N_8: C, 17.7; H, 0.0; N, 82.4. Found: C, 17.9; H, 0.02; N (Dumas), 82.0.

Mol. wt. of dicyandiazide, calcd. for C_2N_8: 136. Calcd. from the following data, 137.

Substance	Solvent	Depression	Mol. wt.
0.1014	($C_6H_5NO_2$), 17.33	0.293°	141
.1073	($C_6H_5NO_2$), 18.40	.308°	134
.1175	($C_6H_5NO_2$), 18.40	.341°	132
.1135	(C_6H_6), 11.83	.347°	141

Hydrolysis of Dicyandiazide by Boiling Water.—The apparatus and procedure used were essentially those used in the determination of carbon dioxide in rock analyses with the exception that a tube containing a 5% solution of silver nitrate was interposed between the reflux condenser and the drying tubes in order to absorb the hydrazoic acid. In solution in boiling water decomposition of the compound was rapid. The silver azide formed was filtered on a Gooch crucible and weighed as such. The carbon dioxide evolved was absorbed in a soda-lime tube at the end of the apparatus. The cyanamide remaining in solution in the reaction flask was determined by precipitation as the silver salt from a slightly ammoniacal solution. When the filtrate from this salt was acidified with dilute nitric acid, a gelatinous silver precipitate was formed which was not further investigated (dicyandiamide).

Anal. Calcd. for CO_2: 32.3. Found: 29.0. Calcd. for HN_3: 63.2. Found: 43.4. Calcd. for $NCNH_2$: 30.9. Found: 21.0.

Although the analytical data show the carbon dioxide which was formed to approximate the theoretical, the hydrazoic acid and the cyanamide obtained are far below the calculated amount.[5]

Hydrolysis of Dicyandiazide with Sodium Hydroxide Solution.—To a suspension of 0.1 g. in 10 cc. of water, 0.6 g. of sodium hydroxide was added and the solution was heated to about 70° for some two minutes. After dilution to about 100 cc.. the cyanamide was precipitated from the slightly ammoniacal solution by adding a solution of silver nitrate. The silver azide was precipitated from the filtrate by acidifying with dilute nitric acid.

Anal. Subs., 0.1000: Ag_2NCN, 0.1926; AgN_3, 0.2115. Calcd. for $NCNH_2$: 30.9. Found: 31.6. Calcd. for HN_3: 63.2. Found: 60.7. 0.1926 g. of Ag_2NCN gave 0.2137 AgCl. Calcd. for Ag: 84.3. Found: 83.5. 0.2115 g. of AgN_3 gave 0.1971 AgCl. Calcd. for Ag: 71.9. Found: 70.2.

Reduction of Dicyandiazide to Dicyandiamide.—One gram of dicyandiazide was dissolved in about 5 cc. of alcohol. After diluting with 30 cc. of water, hydrogen sulfide was passed through the solution. Nitrogen was evolved and sulfur was precipitated immediately. After heating to 80° for a few minutes to coagulate the sulfur, the solution was filtered and the filtrate was evaporated with a current of dry air. The crystals of dicyandiamide thus obtained were, after recrystallization, found to melt at 207.4'. When mixed with pure crystals of dicyandiamide melting at 207.8' the mixture melted at 207.5".

Ammonolysis of Dicyandiazide to Dicyanamidazide.—A slow current of ammonia was passed into a cold solution of 0.39 g. of dicyandiazide in about 150 cc. of dry ether. Ammonium azide separated as a white, flocculent precipitate. After filtration and removal of the ether, colorless, plate-like crystals of dicyanamidazide remained, which after recrystallization from ether melted at 151–152° with evolution of a gas; yield, 0.30 g.

Anal. Calcd. for $NCNC(NH_2)N_3$: C, 21.8; H, 1.8; N, 76.3. Found: C, 21.8; H, 1.8; N (Dumas), 76.2.

Dicyanamidazide is sparingly soluble in water and ether and is very soluble in alcohol and acetone. It is only slightly soluble in chloroform and hot benzene and it is insoluble in petroleum ether. When an aqueous solution of dicyanamidazide is boiled, hydrazoic acid is given off gradually. When heated with a concentrated solution of sodium hydroxide, sodium azide, sodium carbonate, cyanamide and ammonia are formed. When heated in a tube it decomposes with a flash leaving a light brown residue (melon).

Dicyanamidazide from Aminotetrazole (the Opening of a Tetrazole Ring).—Aminotetrazole nitrate, 37 g., suspended in 50 cc. of water, was brought into solution and neutralized by adding a concentrated solution of sodium hydroxide, using phenolphthalein as an indicator. After cooling to about zero degrees, 27 g. of pulverized cyanogen bromide was added in small quantities while agitating. In order to increase the solubility of the cyanogen bromide, about 40 cc. of acetone was advantageously added at this point. Some heat was evolved. After standing for several hours, the solution was extracted with ether and the ether solution was dried with anhydrous sodium sulfate. Pure dicyanamidazide was obtained after evaporation and recrystallization from ether.[11] The crystals gave all the reactions characteristic of dicyanamidazide; melting point, 151–152°. A mixed melting point gave 151°.

Anal. Calcd. for $C_2H_2N_6$: C, 21.8; H, 1.8. Found: C, 21.8; H, 2.1.

Reduction of Dicyanamidazide to Dicyandiamide.—One gram of finely powdered dicyanamidazide was suspended in 30 cc. of cold water, and hydrogen sulfide was passed through the solution for half an hour. Nitrogen was evolved and sulfur was precipitated. The solution was heated almost to boiling in order to precipitate the sulfur and was then filtered. The cold solution was evaporated in a current of air to a small volume. After purification by three recrystallizations, the substance melted at 207.5°. When mixed with pure dicyandiamide melting at 207.8°, the mixture melted at 207.7°.

Dicyanamidazide Hydrochloride, $NCNC(NH_2)N_3 \cdot HCl \cdot H_2O$.—One gram of pure powdered dicyanamidazide was dissolved in 5 cc. of concentrated hydrochloric acid. Within a few minutes needle-like crystals separated out. The excess of acid was absorbed on a porous plate and after air-drying the crystals were dried for a short time in a desiccator. The hydrochloride containing one molecule of water gradually decomposes when heated, losing its crystalline appearance above 150°.

Anal. Calcd. for $C_2H_2N_6 \cdot HCl \cdot H_2O$: Cl, 21 6. Found: 21.7.

Dicyanphenylamidazide, $NCNC(N_3)NHC_6H_5$.—To a solution of 0.55 g. of dicyandiazide in 10 cc. of alcohol, a solution of 0.35 g. of aniline in 10 cc. of alcohol was added and thoroughly mixed. Hydrazoic acid was freely evolved and within half an hour needle-like crystals separated from the solution. After filtration the crystals were washed with a little alcohol. They were recrystallized from alcohol.

Anal. Calcd. for $C_8H_6N_6$: C, 51.6; H, 3.2. Found: C, 51.2; H, 3.2.

Dicyanphenylamidazide decomposes suddenly with evolution of a gas when heated above 145°. It is insoluble in most of the common solvents. It dissolves in concentrated hydrochloric acid, but it is reprecipitated upon dilution. When heated with concentrated sodium hydroxide solution, sodium azide and aniline are two of the products formed.

Sodium Dicyanphenylamidazide, $NCNC(N_3)N(Na)C_6H_5$.—Dicyanphenylamidazide, 0.5 g., was suspended in 3 cc. of water and a normal solution of sodium hydroxide was added until most of the azide dissolved. After filtration, the solution was concentrated to a small volume by a current of dry air. The crystals separated as very minute needles. They were dried in a desiccator.

Anal. Calcd. for $C_8H_5N_6Na$: Na, 11.1. Found: 11.0.

Reduction of Dicyanphenylamidazide to Phenyldicyandiamide.—Approximately 0.5 g. of dicyanphenylamidazide was suspended in a mixture of 5 cc. of alcohol and 5 cc. of water. After warming to 70°, hydrogen sulfide was passed into the solution. At the

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[11] The yield was good (E. C. F.).

end of the reaction the solution was brought to boiling in order to coagulate the sulfur. After filtration, the solution was evaporated to a small volume by dry air. Plate crystals were obtained which after recrystallization from water melted at 195–196°. Phenylcyanguanidine[10] is described as forming needle crystals from water, melting at 190–191°.

Dicyan-α-naphthylamidazide, NCNC(N_3)NHC$_{10}$H$_7$.—One gram of dicyandiazide was dissolved in 15 cc. of alcohol and one gram of a-naphthylamine dissolved in an equal volume of alcohol was added. Hydrazoic acid was freely evolved and after some time beautiful needle crystals separated which were filtered and recrystallized from alcohol. The crystals decomposed slowly when heated. They were found to be insoluble in most of the common solvents. When heated with a concentrated solution of sodium hydroxide, sodium azide was formed and the odor of a-naphthylamine was observed.

Anal. Calcd. for $C_{12}H_8N_6$: C, 61.0; H, 3.4. Found: C, 60.9; H, 3.5.

Sodium Dicyan-a-naphthylamidazide, NCNC(N_3)N(Na)C$_{10}$H$_7$.—Dicyan-α-naphthylamidazide (0.3 g.) was suspended in 10 cc. of water and a little less than the calculated amount of normal sodium hydroxide was added. The solution was heated to boiling and filtered. Upon cooling, the sparingly soluble sodium salt crystallized out as needles.

Anal. Calcd. for $C_{12}H_7N_6Na$: Na, 8.9. Found: 8.9.

Reduction of Cyanurtriazide to Melamine.—Cyanurtriazide[6] (0.6 g.) was suspended in a mixture of 25 cc. of alcohol and 15 cc. of water and hydrogen sulfide was passed into the cold solution for about one-half hour. Nitrogen was evolved and sulfur was precipitated. After boiling and filtering, the solution was evaporated to about 7 or 8 cc. Upon cooling, melamine separated as colorless plate crystals. They were recrystallized once from hot water.

Anal. Calcd. for $C_3H_6N_6$: N, 66.6. Found: 66.2.

Cyanuramiddiazide, $C_3N_3(NH_2)(N_3)_2$.—Two grams of cyanurtriazide were dissolved in 200 cc. of anhydrous ether and a current of ammonia was passed through the solution for one hour. A white precipitate formed consisting of a mixture of ammonium azide and cyanuramiddiazide. After filtration, the mixture was treated with a little water in order to dissolve the ammonium azide. The cyanuramiddiazide remained undissolved as dense, colorless crystals which were recrystallized from a large volume of hot alcohol forming large plate-like crystals.

Anal. Calcd. for $C_3H_2N_{10}$: C, 20.2; H, 1.1. Found: C, 20.1; H, 1.2.

This substance does not melt sharply, but starts to decompose above 200°, gradually turning brown. It decomposes with great violence when heated suddenly to 210°. When treated with a solution of sodium hydroxide it dissolves and is reprecipitated when the solution is acidified. When heated with a strong sodium hydroxide solution, sodium azide, cyanamide and carbon dioxide are formed. It is insoluble in most of the common solvents.

Reduction of Cyanuramiddiazide to Melamine.—Cyanuramiddiazide (0.5 g.) was suspended in a mixture of 10 cc. of alcohol and 10 cc. of water. Hydrogen sulfide was passed into the warm solution. Notwithstanding the slight solubility of the substance the reaction took place with vigorous evolution of nitrogen and deposition of sulfur. After filtration, the solution was evaporated to a small volume, whereupon melamine separated as colorless plate crystals.

Anal. Calcd. for $C_3H_6N_6$: N, 66.6. Found: 66.1.

Cyanurdichloridazide, $C_3N_3(Cl_2)N_3$.—One gram of sodium azide was dissolved in 10 cc. of water and was slowly added to a solution of 3 g. of cyanurtrichloride in 20 cc. of acetone. After shaking for about five minutes, the solvent was allowed to evaporate spontaneously. Plate-like crystals separated which were filtered off, washed with water and recrystallized from a small amount of warm alcohol; m. p. 85°.

Anal. Calcd. for $C_2N_6Cl_2$: Cl, 37.2. Found: 37.7.

Cyanurdichloridazide is sparingly soluble in alcohol and insoluble in water. The usual tests showed the presence of an azide group.

In conclusion, the author wishes to extend his sincere thanks to Dr. Edward Curtis Franklin under whose guidance this work progressed.

Summary

1. The product previously known as cyanogen azide or carbon pernitride is shown to be dicyandiazide.

2. The azides studied are shown to be derived from the ammono carbonic acid, cyanamide and its polymers.

3. Two general tests, which show the distinction between compounds containing azide groups and their isomeric tetrazoles are described and their application demonstrated.

4. The structure of cyanurtriazide containing three azide groups is confirmed, thus eliminating the tetrazole structures which the original investigator considered.

5. A tetrazole ring is opened, revealing the free azide group from which the original tetrazole was derived.

6. The following new compounds are described: (1) dicyanamidazide, (2) dicyanamidazide hydrochloride, (3) dicyanphenylamidazide, (4) sodium dicyanphenylamidazide, (5) phenyldicyandiamide, (6) dicyan-α-naphthylamidazide, (7) sodium dicyan-a-naphthylamidazide, (8) cyanuricamiddiazide and (9) cyanuricdichloridazide.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

CATALYSIS IN THE CONVERSION OF ALLYL ALCOHOL AND ACROLEIN INTO PROPIONALDEHYDE

BY PAUL E. WESTON AND HOMER ADKINS

RECEIVED FEBRUARY 16, 1928 PUBLISHED JULY 6, 1928

F. H. Constable[1] concluded from a study of the rates of the reactions at different temperatures that allyl alcohol over copper showed two primary reactions

$$CH_2{=}CHCH_2OH = CH_2{=}CHCHO + H_2 \qquad (1)$$

$$CH_2{=}CHCH_2OH = CH_3CH_2CHO \qquad (2)$$

He demonstrated that propionaldehyde was not formed, as bad previously been assumed, according to the reaction

$$CH_2{=}CHCHO + H_2 = CH_3CH_2CHO \qquad (3)$$

For some time one of us has been greatly interested in those properties of oxide catalysts which determine the proportion of simultaneous and

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[1] Constable, *Proc. Roy. Soc. (London)*, **A113**, 254 (1926).

competing reactions. In almost all of the cases previously studied in this Laboratory one of the competing reactions involved dehydration of the organic compound. It was therefore a matter of considerable interest to investigate the proportions of two reactions, one of which involved dehydrogenation and the other intramolecular rearrangement, over various catalysts whose characteristics had been previously studied for the reactions of saturated alcohols, esters, etc. The results of this investigation will shortly be submitted for publication, but in this communication we wish to present certain data bearing on the conversion of allyl alcohol and acrolein into propionaldehyde over a zinc oxide and an aluminum oxide catalyst.

The apparatus used in the experimental work is shown in Fig. 1. The method of introducing the alcohol was a modification of that designed by Paul E. Millington in this Laboratory. A constant head of water A, equivalent to **35** cm. of mercury, compressed air in the bottle B. The rate of flow of alcohol from the reservoir, *G*, through the fine capillary, H, could be varied slightly by regulating the pressure of the air by changing the depth of the mercury in *C*. D is a calcium chloride tower to dry the air and E is a manometer. The flow of alcohol could be stopped instantly by releasing the air pressure in the reservoir, G, through the stopcock, F. The limb, J, of the catalyst tube was 2 cm. in diameter and **33** cm. long. The exit tube was a capillary of *2* mm. bore. Six tenths of a cc. of the catalyst in the form of fragments of small pills was placed in a thin layer at L, on top of glass beads which filled the tube to the point J. The catalyst tube was immersed in an electrically heated bath of sodium and potassium nitrates, the temperature of which was kept constant at **330** ± 3° by means of a Leeds and Northrup potentiometer controller. At **400°** considerable charring and side reactions took place but at 330° the amount of side reactions was small, as shown by the composition of the gaseous products.

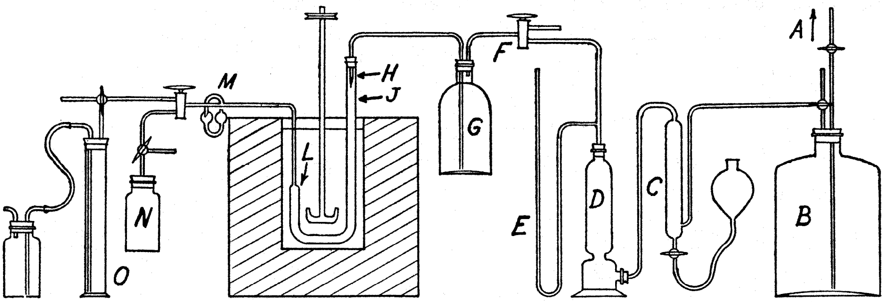
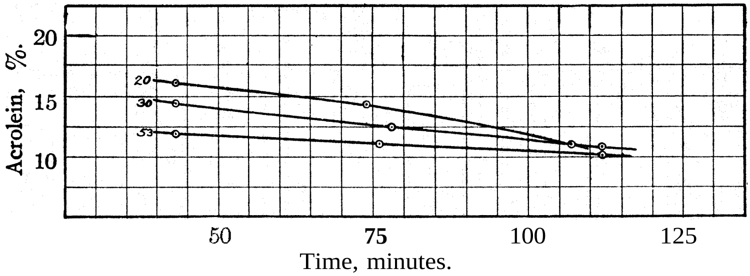


Fig. 1.—Apparatus for the study of the reactions of alcohols over solid catalysts.

The gaseous products of the reaction were collected over an aqueous solution of sodium bromide in the cylinder, O. Sufficient oxygen was added to make the volume **100** cc., and the gas was analyzed over water in an Orsat apparatus. The portion absorbed by potassium hydroxide is reported as carbon dioxide; that removed by bromine as unsaturated hydrocarbons. The hydrogen and carbon monoxide were determined by exploding the residue and measuring the contraction and subsequent absorption by potassium hydroxide. The composition of the gas was approximately 9% carbon dioxide, 6% unsaturated hydrocarbons, 80% hydrogen and *5%* carbon monoxide.

The aldehydes formed in the reaction were determined by precipitation as the *p*-nitrophenyl hydrazones. Seventy cc. of a saturated solution of p-nitrophenyl hydrazine in normal hydrochloric acid was placed in a 250cc. wide-mouthed bottle, N, closed by a rubber stopper bearing a stopcock. Air was removed from the bottle till a pressure of 30 mm. of mercury was reached. The bottle was then attached to the exit of the catalyst tube and the stopcock opened enough to reduce the pressure in the tube (as indicated by the manometer, M) slightly below atmospheric pressure. After a sample had been collected, the stopcock was closed, the bottle shaken occasionally and allowed to stand for four hours. The hydrazone was collected in a Gooch crucible containing an asbestos mat, dried in a calcium chloride desiccator at 50° under reduced pressure and weighed.

The loaded catalyst tube was put in place in the bath and dry air was allowed to pass through it for one and one-half hours before admitting alcohol. Thirty minutes after the flow of alcohol had begun, an aldehyde sample was collected, then a gas sample which in turn was followed by another aldehyde sample, and so on till three gas samples and four aldehyde samples had been collected. Enough aldehyde was collected to give about **0.3** g. of hydrazone, which took from three to six minutes. Enough gas was collected to give about 15 cc. of hydrogen, which required from fifteen to thirty minutes. The allyl alcohol was prepared from formic acid and glycerin and dried by refluxing with potassium carbonate; b. p. 95.5–96.5° (corr.) at 745 mm.[2]



Pig. 2.—Variation in percentage of acrolein with rate of alcohol flow. The percentage of acrolein (ordinates) in the aldehydes produced is plotted against the time of sampling in minutes (abscissas) lor three rates of allyl alcohol flow, namely, 20, **30** and 53 cc. per hour. The zinc oxide catalyst was formed by the thermal decomposition of zinc oxalate.

From the length of the interval for sampling the aldehyde and the weight of the hydrazone produced, the amount of hydrazone that would be formed per hour was calculated. This was plotted against the mean time during which the sample was collected, giving an activity curve as shown in Fig. **3.** The weight of the hydrogen was calculated from the volume of hydrogen found in the gas analysis. Assuming a 96% conversion of acrolein to the hydrazone,[1] the weight of hydrazone formed was calculated and then the weight per hour. This value divided by the activity (from Fig. **3)** at the mean time of collecting the gas sample gave the percentage of acrolein produced at that time. The three values obtained in one experiment were plotted as in Fig. 2.

It was observed in connection with other experiments that the pro-

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[2] "Organic Syntheses," John Wiley and Sons, Inc., New York, 1921, Vol. I, p. 15.

portion of acrolein, as compared to propionaldehyde, was increased by decreasing the rate of passage of allyl alcohol over the catalyst. For example, in an experiment where the percentage of acrolein should have been about 14% with 30 cc. of alcohol per hour, the percentage of acrolein found was actually about 19% when the rate of alcohol flow had decreased to perhaps 15 cc. per hour. (A similar effect is of course produced by increasing the volume of the catalyst.) Following this casual observation, experiments were carried out in order to measure this effect. The results of these experiments are summarized in Fig. 2.

The decrease in proportion of acrolein with increased rate of passage of allyl alcohol suggested the possibility that propionaldehyde is formed through the reaction of acrolein and allyl alcohol

$$CH_2{=}CHCHO + CH_2{=}CHCH_2OH = CH_3CH_2CHO + CH_2{=}CHCHO \qquad (4)$$

This possibility was not considered by Constable in his discussion of the reactions of allyl alcohol over copper. It cannot be eliminated as was the possibility that propionaldehyde resulted from the reaction of acrolein and hydrogen, for in this scheme acrolein is reproduced at exactly the same rate that it is consumed.

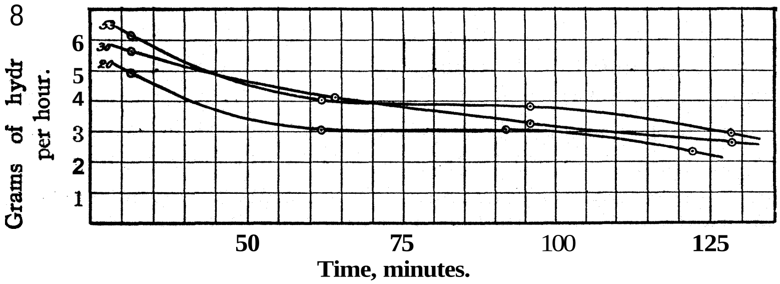

Fig. 3.—Variation of activity with rate of alcohol flow. The rate of hydrazone formation in g. per hour (ordinates) is plotted against the time of sampling expressed in minutes (abscissas) for three rates of alcohol flow.

An increase in the rate of passage of the alcohol over the catalyst would favor reaction (4) because it would increase the probability that an allyl alcohol molecule would be adsorbed by the catalyst on a "point" or area adjacent to an adsorbed acrolein molecule *before* the latter was desorbed.

If propionaldehyde is formed according to reaction (4) then while the *proportion* of acrolein to propionaldehyde decreases with increasing rate of passage of allyl alcohol, the *amount* should remain constant and there should be an increased formation of propionaldehyde, that is, there should be an increase in activity as measured by the amount of hydrazone formation. This is seen to be true from a consideration of Fig. 3, where the highest rate of flow of alcohol gives the highest activity and the lowest rate of flow gives the lowest activity.

That the rate of formation of acrolein is approximately constant and is independent of the rate of flow of alcohol may be readily shown by a consideration of the data given in Figs. 2 and 3. In Fig. 3, the area under the curve between 40 and 110 minutes gives the total weight of hydrazone formed during that time interval at that rate of flow of alcohol. Thus at 53, 30 and 20 cc. per hour, the amounts of hydrazone formed are, respectively, 4.82 g., 4.58 g. and 3.67 g. In like manner the area under a curve in Fig. 2 divided by the length of time gives the mean percentage of acrolein formed during that interval. At rates of flow of allyl alcohol of 53, 30 and 20 cc. per hour, the mean percentages of acrolein are, respectively, 11.0, 12.8 and 14.0%. The product of the weight of hydrazone and the mean percentage of acrolein is the weight of hydrazone equivalent to acrolein. Since 96% of the hydrazone is precipitated, the weights of acrolein formed at rates of flow of alcohol of 53, 30 and 20 cc. per hour are, respectively, 0.16 g., 0.18 g. and 0.16 g. These values are identical within the limit of experimental error.

Furthermore, if reaction (4) takes place, then increasing the concentration of acrolein (as by adding it to the allyl alcohol passed over the catalyst) should increase the amount of propionaldehyde formed and should decrease the amount of acrolein formed over the catalyst. This point was tested experimentally by using allyl alcohol containing 5 cc. of acrolein per 100 cc. of alcohol at a rate of 53 cc. per hour. The weight of hydrazone equivalent to the weight of acrolein already present in the alcohol was subtracted from the total hydrazone found. The remainder was then used in the customary calculations. The percentage of acrolein with pure alcohol would be about 12% at forty-five minutes but with this allyl alcohol–acrolein solution it was only 6.7%. A second determination was made in which the value 6.7% was checked; then over the same catalyst pure alcohol was used and 9.3% of acrolein was obtained. At this time (117 minutes), using pure alcohol throughout, the acrolein would have been 10% of the total aldehyde formed. In another experiment in which a solution of 15 cc. of acrolein in 85 cc. of alcohol was used, 1.5% of acrolein was obtained at the end of forty-five minutes instead of the normal proportion of 12%. The activity in this case was abnormally high, 6.8 g. per hour. This indicated that an abnormally large amount of propionaldehyde was being produced.

The experimental evidence that propionaldehyde is formed through the reaction of acrolein and allyl alcohol would be strengthened if propionaldehyde could be formed under conditions in which the intramolecular rearrangement of reaction (2) could not take place, for example, as in reaction (5)

$$CH_2{=}CHCHO + CH_3CH_2CH_2OH = 2CH_3CH_2CHO \qquad (5)$$

but n-propyl alcohol cannot be used over zinc oxide because it itself is dehydrogenated to propionaldehyde. However, over alumina this latter reaction does not take place. Only traces of aldehyde were formed when n-propyl alcohol was passed over 0.6 cc. of an alumina at 330°. The flow of alcohol was then stopped and in its place over the same catalyst an approximately 10% solution of acrolein in n-propyl alcohol was used. The amount of aldehyde passed over the catalyst was equivalent to 8.7 g. of hydrazone per hour. At the end of seven minutes hydrazone was being produced at the rate of 12.0 g. per hour, at the end of twenty-five minutes the rate was 14.1 g. and at the end of forty-five minutes hydrazone was being produced at the rate of 13.4 g. per hour. There was thus being produced by the reaction of acrolein and n-propyl alcohol, aldehyde equivalent to 3.3 g., 5.4 g. and 4.7 g. of hydrazone per hour. These values correspond to a conversion of acrolein to propionaldehyde of 38, 62 and 54%, respectively. It is thus clearly established that n-propyl as well as allyl alcohol will reduce acrolein to propionaldehyde, and that the reaction takes place over alumina as well as over zinc oxide.

Constable showed that the hydrogenation of acrolein did not occur over copper, so it seems improbable that it should occur over the less active oxide catalysts. In the case of the reaction of acrolein and n-propyl alcohol over alumina there is no possibility of the hydrogenation of acrolein taking place, for alumina does not catalyze the formation of hydrogen from propyl alcohol. It is of course *possible* that a *part* of the propionaldehyde formed over zinc oxide from allyl alcohol results from intramolecular rearrangement or through some other mechanism.

Constable found that sintered copper gave a lower proportion of acrolein than did copper which was not sintered. He suggested that there were two sets of active points, one for each reaction, and that one set was destroyed to a greater extent than the other in the sintering. It is possible that sintering the copper simply reduced its activity, which is similar in effect to increasing the rate of flow of alcohol, and thus reduced the proportion of acrolein.

Summary

The behavior over a zinc oxide catalyst of allyl alcohol and mixtures of it with acrolein has been investigated as has also the reaction over alumina of acrolein and n-propyl alcohol. All of the experimental results indicate that the formation of propionaldehyde from allyl alcohol over zinc oxide results at least in part from the reaction of allyl alcohol with acrolein and not through the hydrogenation of acrolein nor through the intramolecular rearrangement of allyl alcohol.

MADISON, WISCONSIN

DIPIPERIDYLS[1]

BY C. R. SMITH[2]

RECEIVED FEBRUARY 20, 1928   PUBLISHED JULY 6, 1928

There are six possible dipiperidyls corresponding to the six dipyridyls. All of the dipyridyls[3] are known, but up to the time of these experiments only three of the dipiperidyls had been prepared. The author has prepared two additional dipiperidyls, p , ~ and p,&, leaving only the α,γ-derivative for further study.

The method of preparation is that of reduction of the dipyridyls by means of hydrogen in the presence of platinum oxide catalyst. The dipiperidyl is produced in a state of purity equal to that of the dipyridyl. Often it can be purified by suitable means when the dipyridyl cannot be easily purified.

The three dipiperidyls previously known were prepared by means of sodium and ethyl or amyl alcohol reduction and required considerable purification. γ,γ-Dipiperidyl[4] was the first dipiperidyl to be prepared by the sodium reduction and presented considerable difficulty in its purification. Ahrens prepared the dipiperidyl in a pure condition by means of the dinitroso derivative. Blau prepared α,β-dipiperidyl[5] with great difficulty, using steam distillation, crystallization of the hydrochloride from alcohol, distillation of the base and repeating the operations until a maximum melting point (68–69°) was obtained. α,α-Dipiperidyl[6] also was prepared in a pure form by Blau and required almost as much manipulation as γ,γ-dipiperidyl.

The author has prepared the dipiperidyls mentioned, together with β,γ- and β,β-dipiperidyls and also certain derivatives useful for characterizing them. All the dipiperidyls are strong bases which absorb carbon dioxide readily from the air. They are very stable to the action of heat and air. The picrates usually melt with decomposition. The bases may be titrated with two molecular equivalents of strong acid to one of base, phenolphthalein being used as indicator. The bases are very soluble in water, slightly soluble in ether and almost insoluble in petroleum ether.

In no instance does a partial reduction of the dipyridyl molecule appear to take place, either in hydrochloric acid solutions of various strengths, acetic acid solution or various solvents. The reduction goes to completion, calculated as for the formation of dipiperidyl, and stops. When

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[1] This paper was read at the Insecticide Symposium at St. Louis.

[2] Associate Chemist, Insecticide Division, Chemical and Technological Research Bureau of Chemistry and Soils.

[3] Smith, THIS JOURNAL, 46,414 (1924).

[4] Ahrens, *Ber.*, 24, 1479 (1891).

[5] Blau, *Monatsh.*, 13, 330 (1892).

[6] Blau, *ibid.*, 10,375 (1889).

one-half this quantity is used a mixture of dipyridyl and dipiperidyl always results. In alkaline solutions, or solutions without acid, no reduction takes place at all, probably because the catalyst is inactive or rendered so by the production of the alkaline dipiperidyl.

Experimental

The same general procedure was used in the preparation of each of the dipiperidyls. The dipyridyls were usually dissolved in a moderate excess of hydrochloric acid in water or alcoholic solution and reduced at atmospheric or higher pressures. The quantity of hydrogen absorbed agreed with the absorption of twelve hydrogen atoms. The platinum oxide catalyst was prepared by the method of Vorhees and Adams.[7] After reduction the solution was separated from the platinum, evaporated to low volume and precipitated by means of absolute alcohol as the dihydrochloride. (If the original dipyridyls were somewhat impure this precipitation effected a purification but is otherwise unnecessary for the preparation of the bases.)

The bases were freed with caustic potash and extracted with ether. They may be recrystallized from petroleum ether or a mixture of ether and petroleum ether.

The experimental results on five dipiperidyls are given in tabulated form. Only a small amount of crude α,γ-dipyridyl was obtained, boiling at 282–284°, from a large quantity of mixed dipyridyls obtained in the action of sodium on pyridine. The correct quantity of hydrogen was absorbed but the dipiperidyl was too impure to prepare pure derivatives. Further study is required to obtain these α,γ-derivatives.

The phenyl isothiocyanate addition products of the type $C_{10}H_{20}N_2{\cdot}2C_6H_5NCS$ crystallize well from alcohol or alcohol and water mixtures.

Table I

Dipiperidyl Derivatives

	Melting point, ° C.			B. pt., base, °C.	C in base, %	H in base, %	N in Dinitroso, %	S in PhNCS, %
	Base	Dinitroso	PhNCS comp.					
γ,γ[a]	172	149 150	225[b] 229	..	...	...	...	**14.74**
α,α[c]	Liq.	159	178[d]	259	...	...	24.20	14.47
α,β[c]	68 69	88	..	269	...	...	...	...
β,β[e]	105	102	**200**	*282*	71.09	11.83	24.93	14.49
β,γ[f]	159	149	**202**	**270**	70.90	11.85	25.30	14.57
			Calculated		71.40	11.90	24.78	14.64

[a] Ahrens gives **160°** for base and 141-143° for dinitroso compound. Base sublimes long needles below melting point, and boiling point could not be determined.

[b] Needles.

[c] Figures are identical with those given by Blau. The α,β-dipiperidyl picrate, however, melted at 224°, unchanged on recrystallization. Blau gives 215°.

[d] Needles.

[e] Needles arranged in rosets.

[f] Sublimes to needles in rosets. Picrate blackens at **200°** but does not melt at **230°**. The platinum double chloride turns gray at 235° but does not melt at 250". N in base, calcd., 16.7%; found, **16.8%.**

The dipiperidyls resemble nicotine and hexahydronicotine in their chemical structure to a degree which makes it desirable to examine their toxicity to insects. **A** study

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[7] Vorhees with Adams, This Journal, **44,1397 (1922).**

of the insecticidal action of these compounds is being made in cooperation with Dr. C. H. Richardson, Deciduous Fruit Insect Investigations, Bureau of Entomology.

Summary

1. α,α-, β,β-, γ,γ-, β,γ- and α,β-dipyridyls were reduced quantitatively to the corresponding dipiperidyls by means of hydrogen in the presence of platinum oxide catalyst. Impure α,γ-dipyridyl was also reduced to the dipiperidyl but proper purification could not be made.

2. Certain physical constants of the bases, their dinitroso and other derivatives were determined to characterize them.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

AN ORGANIC TITANOUS COMPOUND AND A NEW METHOD FOR THE PREPARATION OF SOLUTIONS OF TITANOUS SALTS

BY DONALD W. MACCORQUODALE AND HOMER ADKINS

RECEIVED MARCH 5, 1928 PUBLISHED JULY 6, 1928

Bischoff in 1923 observed that a blue colored substance insoluble in organic solvents and containing no sodium resulted from the reaction of an alcoholic solution of tetra-ethyl ortho titanate with metallic sodium. He demonstrated that the compound contained trivalent titanium and was presumably an ethyl titanite.

This crude ethyl titanite is readily prepared by converting titanium tetrachloride into tetra-ethyl ortho titanate.[1] The yield may be increased to 81% of the theoretical by centrifuging the mixture containing the sodium chloride and decanting off the alcoholic solution of the ortho titanate instead of distilling it from the salt mixture. The salt should be shaken and centrifuged twice with alcohol in order to wash out the ester. The titanate is readily purified by distillation so that it is entirely free from all metallic or acid impurities.

The trivalent titanium compound is most easily prepared by adding an alcoholic solution of ethyl titanate as rapidly as possible to a flask containing finely divided sodium, the flask being equipped with an efficient reflux condenser which in turn is equipped with a Bunsen valve. When the reaction becomes too vigorous, it is moderated by immersing the flask in an ice-bath for a moment. However, the more vigorous is the reduction, the better the yield of product, so that the reaction should be allowed to proceed as vigorously as the efficiency of the condenser will permit. The separation of the blue precipitate is best effected by centrifuging, after which the solution can be decanted and the precipitate washed by shaking up with absolute alcohol and centrifuging again. The product should be washed in this manner two or three times, after which it can be dried over concentrated sulfuric acid in an atmosphere of hydrogen or nitrogen. From 30 g. of ethyl titanate dissolved in 200 cc. of absolute alcohol, 20 g. of product may readily be obtained, using 10 g. of sodium for the reduction.

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[1] Bischoff and Adkins, THIS JOURNAL, 46,257 (1924).

This dark blue amorphous solid contains from 55 to 70% as much trivalent titanium as would an equal weight of ethyl ortho titanite, $(C_2H_5)_3TiO_3$. It reduces aromatic nitro compounds to amines very readily and aromatic aldehydes to alcohols somewhat more slowly, when used in the form of a suspension in absolute alcohol. It dissolves in hydrochloric acid and in dilute sulfuric acid, forming the titanous salts.

When the dry ethyl titanite is exposed to the air it very rapidly turns olive-green and then white, the odor of acetaldehyde being very pronounced. To obtain samples for analysis the material, in alcoholic suspension, was transferred to small glass bulbs which were filled with nitrogen. The alcohol was removed by heating at 100° for one hour under a pressure of 5–10 mm. and the bulbs were then sealed off, filled with nitrogen. The results obtained were as follows. From 0.2287 g. of substance, 0.1736 g. of water and 0.3368 g. of carbon dioxide were obtained: calcd. for $C_6H_{15}O_3Ti$: C, 39.31; H, 8.25. Found: C, 40.18; 8.49.

Trivalent titanium was determined by titrating the ferrous salt formed by the action of the compound on an excess of ferric alum in an atmosphere of carbon dioxide. All values for trivalent titanium were low. A sample which had been boiled with absolute alcohol in a current of hydrogen for several hours showed 21.31 and 20.77% of trivalent titanium instead of the theoretical 26.25%. This would correspond to a mixture of about 80% of ethyl titanite ($(C_2H_5)_3TiO_3$) and 20% of ethyl titanate ($(C_2H_5)_4TiO_4$). Accordingly, a determination of total titanium was made by dissolving the material in concentrated hydrochloric acid with the addition of a few drops of concentrated nitric acid and precipitating the titanium as titanium dioxide.[2] The results were 24.93 and 24.86% of titanium as compared with the theoretical value of 25.21% calculated for this mixture.

From this analysis it seemed probable that the material was a mixture of the two esters and a further effort was made to effect their separation. It was found impossible to wash out the ethyl titanate but a partial separation was accomplished by heating at 156° and 8–10 mm. for one hour. Under these conditions some of the ethyl titanate distilled out and was condensed in the cold part of the tube. A sample treated in this manner was found to contain 22.85% of trivalent titanium, which corresponds to 87.4% of ethyl titanite in the preparation. Increasing the temperature from 156 to 185° had no effect. Probably the remaining impurity was in part titanium dioxide but we were unable to remove this as we found no non-reactive solvent for the ethyl titanite. It appears probable that if the titanites of the higher alcohols were prepared they would be found to be more soluble and so might be more readily purified, but this has not been attempted.

Summary

An organic trivalent titanium compound has been prepared in an impure state by the reduction with sodium of an alcohol solution of tetra-ethyl titanate. This dark blue compound acts as a reducing agent and also dissolves in hydrochloric or dilute sulfuric acid to form titanous salts. The titanous salt solutions so obtained are entirely free from iron or other metallic or acidic impurities. An improvement in the method of preparation of tetra-ethyl titanate has been described.

MADISON, WISCONSIN

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[2] Scott, "Standard Methods of Chemical Analysis," D. Van Nostrand and Co., New York, 3d ed., 1922, p. 542.

[CONTRIBUTION FROM THE UNIVERSITY OF CALIFORNIA]

THE STRUCTURE OF MERCERIZED CELLULOSE. I. THE SPACE LATTICE OF MERCERIZED RAMIE CELLULOSE AS DEVELOPED FROM X-RAY DATA[1]

BY O. L. SPONSLER AND W. H. DORE

RECEIVED MARCH 5, 1928 PUBLISHED JULY 6, 1928

It has been noted by Herzog[2] and by Katz and Mark[3] that mercerized cellulose gives a diffraction pattern with x-rays which differs somewhat from that of untreated cellulose, but no clearly defined space lattice for mercerized cellulose has been heretofore worked out.[3a] Based upon new x-ray data that we have obtained for mercerized ramie fibers, we have developed a space lattice which appears to agree with all of the observed facts. In the present paper this structure is described and suggestions are made in regard to the probable mechanism of mercerization.

Several lots of ramie fibers were extracted with a mixture of alcohol and benzene and then mercerized by treating for thirty minutes with solutions containing **1**, 8, **14**, **17.5** and 28%, respectively, of sodium hydroxide. The alkali was removed by washing for a long time with distilled water, then digesting for a few minutes in very dilute acetic acid and again washing thoroughly with water. Finally the samples were dried in an oven. In order to keep the fibers from becoming tangled during these treatments, each sample was wound on a glass frame and tied in position, where it remained during all of the operations.

After mercerization the fibers were cut from the frames, laid parallel and cemented with dilute celloidin into tablets from which small blocks were cut. These blocks were used for obtaining the diffraction patterns. A molybdenum Coolidge tube was used as the source of radiation, and a monochromatic beam of x-rays was obtained by using screens of zirconium oxide. The procedure is described in greater detail in an earlier paper.[4]

By revolving the block of fibers through known angles, it is possible to determine the position of the atomic planes with reference to the long axis of the fibers. When that axis, designated here as the *c* axis, is parallel to the line of propagation of the x-ray beam,

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[1] This paper is a joint contribution from the Department of Botany, University of California at Los Angeles, California, and the Division of Plant Nutrition, University of California Experiment Station, Berkeley, California.

[2] Herzog, *J. Phys. Chem.*, **30**, **460** (**1926**).

[3] Katz and Mark, *Z. Elektrochem.*, **31**, **105** (**1925**).

[3a] Since this paper was written, **a** paper by Meyer and Mark. *Ber.*, 61, 593–614 (1928), has appeared in which is proposed a structure for native cellulose resembling in many ways the structure proposed by the present authors in **1926** (see ref. **6**), but differing in several respects from the earlier structure. Based partly upon the data of Herzog, and partly upon new data of their own, Meyer and Mark have calculated lattice dimensions for mercerized cellulose and have made suggestions as to the probable orientation changes accompanying mercerization. The lattice dimensions given by these authors as well as their conclusions are at variance with those of the present paper. Additional data will probably be required before it will be possible to show how far these conflicting views are capable of being reconciled.

[4] Sponsler, *J. Gen. Physiol.*, **9**, **221–233** (**1925**); **9**, 677–695 (**1926**).

the position is called the 0° position; when the beam cuts the fibers at right angles, the position of the c axis is referred to as the 90° position. The interplanar spacings calculated from the diffraction lines obtained from the 0° position are the spacings between planes of atoms which are parallel to the fiber length; when obtained from the 90° position, they are the spacings between planes which are perpendicular to the fiber length.

In Table I the interplanar values obtained from the 0° position for the various mercerization treatments are listed for comparison.

TABLE I

INTERPLANAR VALUES FROM 0° POSITION RAMIE FIBERS

Untreated, Å.	8% NaOH, Å.	14% NaOH, Å	17.5 NaOH, Å.	28% NaOH. Å.
6.10	6.08	7.55	7.53	7.64
5.40	5 45	4.49	4.48	4.51
3.98	3.98	4.10	4.10	4 09
2.65	2.64	2.22	2.22	2.24
1.98	1.96	..	..	..
1.93	1.88	..	..	..

The first and second columns are practically identical; similarly, the third, fourth and fifth columns. Apparently no change had taken place in the first two; while in the remaining three columns the change produced by the alkali was the same regardless of the concentrations used. A critical concentration is indicated between 8 and 14%. From data which we are not presenting completely at this time, that critical point was found to be very close to 13%. For convenience we are using the term "unmercerized" as associated with treatments below the critical concentration, and "mercerized" for all above that. We found that fibers which have been subjected to concentrations near 13% may produce lines of both groups. The significance of that observation is as yet uncertain, but studies now under way may determine whether indvidual fibers have slightly different critical points or whether the same fiber wall may contain both mercerized and unmercerized cellulose.

In Table II values from Table I are summarized into the two groups which we have called "unmercerized" and "mercerized." Instead of tak-

TABLE II

INTERPLANAR VALUES FOR MERCERIZED AND UNMERCERIZED RAMIE FIBERS FROM 0° POSITION

Unmercerized. Treated with 1 or 8% NaOH or untreated		Mercerized. Treated with 14, 17½ or 28% NaOH	
Spacing, Å.	Density of line	Spacing, Å.	Density of line
6.10	Strong	7.55	Medium
5.40	Medium	4.50	Strong
3.98	Very strong	4.10	Strong
2.65	Weak	2.23	Weak
1.98	Very weak		
1.93	Very weak		

ing the averages, however, we have used the values for the strongest clean-cut lines which were obtained, on the assumption that they are most nearly correct.

It may not be out of place to assume at this time that the various planes of atoms producing the diffraction lines have shifted from the spacings given in the first column to those given on the same line in the third column. This assumption will be amply justified later by the facts. In the table it will be noted that with the shift in positions, changes also occur in the densities of some of the lines. Especially significant is the change in density of the line corresponding to the 5.40 spacing into a stronger 4.50, and that of the 3.98 to a weaker 4.10. These density changes are of considerable importance in determining the orientation of the constituent C_6 units in the structure for mercerized cellulose, as will be shown further on.

The patterns from the 90° position of the fibers are identical in all cases regardless of the concentration of sodium hydroxide used, so far as the interplanar spacings are concerned. However, there is a very evident difference in the density of at least three lines, between the mercerized and unmercerized groups; the 5.15 line is slightly stronger, the 3.40 considerably weaker and the 2.58 much weaker from the mercerized material.

TABLE III

INTERPLANAR VALUES FOR MERCERIZED AND UNMERCERIZED RAMIE FIBERS FROM 90° POSITION

Unmercerized. Treated with 1 or 8% NaOH or untreated		Mercerized. Treated with 14, 17½ or 28% NaOH	
Spacing, Å.	Density of line	Spacing, Å.	Density of line
5.15	Strong	5.16	Strong
3.40	Medium	3.36	Very weak
2.58	Very strong	2.59	Strong
2.03	Strong	2.02	Strong
1.70	Strong	1.69	Strong

From the intermediate positions, between 0 and 90°, the mercerized fibers produced fewer lines than the unmercerized. Their values and densities are given in Table IV.

TABLE IV

INTERPLANAR VALUES FOR MERCERIZED RAMIE FIBERS FROM POSITIONS BETWEEN 0 AND 90°

Position of fibers	Spacing, Å.	Density of line
70 to 80°	2.46	Weak
60 to 70°	3.15	Strong
60°	2.19	Weak
55°	4.38	Strong
40 to 50°	2.62	Medium
60 to 70°	1.89	Very weak

Development of Space Lattice

The interplanar spacings for mercerized material given in these tables are in agreement with the calculated spacings for a lattice the elementary cell of which is slightly monoclinic and has the axial ratios, $a:b:c$ = 0.595:1:1.352 (a = 4.53 Å., b = 7.61, c = 10.30).

The angle made by the axes, a and b, is approximately 83°. We have departed here from the conventional nomenclature of crystallography, since, consistent with the terms employed in our earlier work on untreated cellulose, we have found it convenient to retain the long axis of the fiber as the c axis.

The volume of this elementary cell is 4.53 X sin 83° X 7.61 × 10.30 = 353 cu. Å. The volume of the cellulose unit, $C_6H_{10}O_5$, assuming that no chemical change has taken place, is 162.1/1.57 X 1/(6.062 X 10^{23}) = 170 X 10^{-24} cm.[3] or 170 cu. Å., where 162.1 is the sum of the atomic weights of $C_6H_{10}O_5$, 1.57 is the value for the specific gravity of mercerized cellulose determined by us by the de Mosenthal method[5] and 6.062 × 10^{23} is Avogadro's number. There are then two of these C_6 units per elementary cell. 353/170 = 2.08 groups per unit cell.

In Table V the data from the previous tables are brought together for

TABLE V

INTERPLANAR SPACING VALUES ROR MERCERIZED AND UNMERCERIZED RAMIE FIBERS

Basis, $a:b:c$ = 4.53:7.61:10.30, aob = 83°

Unmercerized treated with 1 or 8% NaOH or untreated. Obs. values, Å.[a]	Mercerized treated with 14, 17½ or 28% NaOH				
	Obs. values, Å.	Calcd. values. Å.	Angular position of fibers Obs. approx.	Calcd.	Indices
6.10	7.55	7.55	0°	0°	(010)
5.40	4.50	4.50	0°	0°	(100)
3.98	4.10	4.10	0°	0°	(110)
..	2.23	2.22	0°	0°	(210)
2.65	..	..	...	...	(120)
..	..	10.27	...	90°	(001)
5.15	5.16	5.13	90"	90°	(002)
3.40	3.36	3.42	90°	90°	(003)
2.58	2.59	2.56	90°	90"	(004)
2.03	2.02	2.05	90°	90"	(005)
1.70	1.69	1.71	90°	90°	(006)
4.35	4.38	4.37	55°	58°	(114)
2.17	2.19	2.18	60°	58°	(114)
2.62	2.62	2.63	45"	50°	(113)
2.35	2.46	2.44	75°	71°	(014)
2.97	3.15	3.13	65°	65°	(013)
1.94	1.89	1.88	65"	65°	(105)

[a] Figures in this column are taken directly from an earlier paper, *J. Gen. Physiol.*, 9, 221–233 (1925).

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[5] H. J. de Mosenthal, *J. Soc. Chem. Ind.*, 26,443 (1907).

comparison, and the corresponding crystallographic indices and calculated values for the interplanar spacings and for the angular positions have been added. The observed angular position refers to a relationship between the long axis of the fiber and the path of the beam, the calculated position to the angle between the long axis and the diffracting plane as determined from the elementary cell. These two values should agree within a few degrees. The calculated values are based upon the axial dimensions as given above and upon the value of 83° for the angle between the axes *a* and b.

The close agreement between observed and calculated values seems to indicate that the space lattice for mercerized ramie cellulose, which we have described, meets the requirement of the x-ray data.

Discussion

A comparison of the lattice which we have just deduced for mercerized ramie cellulose with our earlier lattice for unmercerized cellulose[4,6] reveals rather definitely, we believe, the rearrangement of the structural units which has taken place during mercerization of the fiber.

In the earlier paper[6] it was shown that untreated ramie cellulose is apparently made up of glucose units arranged in parallel chains of indefinite length running lengthwise of the fiber, the C_6 units of the chain being united throughout by glucosidal linkages. The chains themselves, in a cross section of the fiber, are rectangularly spaced 6.10 by 5.40 Å.

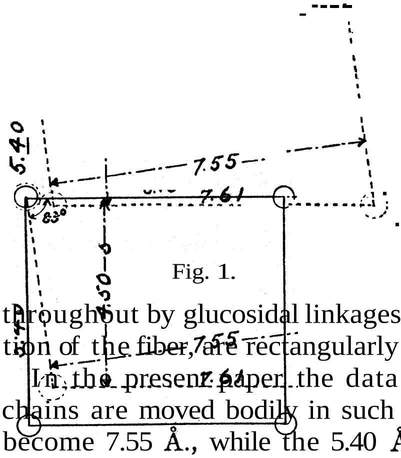

Fig. 1.

In the present paper the data indicate that during mercerization the chains are moved bodily in such a manner that the 6.10 Å. spacing has become 7.55 Å., while the 5.40 Å. spacing has become 4.50 Å. This is illustrated in Fig. 1, which shows a section through the unit cells perpendicular to the *c* axis. The solid circles indicate the centers of the C_6 groups as they occur in the unmercerized fibers; the dotted circles show the new positions after mercerization.

As pointed out in our earlier paper,[6] each of the constituent glucose units of cellulose contained a six-membered ring which gave the unit a flattened structure having a maximum dimension of about 7 Å. at right angles to the *c* axis. In the unmercerized fibers this dimension was regarded as lying along one of the diagonals of the 6.10 by 5.40 rectangle as indicated in Fig. 2.

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[6] Sponsler and Dore, "Fourth Colloid Symposium Monograph," Chemical Catalog Company, New York, 1926, pp. 174–202.

This view is in agreement with the x-ray data, since the diagonal 3.98 line is much denser than either the 6.10 or the 5.40 lines. The density of the lines from the mercerized fibers, however, forces a different interpretation in regard to the position of the flattened C_6 units. Here the 4.10 line, a diagonal, is of equal density to the 4.50 line, which may correspond to the 5.40 of the unmercerized material. The equality of density of these two lines strongly suggests that in the mercerized material one-half of the number of C_6 groups have their long dimension (7 Å.) along the diagonal and the other half along the 4.50 planes, that is, parallel to the b axis. This may be more clearly seen from Pig. 3, where several possible arrangements are shown, each diagram representing a section through the unit cell perpendicular to the *c* axis. In A and B the long dimensions of all the C_6 units of any one chain lie in the same direction, but all those of two of the chains lie along the 4.50 planes and of the other two chains along the diagonal planes. By either arrangement a given chain would contribute mostly to one line or to the other, but by the arrangement shown in C every chain would contribute equally to each line. Here the dotted circles indicate a level below the solid circles. A study of three-dimensional models seems to indicate the C arrangement as the most probable one.

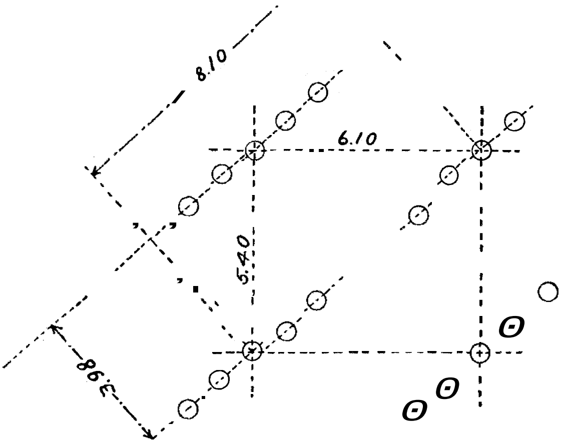
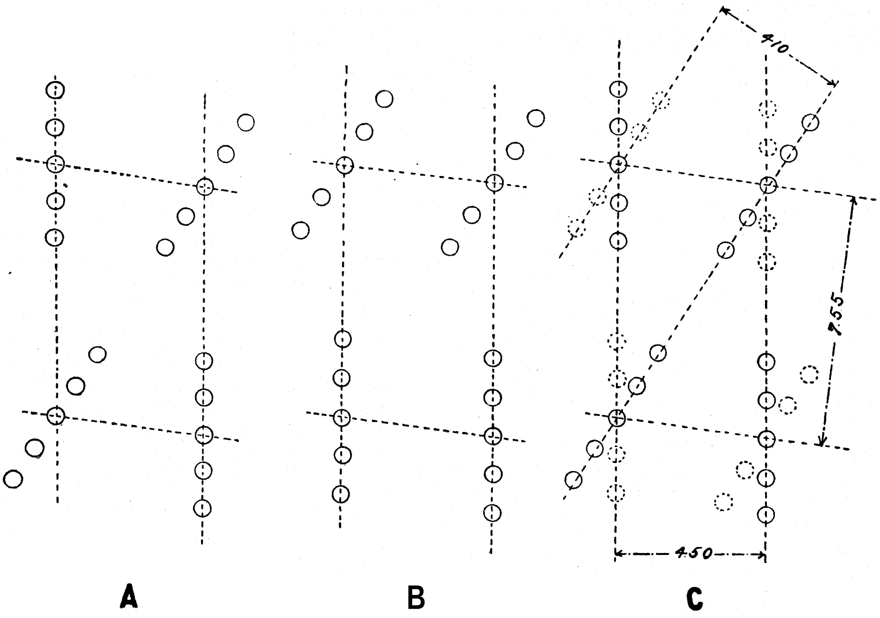


Fig. 2.

In attempting to fit a three-dimensional model of the glucose unit to our original elementary cell of untreated cellulose, we were forced to place the long dimension of the unit (7 Å.) on a diagonal of the cell because the axial dimensions were too short (6.10 and 5.40). This diagonal position furnished very satisfactory agreement with the densities of the diffraction lines produced. A similar agreement between position of the units and density of lines should occur, of course, with the mercerized cellulose. It is interesting to note that the density of the lines demanded that about half of the units should change their position from the diagonal to the b axis, and then to find that the axial dimension along that axis had actually increased sufficiently (to 7.61 Å.) to allow for the new orientation of the long axis of the glucose unit.

In the above discussion we have attempted to show that the chains of C_6 units have been shifted in their relative positions and that the individual units in each chain have assumed new relative positions with respect to one another. It now remains to be considered whether in addition to these larger shifts there have also occurred internal rearrangements in the structure of the chain and of the C_6 unit.



A B C

Fig. 3.

The fact that identical diffraction lines were obtained from both untreated and from mercerized fibers in the 90° position shows that the planes of atoms at right angles to the *c* axis have not shifted during the mercerization process. Since it has been shown in our earlier paper that the arrangement of these particular planes of atoms is produced by the arrangement of atoms in the amylene oxide ring of the constituent glucose units, the absence of change in the arrangement of the planes would appear to indicate that the ring formation has not been disturbed. Although the same planes of atoms exist after as before mercerization, a distinct change in the intensities of three lines shows that there has been some change in the spacial relationship of some of the constituent atoms of the C_6 group. An adequate explanation may be found in the mobility of the hydroxyl group attached to the sixth carbon atom. An examination of the three-dimensional model[7] will show that while the rest of the atoms in the molecule are in practically fixed positions, this particular hydroxyl is capable of rotation about the axis of the bond joining the fifth and sixth carbon atoms. A rotation from position A to position B, as shown in Fig. **4,** would have a tendency to produce the changes observed, namely, a decrease in the density of the 2.58 and the **3.40** lines and an increase in that of the 5.15 line.

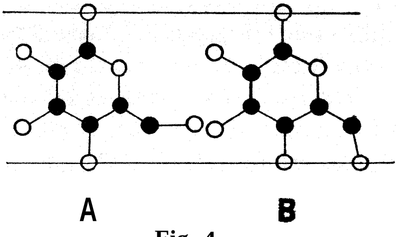


Fig 4

The Nature of the Mercerization Change

From the preceding considerations mercerization appears to be the result of rearrangements in three different ways: (1) a shift in the position of the chain with respect to the neighboring chains, **(2)** a partial rotation of the alternate glucose units in each chain and **(3)** a shift in the position of the hydroxyl attached to the sixth carbon atom. We are not prepared to discuss at present either the time relation or the causal relation of these three events; that is, we do not know whether the movement of the whole chain is due to the partial rotation of the alternate glucose groups nor whether those movements are influenced by the probable shifting of the hydroxyl mentioned.

Regardless of the relationship existing between these three rearrangements, the new positions taken by the chains and by the constituent units and parts seem to dispose of several suggestions which have appeared in the literature concerning the nature of mercerization. It seems extremely unlikely that the mercerization process involves *(a)* a migration of an oxygen bridge,[8] (b) an enolization,[9] (c) an isomeric change,[3] or in fact any type of molecular rearrangement of the constituent glucose, since any such change would almost certainly produce a different diffraction pattern than that which is obtained from the 90° position of the fibers.

It appears also unlikely that mercerization is a progressive change varying in degree with the strength of the alkaline solution employed, as Herzog[2] contended. Herzog recognized three stages of mercerization; the first with 8 to 10% NaOH, the second with about 14% and the third or "total mercerization" with **28%** NaOH.

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[7] Ref. 6, Fig. 3, p. 179.

[8] Herzog and Londberg, *Ber.*, 57, 329 (1924).

[9] Gebhard, *Chem.-Ztg.*, 37,663 (1913).

Our data indicate that there is a critical concentration of alkali below which the treatment does not produce a permanent effect on the arrangement of the C_6 units. This critical concentration is in the neighborhood of 13% for sodium hydroxide. Material treated with alkali of about that concentration is quite likely to give diffraction lines of both the mercerized and unmercerized fibers, as previously mentioned. It is probable that certain discrepancies between our data and those of Herzog are due to this partially mercerized condition. In his data from the 14% material, the interference points A_1 and A_2 were apparently produced by the parts of the fibers which were unmercerized, since they appeared from the 8% and not from the 28%; while opposed to this the A_3 and A_4 lines were produced by the mercerized parts of the fibers since they appeared from the 28% and not from the 8% treatments. With that explanation his data, but not his conclusions, are in agreement with ours with one further exception. Apparently he has made the error of accepting interference points produced by K_β wave lengths as though they were of K_α origin. His point A_3 from 8% treatment is quite clearly of K_β origin, while A_4 is of K_α origin from the same set of planes. Of course that A_3 point should be discarded and, without that, there is no basis for Herzog's conclusion that mercerization is a progressive change.[10] On the other hand, both his data and ours seem to indicate that only two general types of x-ray diffraction patterns are obtainable, one from unmercerized and the other from mercerized material, and that the spatial rearrangement of the groups of atoms which exist in mercerized material is produced by a definite concentration of the alkali. Although the fibers are swollen to a different extent with different concentrations of alkali, the component chains, upon washing, seem to behave in only two ways: for concentrations below 13% they return to their original position, for those'above that concentration they take on new positions as described above.

We desire to call attention here to the additional support which the observations recorded in the present paper give to the conception of a cellulose structure as being made up of continuous chains of glucose units which are held together by primary valence linkages. As we have shown, mercerization produces a separation of the chains and a partial rotation of the units within the chains. This rotation is definitely a rotation about an axis which is parallel to the long axis of the chain. Throughout these changes the chains as such remain intact; that is, the C_6 units have not become detached from the chain.

If the units were held together by secondary valence forces only,[11] then the alkali treatment should produce a separation of the units lengthwise of the fiber, just as it produces the separation of the chains laterally.

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[10] Sponsler has discussed this error in greater detail in Nature, 120,767 (1927).

[11] K. Hess and others, Ann., 435, 1–144 (1923); 443, 71–112 (1925).

Our x-ray evidence, however, shows that no separation of the C_6 groups occurs lengthwise of the fiber, but that the chains have become separated, indicating that the forces existing between the units in the chain must be greater than those exerted laterally from chain to chain. We consider that the greater forces holding unit to unit correspond to primary valences and the lesser ones between the chains to secondary valences.

Again, if cellulose were composed of detached C_6 units held in space by secondary valence only, it is scarcely conceivable that the forces which produce mercerization would be exerted so as to produce partial rotation on one axis only and that axis the long axis of the chain. It would seem more likely that rotation would occur on several axes rather than only one which happens to be always the long axis of the chain, and, further, it would seem that the units would be forced out of their linear arrangement unless the forces which hold the units together, and incidentally act as pivots, are stronger than the laterally acting forces.

The x-ray evidence which we have brought forward points very strongly to a linear arrangement of the units and shows that the mercerization process produces rotation of some of the units about the long axis of the chain but does not disturb their linear arrangement. This evidence indicates that the forces holding the units together in a linear chain are too strong to be overcome by the mercerization process and that, on the contrary, the forces acting laterally unquestionably have been overcome. These stronger linear forces correspond to our conception of primary valence forces; the weaker lateral forces, to secondary valences.

We have not yet attempted to correlate the gross changes of swelling, shrinking and twisting which accompany mercerization with the changes observed in the lattice structure.

We have so far been concerned with the structure of mercerized cellulose rather than with the mercerization process. Accordingly, we have as yet no insight into the mechanism by which treatment of cellulose fibers with strong sodium hydroxide solution is able to produce the changes we have been discussing., but studies are now under way with swollen fibers which may give some suggestion as to the mechanism involved in mercerization.

Summary

1. X-ray diffraction data are given for ramie cellulose which has been subjected to mercerization processes with various strengths of sodium hydroxide solutions. The evidence shows that there is a critical concentration of the alkali at about 13%, above which the fibers are mercerized, below which they remain unmercerized.

2. From the diffraction patterns of mercerized ramie cellulose a space lattice has been developed, When compared with the unmercerized lattice the *c* axis is seen to be unchanged while the a and *b* axes have been

changed from $a = 5.40$ in the unmercerized to $a = 4.53$ in the mercerized and from $b = 6.10$, to $b = 7.61$ Å. The angle between axes a and b has been changed from 90 to 83°.

3. As a result of mercerization the chains of glucose units have been shifted laterally in the wall of the fiber and have remained unbroken.

4. Within the chain the original glucose unit has remained unchanged except for a shift of the hydroxyl of the sixth carbon atom. The x-ray diffraction patterns indicate that there has been a partial rotation of some of the glucose units about the long axis of the chain.

5. A comparative study of the structures of mercerized and unmercerized cellulose has produced additional support to the view that the constituent units of cellulose are united in chains by primary valence linkages.

LOS ANGELES, CALIFORNIA
BERKELEY, CALIFORNIA

[COMMUNICATION FROM THE DEPARTMENT OF INDUSTRIAL AND CELLULOSE CHEMISTRY, MCGILL UNIVERSITY]

STUDIES ON REACTIONS RELATING TO CARBOHYDRATES AND POLYSACCHARIDES. XIV. POLYMERIZATION OF ALDEHYDES

BY HAROLD HIBBERT, W. F. GILLESPIE[1] AND R. E. MONTONNA[2]

RECEIVED MARCH 8, 1928 PUBLISHED JULY 6, 1928

The nature of polymerization, aggregation and disaggregation is one of peculiar importance in relation to the valence, surface tension, crystal and absorption forces which come into play in the formation of large crystalline and colloidal aggregates in plant and animal life, since "permanence of form" and "capacity to exist" are both dependent on the ability of specific substances to exhibit the pheonomenon of "aggregation." The nature of the forces through which this increased permanence and stability are attained is, as yet, quite unknown, as is evident from the work of Bergmann,[3] R. O. Herzog,[4]

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[1] Presented to the Faculty of the Graduate School, McGill University, June, 1927, in candidacy for the degree of Master of Science.

[2] Taken in part from the thesis of R. E. Montonna as presented to the Graduate School of Yale University in June, 1924, in candidacy for the degree of Doctor of Philosophy.

[3] Bergmann, "Allgemeine Strukturchemie der complexen Kohlenhydrate und Proteine," *Ber.*, 59, 2973 (1926); "Beitrage zur Chemie hochmolekularer Stoffe," *Ann.* 445, 1 (1925); "Über den hochmolekularen Zustand von Kohlenhydraten und Proteinen und seine Synthese," *Z. angew. Chem.*, 38, 114 (1925); *Naturwissenschaften*, 1925, p. 1045; "Über ein assoziierendes Hexosan," *Ann.*, 448, 76 (1926).

[4] Herzog, "Published Researches from the Kaiser Wilhelm Institut für Faserstoffchemie," 1920–1927.

H. Mark,[5] Hess,[6] Pringsheim,[7] Staudinger,[8] Karrer,[9] Waldschmidt-Leitz[10] and others.[11]

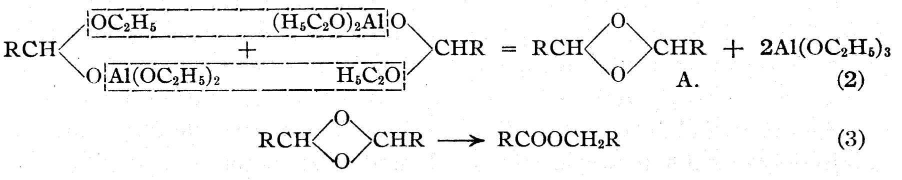
As illustrating the complexity of the problem involved, the recent work of Bergmann,[12] on cellobiose anhydride and of Hess[6d] on cellulose may be cited. In the Form of their acetates these substances are present in solution as monomolecular derivatives which, however, on saponification yield the original, highly polymerized, hydroxy compounds.

There seems to be little doubt, as suggested by Bergmann,[13] that in the case of the polysaccharides the factors responsible for the polymerization are concerned with the entire molecule (a) the hydroxyl groups, (b) latent aldehyde groups and (c) oxygen bridge rings.

In order to throw some light on the subject, work has been carried out for some considerable time by the author and his co-workers on the properties of the carbonyl group.

In connection with an investigation carried out several years ago on the mechanism of the formation of esters from aldehydes by the catalytic action of an aluminum alkylate (Tischtschenko)[14] it seemed possible that the function of the catalyst might be explained by the formation of an intermediate, unstable four-membered oxygen ring (A) which, through

$$2RCHO + 2Al(OC_2H_5)_3 = 2RCH(OC_2H_5)[OAl(OC_2H_5)_2] \qquad (1)$$


A.
(2)
(3)

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[5] Mark, "Über die roentgenographische Ermittelung der Struktur organischer besonders hochmolekularer Verbindungen," *Ber.*, 59, 2982 (1926).

[6] (a) Hess, "Über Cellulose," *Ann.*, 435, 1 (1923); (b) *Papierfabrikant,* 35, 541 (1927); (c) *Kolloid-Chemische Beihefte,* 1926, p. 93; (d) "Ueber Lösung und Abbau von Cellulose, ein Beitrag zur Chemie hochmolekularer Korper," *Z. angew. Chem.*, 39, 1189 (1926); see also (e) *Naturwissenschaften,* 19, 435.

[7] Pringsheim, "Abbau und Aufbau der hochmolekularen organischen Stoffen," *Ber.*, 59, 3008 (1926).

[8] Staudinger, "Die Chemie der hochmolekularen organischen Stoffen," *Ber.,* 59, 3019 (1926).

[9] Karrer, "Der Aufbau der polymeren Kohlenhydrate," see *Ergebnisse der Physiologie,* 20, 443 (1922).

[10] Waldschmidt-Leitz, "Zur Struktur der Proteine," *Ber.*, **59, 3000** (1926).

[11] For synopsis see "Handbuch der normalen und pathologischen Physiologie," 1927, pp. 922–924.

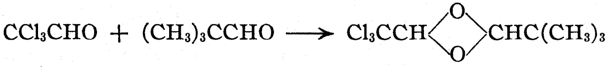
[12] Bergmann, *Ber.*, 57, 1276 (1924).

[13] Bergmann, *Ann.*, **445,** 5 (1925).

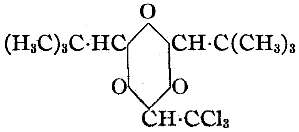
[14] Tischtschenko, *J. Russ. Phys. Chem. Ges.*, **38,** 355, 482 (1906); *Chem. Centr.*, 1906, (II), 1309, 1552.

the wandering of a hydrogen atom would be capable of yielding the corresponding ester.'[5]

An attempt to prepare such a ring by the interaction of chloral with trimethylacetaldehyde



yielded instead a mixed paraldehyde, formed from the union of two moles of trimethylacetaldehyde with one of chloral



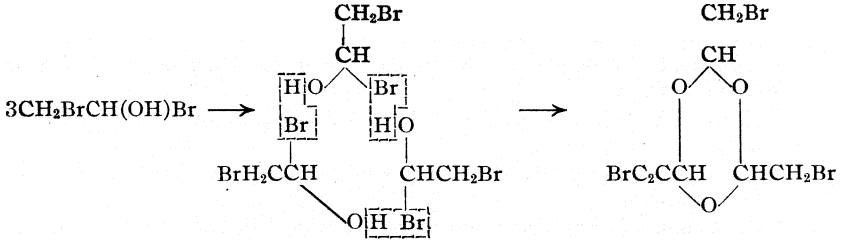
The substance[16] is a crystalline product, remarkably stable toward aqueous and alcoholic alkali. Owing to a temporary interruption in the work it was not possible to carry it further and in the meantime two other interesting communications on the same subject have appeared.

Helferich[17] has shown that mixed paraldehydes can be obtained readily from acetaldehyde and both the halogenated butyraldehydes and chloral in which two moles of acetaldehyde are united with one mole each of the chlorinated aldehydes.

These products are oils which possess a strong paraldehyde odor, are difficultly soluble in water and decompose slowly into their component parts on standing, more rapidly under the influence of acids.

Stepanow and co-workers[18] in an interesting re-investigation of the work of Hibbert and Hill[19] on the synthesis of bromo-acetaldehyde from paracetaldehyde were able to prepare mono-, di- and tribromoparacetaldehydes.

They also were able to isolate α,β-dibromo-ethyl alcohol [$CH_2BrCH(OH)Br$] and to show that the product readily loses hydrobromic acid to give tribromoparacetaldehyde, thus indicating the mechanism by which the acid probably functions as a catalyst in paraldehyde formation.



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[15] A review of this and similar reactions is to be given in a series of forthcoming papers on "The Mechanism of Organic Reactions."

[16] This product was first prepared by R. E. Montonna in February, 1924.

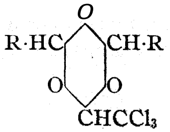
[17] Helferich, *Ber.*, 59, 1276 (1924).

[18] Stepanow, *Ber.*, 58, 1718 (1925); 59, 2533 (1926).

[19] Hibbert and Hill, THIS JOURNAL, 45, 734 (1923).

The action of other catalysts such as sulfuric acid, zinc chloride, etc., may thus be satisfactorily explained.

In the present investigation the work of Stepanow and co-workers on the bromoparaldehydes was confirmed and in addition new paraldehyde derivatives were prepared from both propionaldehyde and *iso*butyraldehyde with chloral in which two moles of each of the former are combined with one of chloral. Each of the members of a series of substituted acetaldehydes, namely, $H{-}CH_2CHO$, $CH_3{-}CH_2CHO$, $(CH_3)_2{=}CHCHO$, $(CH_3)_3{\equiv}CCHO$, is thus found to condense readily with chloral **to give** a mixed paraldehyde of the general type:



These paraldehydes are stable crystalline products which are insoluble in water and show no tendency to alter on standing. They decompose on continued boiling with sulfuric acid but are very stable toward alkali.

All attempts to prepare mixed paraldehydes involving three different aldehydes were unsuccessful. Thus with molecular proportions of *iso*butyraldehyde (A), propionaldehyde (B) and chloral (C), instead of the expected A B C paraldehyde derivative, there was obtained a mixture of two paraldehydes, the one being formed from two moles of propionaldehyde, the other from two moles of di-isobutyraldehyde with one mole of chloral.

Similar attempts using bromo-acetaldehyde in place of chloral were also unsuccessful.[20] It is of interest that a paraldehyde of hydroxypyruvic aldehyde has been isolated[21] and that the recent work of Klason[22] assigns to lignin the role of a paraldehyde derivative of coniferyl aldehyde.

Practical Part

Paraldehyde Formation from Trimethylacetaldehyde and Chloral, $CCl_3CHO + 2(CH_3)_3C{\cdot}CHO$.—14.75 g. of chloral (1 mole) was mixed with 8.6 g. of trimethylacetaldehyde[23] (1 mole) (b. p. 74–78°) at room temperature. There was an increase in tem-

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[20] The explanation apparently lies in the different reaction velocities with which the components unite. From this standpoint it might be of interest to see whether acetol, dioxyacetone and glyceric aldehyde are capable of forming a mixed paraldehyde of the A B C type, since there is the possibility that abnormal biochemical changes possibly may be due in certain cases to the formation of the relatively stable paraldehyde derivatives, thus interrupting the normal course of oxidation, etc.

[21] Evans and Waring, THIS JOURNAL, 48, 2679 (1926).

[22] Klason, *Ber.*, 58, 1761 (1925); 61, 171 (1928).

[23] This was prepared by Richard's method, Ann. *chim. phys.*, [8] 21, 360 (1910), by first decomposing the trimethylpyruvic acid with aniline. It was found better to hydrolyze this reaction product by refluxing with 20% sulfuric acid for two hours instead of attempting to distil it as he recommends. After washing the bisulfite compound with ether and drying, it should then be decomposed with sulfuric acid and steam distilled, since sodium carbonate tends to cause polymerization.

perature of about 6°. After standing for two days the product had become almost solid. The crystals were separated from the small amount of mother liquor and recrystallized from hot, absolute alcohol, m. p. 114–115°; yield, 16 g.

Anal. Subs., 0.2700, 0.2548: H_2O, 0.1570, 0.1510; CO_2, 0.4436, 0.4222. Subs., 0.1149, 0.2183: AgCl, 0.1537, 0.2908. Calcd. for $C_{12}H_{21}O_3Cl_3$: H, 6.62; C, 45.06; Cl, 33.29. Found: H, 6.51, 6.63; C, 44.75, 45.17; Cl, 33.09, 32.96.

Mol. wt. Subs., 0.2564, 0.2817, 0.2982: benzene, 17.543. ΔT, 0.241, 0.259, 0.280. Calcd.: 319. Found: 311, 333, 311.

The substance is insoluble in hot and cold water and in dilute alcohol, readily soluble in hot absolute alcohol and cold benzene. It is very stable toward aqueous and alcoholic alkali.

The product may be obtained more readily by using a trace of concentrated sulfuric acid as a catalyst and warming until solution occurs. After standing for two hours at room temperature the semi-solid, crystalline mass is filtered and the product recrystallized.

Propionaldehyde and Chloral ($CCl_3CHO + 2CH_3CH_2CHO$).—Fourteen and one-half grams of propionaldehyde (2 moles) was mixed with 18.4 g. (1 mole) of chloral, the flask placed in a freezing mixture (–10°) and a few bubbles of dry hydrogen chloride gas passed into the mixture. The contents were allowed to stand at 0° for about twelve hours, the crystals formed removed by suction filtration, washed with a small quantity of 50% alcohol and then dissolved in absolute alcohol. The solution was diluted by adding one-fifth its volume of water and the oil separating out redissolved by warming. It was filtered hot and allowed to crystallize slowly. The crystals, after filtering, washing with alcohol (50%) and drying, melted sharply at 62.5°; yield, 35–40%.

The same product was also obtained without the use of a catalyst (HCl).

Anal. Subs., 0.1804, 0.1760: H_2O, 0.0798, 0.0791; CO_2, 0.2387, 0.2391. Subs., 0.1287: AgCl, 0.2097. Calcd. for $C_8H_{13}O_3Cl_3$: H, 4.93; C, 36.43; Cl, 40.39. Pound: H, 4.92, 4.98; C, 36.40, 37.00; Cl, 40.27.

Mol. wt. Subs., 0.4365, 0.8884: benzene, 17.60. ΔT, 0.490, 1.001. Calcd.: 263.5. Found: 259, 256.

*Iso*butyraldehyde and Chloral ($CCl_3CHO + 2(CH_3)_2CHCHO$).—This compound was prepared similarly, both with and without a catalyst; needle crystals from 80% alcohol; m. p. 68.5–69°; yield, 39%.

Anal. Subs., 0.1674, 0.1718: H_2O, 0.0896, 0.0891; CO_2, 0.2565, 0.2601. Subs., 0.1123, 0.1061: AgCl, 0.1680, 0.1569. Calcd. for $C_{10}H_{17}O_3Cl_3$: H, 5.83; C, 41.30; Cl, 36.58. Found: H, 5.93, 5.78; C, 41.80, 41.30; Cl, 36.84, 36.60.

Mol. wt. Subs., 0.3057, 0.8806: benzene, 17.60. ΔT, 0.310, 0.890. Calcd.: 291.5. Found: 287, 289.6.

All three paraldehydes are very insoluble in hot and cold water but are readily soluble in organic solvents. They show no sign of decomposition on standing for several months; are stable toward alkalies, but decompose on boiling with dilute sulfuric acid.

All attempts to prepare paraldehydes involving three different aldehydes (propionaldehyde, *iso*butyraldehyde and chloral; acetaldehyde, *iso*butyraldehyde and chloral, etc.) were unsuccessful, only mixtures of paraldehydes containing two moles of the aldehyde to one mole of chloral being obtained. Negative results were also obtained using bromoacetaldehyde in place of chloral.

It was not found possible to condense acetaldol with chloral to give a mixed paraldehyde.

Summary

1. Chloral either alone or, better, in the presence of a trace of hydrogen chloride, combines with acetaldehyde,'' propionaldehyde, *iso*butyraldehyde and trimethylacetaldehyde to give paraldehydes corresponding to the general type ($2RCHO + CCl_3CHO$).

2. It apparently does not combine with acetaldol under similar conditions.

3. Attempts to prepare a mixed paraldehyde containing three different aldehydes were unsuccessful.

4. The possible role played by such derivatives in plant and animal life would seem to call for some consideration.

MONTREAL, CANADA

[CONTRIBUTION FROM THE CHEMICAL LABORATOPY OF THE RICE INSTITUTE]

ALPHA-FURFURYL CHLORIDE (FURYL-2-METHYL CHLORIDE) AND ITS DERIVATIVES.

I. THE PREPARATION AND PROPERTIES OF ALPHA-FURFURYL CHLORIDE AND A FEW ALPHA-FURFURYL ETHERS[1]

BY W. R. KIRNER

RECEIVED MARCH 12, 1928 PUBLISHED JULY 6, 1928

The synthesis of many relatively simple derivatives of furan has hitherto been impossible or, at best, extremely difficult and complicated, due to the fact that reactive starting materials such as the ω-halogen derivatives of furan homologs have been practically unknown. A halogen in the side chain of a furan ring corresponds in reactivity to that possessed by a halogen in the side chain of a benzene ring.

Fenton and co-workers[1a] were the first to prepare a reactive halogen derivative of methylfuran when they succeeded in isolating 2-chloromethyl- and 2-bromomethyl-5-furfuraldehyde from a large variety of carbohydrates using a non-aqueous solvent (for example, ether, chloroform or carbon tetrachloride) saturated, respectively, with hydrogen chloride and hydrogen bromide. They pointed out the high order of reactivity of the halogen and prepared a number of derivatives in which the halogen was substituted by groups such as H, OH, $OCOCH_3$, $OCOC_6H_5$, C_6H_5 and $CH_2C_4H_2OCOH$, while subsequent workers[2] extended the list of sub-

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[1] Presented before the Organic Chemistry Division of the American Chemical Society at the St. Louis meeting. April. 1928.

[1a] Fenton and Gostling, J. *Chem. Soc.*, 73, 556 (1898); *ibid.*, 75, 423 (1899); *ibid.*, 79, 361,807 (1901); Fenton and Robinson, *ibid.*, 95, 1334 (1909).

[2] Erdmann, *Ber.*, 43, 2392 (1910); Cooper and Nuttall, *J. Chem. Soc.*, *99*, 1197 (1911); E. Fischer and v. Neyman, Ber., 47, 974 (1914); see also Middendorp, *Rec. trav. chim.*, 38, 23–38 (1919).

stitutions to include the OCH_3 and OC_2H_5 groups. Rill and Jennings[3] obtained the 2-bromomethylpyromucic acid by direct bromination under specific conditions and noted the easy hydrolysis to form the hydroxy compound.

Only recently has the preparation of the parent w-halogen methylfuran been successful. Zanetti[4] has succeeded in preparing ethereal solutions of both the a-furfuryl bromide and iodide from a-furfuryl alcohol by simple procedures. In the case of the iodide at least 40% of the alcohol is transformed and 70% in case of the bromide. Using these reactive agents, Zanetti prepared five ethers which had previously been unknown. Zanetti did not isolate the bromide or iodide in a pure condition but merely obtained them in an ethereal solution. Von Braun and Kohler were the first to have prepared an ethereal solution of the bromide[6] by the treatment of a-furfurylethylmethylamine with cyanogen bromide, which resulted in an 80% conversion of the base (by weight) to the bromide. This method is not as convenient, however, as that of Zanetti. Von Braun and Kohler describe the properties of the ethereal solution, particularly its gradual decomposition on standing, and add that when an attempt was made to distil it, it completely decomposed. They consider it a surprisingly satisfactory result that a-furfuryl bromide is stable even for several hours. They also predicted that the same ease of decomposition would probably be found in the chloride.

Von Braun and Kohler attempted to make a-furfuryl chloride by the well known Von Braun reaction which, in this case, consisted in the treatment of the benzoyl derivative of a-furfurylmethylamine with phosphorus pentachloride. The reaction resulted only in the complete resinification of the substances present, the same result being obtained with phosphorus pentabromide. Gilman and Vernon[6] also attempted to prepare the chloride by treatment of an ethereal solution of a-furfuryl alcohol with thionyl chloride at low temperature and by passing dry hydrogen chloride into an ethereal solution of the alcohol in the presence of a dehydrating agent (calcium carbide), The yield in the first case was 10% (based on the amount of a-furfuryl ethyl ether obtained) and 5% in the second case. Both of these methods are therefore decidedly unsatisfactory and impractical. Gilman and Vernon state that "all efforts to distil the chloride were futile. After some 80–90% of the ether had been distilled at reduced pressure, the contents of the flask suddenly and violently decomposed into a hard, intractable tar. The temperature of the water-bath in which the flask was immersed did not exceed 30°."

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[3] **Hill and Jennings, Am. *Chem.* J., *15*, 180 (1893).**

[4] **Zanetti, THIS JOURNAL, 49, 1061, 1065 (1927).**

[5] **Von Braun and Kohler, Ber., 51, 87 (1918).**

[6] **Gilman and Vernon, THIS JOURNAL, 46, 2576 (1924).**

It is the purpose of this paper to demonstrate that *under certain conditions it is possible to prepare the chloride and isolate it in a pure state by vacuum distillation, to obtain a satisfactory analysis, determine its physical properties and prepare derivatives of it.* Zanetti has shown that the bromide is more stable than the iodide toward potassium hydroxide[7] and in this work it is proved that the chloride is more stable toward potassium hydroxide than the bromide The relative stabilities of these furfuryl halides thus coincide with the order usually given for organic halides, namely, chloride > bromide > iodide. Although the chloride is a relatively unstable substance it is of a much higher order of stability than the statements of previous investigators would lead one to believe.

Since the furan nucleus is sensitive to halogen acids, it is imperative in the successful preparation of the furfuryl halides to avoid so far as possible the presence of halogen acids in an uncombined state. The Darzens method for the preparation of chlorides from alcohols,[8] which consists in the treatment of the alcohol in a solution of a tertiary amine (pyridine was used in this work) with thionyl chloride, is ideal in this case since the hydrogen chloride which is liberated from the alcohol and thionyl chloride is immediately taken up by the base and therefore causes no decomposition of the sensitive alcohol. By this method *α-furfuryl alcohol has been converted into α-furfuryl chloride with a 63% yield of distilled material.* The boiling point observed was 49.6–50° at 27 mm. The substance distils as a water-white liquid which is sufficiently stable, in the absence of moisture, to permit its analysis and the determination of its density and refractive index. It is insoluble in water but soluble in the common organic solvents. It possesses a characteristic odor and is a weak lachrymator. On standing it gradually turns yellow, then green and finally black and deposits a black, resinous precipitate. An ethereal solution remains nearly colorless for several days at room temperature and gradually turns yellow with the formation of a black, gummy precipitate. There is no difficulty whatsoever in preparing and keeping the substance long enough for use in any reaction.

From the pure chloride a number of ethers were prepared using the procedure given by Zanetti.[4] The ethers were chosen as the first derivatives to be prepared since Zanetti has recently prepared a considerable number of them by a convenient procedure and in good yield. They are listed below together with their boiling point, density, yield, refractive index and calculated and observed molecular refraction. It is interesting to note that Zanetti was unable to prepare the allyl ether by treatment of the a-furfuryl bromide with allyl alcohol; he states "the heat of formation was so great as to decompose the α-furfuryl bromide, giving only resinous

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[7] Ref. 4, p. 1067.

[8] Darzens, *Compt. rend.*, **152, 1314 (1911).**

products." Using the chloride no difficulty whatsoever was experienced; in fact, the highest yield of the eight ethers prepared was obtained in this *case.*

TABLE I

α-FURFURYL ETHERS

Name	B. p., °C.	Press., mm.	Density, 20°/4°	Yield, %	Refractive index, $N_D^{20°}$ (Abbé)	Molecular refraction	
						Obs.	Calcd.
Methyl	134–135	762	1.0163	66[a]	1.4570	30.031	30.060
Ethyl	149.5–150.5	770	0.9844	81	1.4523	34.573	34.678
n-Propyl	168–170	767	0.9656	79	1.4523	39.164	39.296
n-Butyl	189–191	777	0.9516	78	1.4522	43.707	43.914
Allyl	173.5–174.5	772	1.0025	88	1.4718	38.554	38.829
Benzyl	108–109	1	1.0865	83	1.5372	54.082	54.167
α-Furfuryl	88–89	1	1.1405	84	1.5088	46.604	47.041
Cinnamyl	141–142	1	1.0802	85	1.5661	64.670	62.936

[a] Some material was lost accidentally.

Experiments are already under way in this Laboratory using the chloride for the preparation of a large number of other furan derivatives such as the amines, acetoacetic and malonic ester derivatives, those obtained from the Grignard reagent, etc.

I wish to thank my friend, Dr. John R. Johnson of Cornell University, for the first generous sample of furfuryl alcohol used in this work.

Experimental

A. Preparation of α-Furfuryl Chloride

The a-furfuryl alcohol was always freshly distilled just before using; it boiled at 84.5–85.0° at 26 mm. The pyridine was obtained from the Eastman Kodak Company, and was thoroughly dried over solid potassium hydroxide and distilled. The thionyl chloride was distilled from cotton seed oil through a Glinsky column and then re-distilled; it was practically water white.

The following procedure is typical of a number of experiments which were made: 46.2 g. (0.47 mole) of freshly distilled furfuryl alcohol was placed in a 500cc. three-necked Pyrex round-bottomed flask, the center neck being fitted with a stirrer, one side neck with a 50cc. dropping funnel and the other with a loosely stoppered thermometer; 44.7 g. (0.565 mole, 20% excess) of pyridine was added, which caused a slight evolution of heat, and then 50 cc. of dry ether (prepared in the same way as one prepares Grignard ether). The flask was immersed in an ice-bath and the stirrer started. When the temperature fell to about 2–3°, 61.7 g. (0.52 mole, 10% excess) of thionyl chloride dissolved in 50 cc. of dry ether was added from the dropping funnel, dropwise, in 10cc. portions, to the mixture in the flask, each 10cc. portion being added over a period of about twenty minutes. In this way the temperature of the reaction mixture remained at 7–9° during practically the entire reaction. The reaction was very vigorous, each drop of thionyl chloride producing a hissing noise and a spattering of the liquid.

During the addition of the second 10cc. portion, each drop of thionyl chloride produced a local turbidity and after about half of this portion had been added a heavy, oily layer started to separate. During the addition of the seventh portion the lower layer crystallized and the temperature rose rapidly to about 15° and then gradually fell again. After this portion was all added the thermometer was temporarily removed while a bent glass rod was inserted to break up the crystalline lumps as much as possible. The last portions of the thionyl chloride caused the crystalline material, which was originally a light brown color, to turn greenish-black. After all of the thionyl chloride had been added the mixture was stirred for an additional twenty-five minutes.

Darzens recommends that, after the addition of the thionyl chloride to the alcohol-pyridine mixture, the mixture be heated until evolution of sulfur dioxide ceases. In this case such a procedure was not possible for it was found that the heating resulted in nothing but a black tar; presumably the furan ring was destroyed or else polymerization occurred, Since heating was not required in this case to give a fair yield it may not be necessary in other cases in which, following Darzens, heating is usually carried out. The removal of the ethereal solution from the flask fortunately was extremely easy since the brownish lumps were rather large and pasty. The thermometer was removed and in its place a glass siphon tube was tightly stoppered, the short end of which reached to the very bottom of the flask. By having an electric light bulb behind the flask so as to be able to see through the ethereal solution the siphon tube could be placed in a space cleared up by the stirrer. Slight air pressure was then applied through the dropping funnel and the ethereal solution completely siphoned off into an Erlenmeyer flask. The ethereal solution was light yellow in color and transparent. The siphon tube was removed, 50 cc. of dry ether added to the reaction flask and the mixture stirred for five minutes after again breaking up the lumps with a bent glass rod. Then the ethereal solution was again siphoned off. This extraction was repeated three times, the last time the flask being removed from the ice-bath to permit it to warm up slightly. The total ethereal solution, which reacted acid to litmus paper, was thoroughly extracted with 50 cc. of 50% potassium hydroxide solution, everything being kept very cold and the potassium hydroxide solution being added in small portions in order not to cause undue heating. The ethereal solution was then removed and dried over anhydrous sodium carbonate.

In the distillation of the furfuryl chloride 75cc. portions of the ethereal solution were used and the distilled product was converted into the various ethers described later. The ether solution was added in portions to a 25cc. Claissen fractionating flask the side arm of which was fitted with a short water condenser, a 50cc. distilling flask being used as the receiver. The air entering the flask during the distillation was dried with a soda lime tube and a similar large soda lime tube was placed between the receiver and manometer; a water pump furnished the suction. It is the custom in this Laboratory to clean glass apparatus by immersion in a bath of very hot sulfuric acid. It was found that unless certain precautions were taken some of the acid remained adsorbed on the walls of the apparatus and that when the furfuryl chloride was distilled decomposition occurred in the side arm and receiver. This difficulty was overcome by carefully washing all apparatus a large number of times in tap water followed by washing with distilled water, then allowing the apparatus to soak in a large bath of distilled water overnight and subsequently re-washing with distilled water. The distilling flask was also steamed to remove completely any acid from the side arm and indentations of the fractionating column. The apparatus was then dried in an oven at 130°.

After removal of the ether in vacuum in the apparatus described above, a yellowish-brown, oily residue remained. On distilling this from a water-bath the liquid distilled very readily and yielded a water-white distillate. Various boiling points observed were: 49.1–49.4° (26 mm.); 49.6–50.0' (27 mm.); 54.0–54.4° (33 mm.), $d_{20}^{20} = 1.1804$; $d_4^{20} = 1.1783$; $N_D^{20} = 1.4941$ (Abbé). M_D, calcd. = 28.666; M_D, obs., = 28.788.

Anal. Subs., 0.2072, 0.2253; AgCl, 0.2538, 0.2747 Calcd. for C_5H_5OCl: Cl, 30.436. Found: 30.299, 30.16.

The analyses are slightly low due to the fact that during the time necessarily required to weigh out the sample and introduce it into the Carius tube some decomposition was taking place. This was evident from the fact that the sample gradually turned yellow.

B. Preparation of α-Furfuryl Ethers

The ethers were prepared by treating a given weight of the distilled chloride in 75 cc. of dry ether with 100% excess of dry, pulverized potassium hydroxide and with 200% excess of the desired alcohol, the alcohol being added in portions. In the case of methyl and α-furfuryl alcohol the reactions were vigorous enough to cause the ether to boil, so that cooling was necessary; large amounts of a flocculent precipitate of potassium chloride formed. In the case of the other alcohols the reaction proceeded more slowly and only small quantities of heat were evolved and small amounts of potassium chloride deposited. The reaction mixtures were allowed to stand overnight. Then the ether was evaporated on a hot-plate until the temperature of the flask contents reached 75°. The flask was then heated in a water-bath at 75–80° for a half hour, cooled, 100 cc. of distilled water added and the oily layer which separated removed with a separatory funnel. The aqueous layer was extracted four times with 25cc. portions of ether and the total oily layer–ether extract was dried over anhydrous sodium carbonate.

The ether was removed in vacuum and the residue subjected to fractional distillation, either at atmospheric pressure or in vacuum, depending on the boiling point of the furfuryl ether. The boiling points and densities, in general, agree quite well with those given by Zanetti except in the case of the a-furfuryl and benzyl ethers. In these cases the boilng points observed were about 10" lower than reported by Zanetti; his distillations were made at 2 mm., while in this work the pressure was 1 mm. The fact that the boiling points of the cinnamyl ethers agree even though distilled at two slightly different pressures makes it probable that the 10° difference in the boiling points in these two instances does not correspond to the decrease occasioned by a 1mm. change in pressure. Both of these ethers were systematically fractionated twice and they boiled very uniformly over the small range of temperature indicated. The close agreement between the calculated and observed molecular refractions indicates that the substances were pure. The value obtained for the refractive index of the ethyl ether does not agree with the value ($N^{20} = 1.4316$) given by Gilman and Vernon. They do not state their light source, but assuming that they used the D line their observed molecular refraction is 33.046, which is quite far from the calculated value of 34 678. It thus appears that their value for the refractive index is incorrect or their substance was impure. . The agreement between the observed and calculated values for the molecular refraction of the substances listed is good in all cases except the cinnamyl ether. In this case there is the usual exaltation due to the conjugated system present in the cinnamyl group. It is also interesting that the refractive indices of the ethyl, *n*-propyl and *n*-butyl ethers are almost identical.

Using the iodide for the preparation of ethers Zanetti obtained a mixture of ethers which contained as much as 30% of the di-α,α′-furfuryl ether formed by the reaction of the iodide with furfuryl alcohol. The latter was present, either because it was not reacted upon during the preparation of the iodide, or was formed by the hydrolysis of the iodide. Using the bromide practically no di-α,α′-furfuryl ether appeared to be formed. This is also true in the case of the synthesis using the choride. The crude ethers are nearly pure and leave practically no residue when distilled.

The remarks of Zanetti concerning the instability of the furfuryl ethers have been confirmed. When placed in tubes at atmospheric pressure they gradually darken, but if sealed off in tubes at about 1 mm. pressure with a trace of hydroquinone, they remain nearly colorless for a considerable length of time.

Summary

1. α-Furfuryl chloride has been isolated in a pure state, analyzed and its physical properties have been determined. It is a relatively unstable substance but of sufficient stability to be distilled in a vacuum and used in a variety of reactions. It seems obviously more stable than the corresponding bromide and iodide. This is the first time the parent w-halogen methyl furan has been obtained in a pure, free condition, having previously been known only in solution.

2. The chlorine atom possesses a high order of reactivity, comparable to that of the chlorine in benzyl chloride. Eight ethers have been prepared from the α-furfuryl chloride and their physical properties determined. The allyl-α-furfuryl ether has been prepared by the direct reaction between the chloride and allyl alcohol.

3. The synthesis of this reactive chloride has opened up new possibilities in the furan series and investigations of other reactions using a-furfuryl chloride are being continued.

HOUSTON, TEXAS

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

A METHOD FOR THE MEASUREMENT OF INTERFACIAL TENSION OF LIQUID–LIQUID SYSTEMS[1]

BY F. E. BARTELL[2] AND F. L. MILLER[3]

RECEIVED MARCH 17, 1928 PUBLISHED JULY 6, 1928

Recently the authors were confronted with the problem of measuring the interfacial tension between water and a series of crude petroleum oils. Some of these oils were very dark, practically black; consequently, the methods most generally used for interfacial tension measurements were not satisfactory. With the more transparent oils the Reynolds capillary tube method[4] was used, but with the darker oils the liquid interface within the capillary could not be seen. After considerable experimentation a method was developed by means of which it was possible to determine the interfacial tension between the dark oils and water and subsequently it was found that this method gave results which checked well with what

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[1] This paper contains preliminary results obtained in an investigation on the "Displacement of Petroleum Oils from Oil Bearing Sands by Means of Selected Aqueous Solutions," listed as Project No. 27 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 27.

[3] American Petroleum Institute Research Assistant.

[4] Reynolds, Trans. Chem. *Soc.*, **119**, 460–466 (1921).

we believe to be some of the most reliable values to be found in the literature. The apparatus is simple in construction, is easy to operate and measurements can be quickly carried out.

Ferguson[5] has presented discussions covering the different methods which have been used for interfacial tension measurements; accordingly, no comprehensive discussion will be presented in this paper. It is well known that the most generally used methods have involved either the principles of the drop weight or the capillary rise method. The capillary rise method has been used with modification by Lerch,[6] Clark,[7] Reynolds,[7] Harkins and Humphery[8] and others, and not always with agreement in results. It is believed that the results reported by Harkins and Humpherys represent about the most accurate values obtained to date with a method based upon capillary rise.

The result of our experience with a number of the existing methods led first to the construction of an exceptionally simple apparatus with which apparently very satisfactory results were obtained (Fig. 1). The apparatus consists of a glass cup, A, about 4 cm. in diameter and 8 cm. in depth to the bottom of which is sealed a capillary tube outlet of about 0.3mm. radius. The remainder of the apparatus consists only of an open dish, B, which is large enough to eliminate effects due to capillarity.

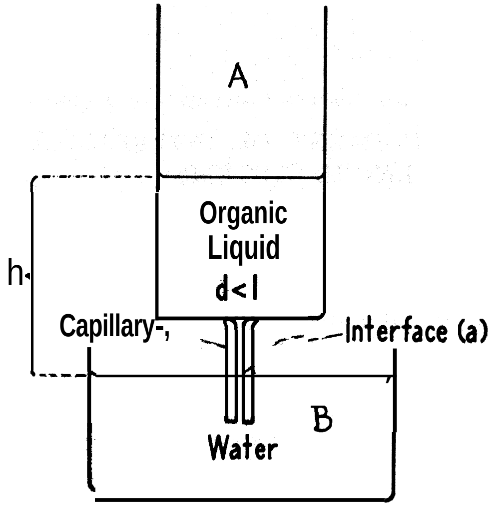

Fig. 1.

For the determination of interfacial tension, one immerses the capillary in the dish of water (B) until the calibration mark (a) is exactly level with the surface. Water will rise in the capillary to the bottom of the cup, thereby wetting the capillary throughout its length. The organic liquid (or oil) to be used is then slowly added from a buret, at the later stages drop by drop, until the water-organic–liquid interface is forced downward to the calibrated mark (a). The height of the organic liquid is then readily measured by means of a cathetometer. Knowing the density of the organic liquid, the interfacial tension, S_{23}, is calculated from the formulation

$$S_{23} = \frac{rhdg}{2} \qquad (1)$$

The results obtained with this apparatus for different organic liquids

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[5] Ferguson, Brit. Assn. Adv. Sci., ***Fifth Report,*** Colloid Chem., 1923, pp. 1–13.

[6] Lerch, ***Ann. Physik,*** 9, 434 (1902).

[7] Clark, ***Proc. Amer. Acad.,*** 41,361 (1906).

[8] Harkins and Humphery, THIS **JOURNAL,** 38,242 (1916).

against water showed close agreement with those obtained by Harkins and co-workers.[9]

The advantages of this apparatus are that it can be constructed from the materials to be found in almost any chemical laboratory and by one not expert in the art of glass blowing. The only precaution to be observed in construction is that excessive constriction or enlargement of the capillary at any point must be avoided; otherwise, difficulty will be encountered in bringing about a gradual descent of the liquid–liquid interface to the mark of calibration. Although this apparatus appeared to give good results, certain disadvantages were encountered such, for example, as the impracticability of using liquids denser than water, as also difficulty in obtaining exact temperature control.

A detailed description of this simple apparatus is given herewith, inasmuch as it is felt that this apparatus may prove to be well suited to the needs of some investigators and, further, it has been found to be satisfactory when placed in the hands of students in the regular laboratory courses.

An apparatus was next constructed which could be used with liquids of any density and which could be placed in a water thermostat and held at any desired temperature. In our experiments a thermostat with plane glass sides was used and readings were made through this glass.

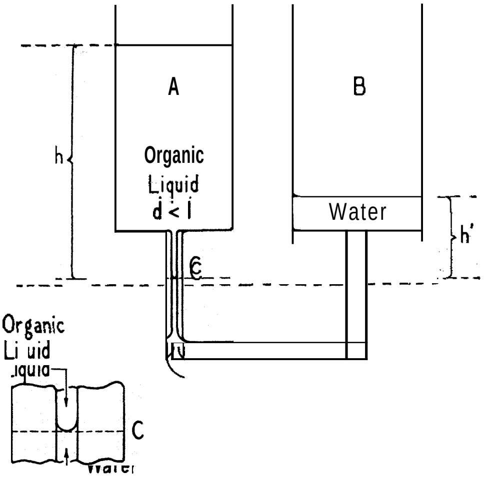

Fig 2

The apparatus is shown in Pig. 2. It consists of two cups, A and B about 4 cm. in diameter and 8 cm. in height. These are connected by glass tubing, one arm of which is a capillary tube of approximately 0.3-mm. radius. The operation of this apparatus is similar in principle to that previously described. In case the organic liquid to be used is less dense than water, the latter (about 10 cc. or more) is put into cup B. It will completely fill the glass tube and will mount to the top of the capillary tube. Immediately the organic liquid is introduced at A so that a liquid–liquid interface is formed at the upper end of the capillary. More liquid is added, finally drop by drop, until the interfacial meniscus is forced down even with the calibration mark at C. Readings h and *h'*, the heights of the organic liquid and water, respectively, above this meniscus, are now taken by means of a cathetometer.

In case the organic liquid is denser than water, the operation is somewhat different. Water (about 10 cc.) is put into cup A until it mounts just to the top of the tube in the

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[9] Numerous papers on interfacial tension.

bottom of cup B (Fig. 3). The organic liquid (as chloroform, etc.) is now added slowly to cup B, so that the water is forced back until the liquid interface enters the lower end of the capillary and finally reaches the mark C. Readings are taken with the cathetometer as before.

In either of the above cases the procedure is simple and the time required for a determination is not over ten to fifteen minutes. The formulation used in this case is as follows

$$S_{23} = \frac{rg}{2}(hd - h'd') \qquad (2)$$

in which h and d are the height and density of the organic liquid and h' and d' are the height and density of water, respectively.

The radius of the capillaries in both types of apparatus is determined by suspending the inverted cup at a given temperature in a pure liquid (as benzene) of known surface tension (S for benzene is taken as 28.25) for this temperature (25°). By carefully adjusting the apparatus the meniscus is brought to the etched mark on the capillary. The height of this meniscus above the level of the liquid in the container is measured with a cathetometer. The radius, r, is thus determined from the formula

$$S = \frac{rhdg}{2} \qquad (3)$$

or

$$r = \frac{2S}{hdg} \qquad (4)$$

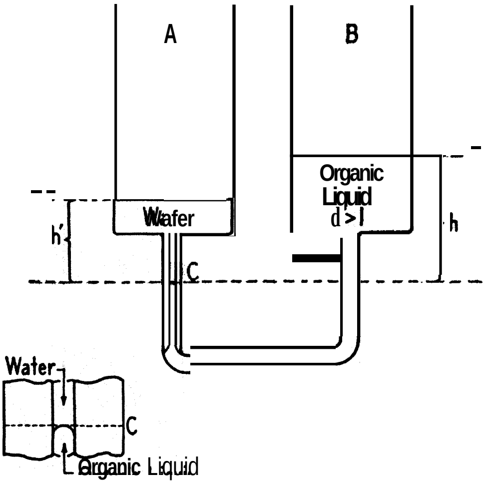

Fig. 3.

Meniscus Corrections.—In the determination of surface tension of a liquid by the capillary rise method, the height of the liquid is measured only to the lowest point of the meniscus. This leaves a small quantity of liquid above this point which should be considered and for which a correction in the reading should be made. In order to determine the height representative of the true mass of the liquid column supported by the force of surface tension, a correction must be added. The actual value in terms of height of liquid which should be considered in this correction is approximately one-third that of the height of the meniscus itself. Different investigators[10] have employed somewhat different meth-

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[10] Laplace, "Mécanique Celeste," Supp. au livre 10, 1805; Poisson, "Nouvelle Theor. de l'Action Capill.," 1831; Mathieu, "Théorie de la Capillarité," Ch. II, Ch. IV, 1883; Lohnstein, *Wied. Ann.*, 54, *713* (1895); Rayleigh, *Proc. Roy. Soc.*, 92A, *184* (1915); Schrodinger, *Ann. Physik.*, 46, *111, 413* (1916).

ods in making this correction. A generally accepted correction is that given by Poisson,[11] who expressed the correction as a function of the radius of the capillary. The equation follows (h_0 represents the observed height of the liquid column)

$$h = h_0 + {}^1/_3\, r - 0.12\% \frac{r^2}{h_0} \tag{5}$$

accordingly, substituting for the value of h in equation (3)

$$S = \frac{rh_0dg}{2} + \frac{r^2dg}{6} - 0.1288 \frac{r^3dg}{h_0} \tag{6}$$

This correction may be used for small capillaries, that is, those with radius less than 1 mm., but does not hold strictly for larger ones.

Richards and Coombs[12] have justified a simple treatment which involves only a correction for the measurement of the height of the meniscus itself. Letting h_0 represent the observed height and h_m equal the height of the meniscus

$$h = h_0 + {}^1/_3\, h_m \tag{7}$$

from which

$$S = rdg/2\,(h_0 + {}^1/_3\, h_m) \tag{8}$$

They have measured h_m directly and the values obtained by them show satisfactory agreement with those calculated with the Poisson formulation.

The radius of the capillaries used by us came well within the limits demanded by these formulations; accordingly, the Poisson equation was applied to our data for the calculation of capillary radius and comparisons were made between the values obtained when such meniscus corrections were applied and results obtained when no meniscus corrections were made.

Results.—Data will be given which were obtained with two different sets of apparatus (double cylinder type), designated as apparatus No. 1, and apparatus No. 2. The diameter of the capillary in No. 1 was uncorrected, 0.2530, corrected, 0.2522; in No. 2 it was uncorrected 0.3551, corrected 0.3329. In the first case there was an apparent error due to meniscus reading of −0.3%, in the second an error of −0.6%.

In the measurement of interfacial tension a meniscus is also involved, and again when water forms a zero contact angle the general shape of the meniscus is the same as that encountered in the determination of pore radius. Similar theoretical treatment was applied and similar corrections were made. It was found that in the case of liquids whose interfacial tension values ranged between 25 and 40 dynes, the corrections were well within the limits of experimental error. For example, results for the interfacial tension of benzene and water were almost identical when calculated, first, making no meniscus corrections whatsoever and, secondly, making meniscus corrections, that is, making meniscus height corrections

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[11] Poisson, "Nouvelle Theor. de l'Act. Capill.," 1831, pp. 112.

[12] Richards and Coombs, THIS JOURNAL, 37, 1656 (1916).

both in the calculation of radius of the capillary tube and in the subsequent calculation of the interfacial tension using this corrected radius value. It happens that in each of these cases in which the interfacial values are within the range indicated, the magnitude of the corrections for the interfacial tension values and for the capillary radius bear the same percentage relationships. In other systems having interfacial tension values outside the range indicated, the corrections for these values do not bear the same percentage relationships to the capillary radius corrections, and failure to apply the meniscus corrections in these cases does involve a perceptible error; even in these cases, however, the error is not great and the deviation still comes within the limits encountered in almost any one of the methods in present use. In fact, as shown in the table below, the deviation is not greater than errors involved in the calibration and use of different apparatus. It may be found that when liquids of an exceptional degree of purity are used and when further refinements are made and precautions are observed in the use of the apparatus, results even more consistent may be obtained.

The following table contains the results obtained with apparatus No. 1 and apparatus No. 2 (each of the double cylinder type) with six different liquids. Both corrected and uncorrected results are given.

TABLE I

INTERFACIAL TENSION VALUES OBTAINED WITH APPARATUS

Temperature, 25; apparatus No. 1; r, 0.2530 (uncorr.); r, 0.2522 (corr.)

Organic liquid against water	h (water)	h' (org. liquid)	$hd-h'd'$	S_{23} (uncorr.)	S_{23} (corr.)
Benzene	50.93	16.66	27.85	34.56	34.56
Toluene	61.47	2384	29.04	36.04	36.04
Ether	4305	22.13	8.50	10.55	10.62
Chloroform	29.20	18.06	25.50	31.65	31.65
Carbon disulfide	44.80	16.17	3868	4800	47.95
Crude petroleum oil "M"	50 04	19 73	19.70	24.45	24.47

Temperature, 25; apparatus No. 2; r, 0.3551 (uncorr.); r, 0.3529 (corr.).

Liquid	h	h'	$hd-h'd'$	S_{23} (uncorr.)	S_{23} (corr.)
Benzene	37.64	12.99	19.90	34.66	34.65
Toluene	40 10	13.78	20.74	36.12	36.10
Ether	30.10	15 33	6.09	10.61	10.74
Chloroform	23 86	17.45	18.16	31.63	31.64
Carbon disulfide	3492	16.10	27.60	48.08	47.98
Crude petroleum oil "M"	34.61	13 25	14.06	24.50	24.54

Summary

1. A method based upon the capillary tube principle was developed for the determination of the interfacial tension of liquid-liquid systems.

2. Two somewhat different types of apparatus were designed. Both types were constructed and used in the experimental work described herein. Both gave satisfactory results.

3. The method is rapid. The apparatus can be cleaned easily. Non-transparent liquids can be used, likewise liquids of any density. The apparatus can be placed in a water thermostat and kept at constant temperature while readings are being made.

4. In constructing this apparatus, it is not essential that the diameter of the capillary be strictly uniform throughout. Calibration of capillary radius is necessary only for a given point on the capillary tube; also for work of ordinary accuracy no capillary corrections for meniscus height readings are necessary.

5. Results which have been obtained show a close agreement with what are believed to be the most accurate interfacial tension data available in the literature.

ANN ARBOR, MICHIGAN

[CONTRIBUTION FROM THE LABORATORY OR ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

SYNTHESIS OF HEPTANE DICARBOXYLIC ACID-1,5[1]

BY ALBERT S. CARTER

RECEIVED MARCH 19, 1928 PUBLISHED JULY 6, 1928

Perkin[2] attempted to prepare heptane dicarboxylic acid-1,5 through the condensation of diethyl ethyl malonate with trimethylene bromide and subsequent condensation with diethyl malonate to yield heptane tetracarboxylic ester-1,1,5,5. This was hydrolyzed and partially decarboxylated with the formation of an acid which seemed to be ethyl pimelic acid (heptane dicarboxylic acid-1,5). This product could not be purified to yield a solid acid, such as might be expected from the melting points of the other isomers of azelaic acid, consequently Perkin expressed doubt as to the purity of his product. This work was repeated with the utmost care and it was found that the results duplicated those obtained by Perkin. It was found, however, that small amounts of nonane tetracarboxylic ester-3,3,7,7 could be isolated from the reaction product and it was thought probable that the corresponding diethyl pimelic acid might be the impurity which inhibited the crystallization of the product.

The use of trimethylene chlorobromide or the addition of the sodium derivative of ethyl malonic ester to trimethylene bromide instead of the addition of the bromide to the sodium derivative would decrease the tendency to form the nonane tetracarboxylic acid (the former was tried by Perkin), but neither of these methods would insure that none of the second-

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[1] **From an investigation carried out under the direction of Professor Richard Fischer which constituted a part of a thesis presented by A. S Carter to the Graduate School Faculty of the University of Wisconsin in partial fulfilment of the requirements for the degree of Doctor of Philosophy.**

[2] Perkin, J. Chem. *Soc.*, *65*, 991 (1894).

ary product would be formed. The idea of adding the sodium derivative to the bromide in order to have constantly an excess of the bromide present was tried without success.

To avoid completely the condensation of two molecules of the malonic ester with trimethylene bromide, a synthesis involving the use of phenoxypropyl bromide was carried out to yield phenoxypropylmalonic ester and phenoxyvaleric acid. This was hydrolyzed to form iodovaleric acid, esterified and condensed with diethyl malonate.

$$C_6H_5O(CH_2)_3Br \xrightarrow[C_2H_5ONa]{CH_2(COOC_2H_5)_2} C_6H_5O(CH_2)_3CH(COOC_2H_5)_2 \xrightarrow{H_2O}$$

$$C_6H_5O(CH_2)_3CH(COOH)_2 \longrightarrow C_6H_5O(CH_2)_4COOH \xrightarrow{HI} I(CH_2)_4COOH \xrightarrow[HCl]{C_2H_5OH}$$

$$I(CH_2)_4COOC_2H_5 \xrightarrow[NaOC_2H_5]{HCC_2H_5(COOC_2H_5)_2} C_2H_5OOC(CH_2)_4CC_2H_5(COOC_2H_5)_2 \xrightarrow{H_2O} \xrightarrow{Heat}$$

$$HOOC(CH_2)_4CH(C_2H_5)COOH$$

Experimental Part

8-Phenoxypropyl Malonic Ester.—Following the general course of some work by Marvel and MacCorquodale,[3] phenoxypropyl malonic ester was prepared as follows: 32 g. of sodium was added to 500 cc. of absolute alcohol and to this was added 225 g. of diethyl malonate through a dropping funnel, with frequent shaking. During a period of about one hour, 325 g. of phenoxypropyl bromide was added to the reaction mixture, which was then refluxed for four hours. Most of the alcohol was distilled from the neutral product and it was shaken with water to remove the sodium bromide. The ester layer was collected in a little ether, separated from the water and dried over sodium sulfate. From this ether solution, phenoxypropyl malonic ester was obtained by fractionation under diminished pressure. The fraction containing the ester was collected at 228–235° (26 mm.); yield, 310 g. or 76%.

Anal. Subs., 0.2000: CO_2, 0.4770; H_2O, 0.1334. Calcd. for $C_{16}H_{22}O_5$: C, 65.30; H, 7.48. Found: C, 65.05; H, 7.41.

8-Phenoxypropyl Malonic Acid.—One liter of 20% sodium hydroxide and 300 g. of phenoxypropyl malonic ester were refluxed for about five hours. The resulting solution was cooled and acidified with dilute sulfuric acid. The precipitated phenoxypropyl malonic acid was filtered off and recrystallized from hot water; yield, 218 g. or 90%; m. p. 72–78' with some decomposition. The melting point is given in the literature[4] as 75–80°.

δ-Phenoxypropyl Valeric Acid.—Two hundred g. of the malonic acid derivative was decarboxylated by heating in a 2-liter flask in an oil-bath at 175° until the evolution of carbon dioxide was complete. The product was cooled and recrystallized from petroleum ether, giving 147 g. (90%) of the phenoxypropyl valeric acid; m. p. 55–56° (Gabriel gives 65–66"). The silver salt of this acid was prepared by crystallization from a hot solution of the ammonium salt by the addition of silver nitrate.

Anal. Subs., 0.2000: AgCl, 0.0957. Calcd. for $C_{11}H_{13}O_3Ag$: Ag, 35.85. Found: Ag, 36.01.

8-Iodovaleric Acid.—One hundred g. of phenoxyvaleric acid was refluxed for four

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[3] Marvel and MacCorquodale, THIS JOURNAL, 46, 2838 (1924).

[4] Gabriel, Ber., 25, 418 (1892).

hours with 400 cc. of hydriodic acid (sp. gr. 1.70) and the mixture was diluted with several times its volume of water and extracted with ether. To separate the iodovaleric acid from phenol, the ether solution was extracted with saturated sodium carbonate from which the acid was precipitated with hydrochloric acid, filtered and dried. This crude product was partly purified by dissolving in 75% alcohol and pouring over ice. After drying and recrystallization from warm petroleum ether, white needles were obtained, melting at 54–56°, which agrees with the melting point previously reported;[5] yield, 80 g. or 68%. An attempt to prepare bromovaleric acid in a similar manner using 48% hydrobromic acid gave poor yields.

Ethyl **δ-Iodovalerate.**—A mixture containing 100 g. of the iodovaleric acid in 500 g. of a 5% solution of dry hydrogen chloride in absolute alcohol was refluxed for four hours and then the greater part of the alcohol and hydrogen chloride was removed by distillation. The solution was diluted with an equal volume of water, the ester layer extracted with ether and the ether solution washed with saturated sodium carbonate to remove free acid. The ether solution of the ester was dried over sodium sulfate and distilled under diminished pressure; the ester was collected in the fraction boiling from 108 to 118° (20 mm.); yield, 68 g., representing 61% of the theoretical (this is almost 90% if corrected for the acid reclaimed from the carbonate extract of the reaction product).

Anal. Subs., 0.5000: AgI, 0.4490. Calcd. for $C_7H_{13}O_2I$: I, 49.61. Found: I, 48.54.

Triethyl Ester of Heptane Tricarboxylic **Acid-1,5,5.**—Four g. of sodium was dissolved in 50 cc. of absolute alcohol and to this was added 34 g. of diethyl ethylmalonate followed by 44.1 g. of ethyl iodovalerate. The reaction mixture was worked up in the same manner as in the preparation of phenoxypropyl malonic ester, the product being obtained in a fraction boiling between 195 and 200" at 20 mm.

Heptane Tricarboxylic **Acid-1,5,5.**—As in the case of phenoxypropyl malonic acid, 31.5 g. of the tricarboxylic acid ester was hydrolyzed with 150 cc. of 20% sodium hydroxide to yield a product of oily crystals melting at 86–88' and decomposing with the evolution of carbon dioxide at temperatures above 140°.

Heptane **Dicarboxylic Acid-1,5.**—Decarboxylation of 20 g. of the tricarboxylic acid between 140 and 180° gave 16 g. of yellow oil which was distilled under diminished pressure from a Claisen flask carrying a modified arm. Upon fractionation almost the entire product was collected at 218–223° at 17 mm. (Perkin records 260" at 82 mm.) The fraction was a thick, colorless oil which seemed to resist all attempts to obtain a crystalline product from it, but after standing as a liquid for several days, it suddenly completely crystallized. This crystalline material melted at 41.5–43.0° and was soluble in hot water, alcohol and hot benzene. The silver salt was prepared by dissolving in dilute ammonium hydroxide, boiling out the excess ammonia and precipitating from the cooled solution of the ammonium salt by adding silver nitrate solution.

Anal. Subs., 0.3000: AgCl, 0.2125. Calcd. for $C_9H_{14}O_4Ag_2$: Ag, 53.68. Found: Ag, 53.32.

These analyses, while slightly low for silver, considered with the method of preparation, indicate that the product is heptane dicarboxylic acid-1,5.

Summary

Heptane dicarboxylic acid-1,5 has been synthesized through the following steps: trimethylene bromide, phenoxypropyl bromide, phenoxypropyl malonic ester, phenoxyvaleric acid, iodovaleric acid, heptane tricarboxylic acid-1,5,5 and heptane dicarboxylic acid-1,5.

[5] Cloves, *Ann.*, 319, 367, 388 (1901).

Heptane dicarboxylic acid-1,5 has been obtained as a solid.

In the course of the synthesis, the following new compounds were prepared: ethyl δ-iodovalerate, triethyl ester of heptane tricarboxylic acid-1,5,5, heptane tricarboxylic acid-1,5,5 and the silver salt of heptane dicarboxylic acid-1,5.

WILMINGTON, DELAWARE

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

THE USE OF PLATINUM-OXIDE PLATINUM BLACK IN THE CATALYTIC REDUCTION OF AROMATIC HYDROCARBONS. XVII[1]

BY ROGER ADAMS AND J. R. MARSHALL[2]

RECEIVED APRIL 2, 1928 PUBLISHED JULY 6, 1928

One of the few classes of reducible compounds which does not lend itself readily to reduction under ordinary laboratory conditions is the aromatic hydrocarbons. These compounds have frequently been reduced at high temperatures, using nickel or other metals as a catalyst, but no satisfactory method is available for their reduction under such conditions as are most conveniently used in a scientific laboratory, namely, room temperature or slightly above, atmospheric pressure or pressures not over two or three atmospheres and readily prepared catalyst. The reactions should be comparatively rapid and it should be possible to reduce large enough quantities to be sufficient for ordinary research purposes. The success of platinum-oxide platinum black as a catalyst for the addition of hydrogen to many unsaturated compounds, as compared with other forms of catalytic platinum, led to a study of its use in the reduction of aromatic hydrocarbons.

Willstatter[3] and his associates report the hydrogenation of benzene and toluene at ordinary pressures and temperatures by means of hydrogen and platinum black prepared by the reduction of chloroplatinic acid and formaldehyde. However, the large amount of catalyst needed compared with the amount of material to be reduced renders the method impractical for ordinary work. For the reduction of 3.0 g. of benzene in 13 cc. of glacial acetic acid with 0.1 g. of platinum black, six hours was required; for 1.8 g. of toluene in 3 g. of acetic acid with 0.5 g. of platinum black, three and one-half hours; for 6 g. of xylene in 4 g. of acetic acid with 0.9 g. of platinum

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[1] The previous article in this field is by Bray and Adams, THIS JOURNAL, 49, 2101 (1927). Reference to the other work will be found in this article.

[2] This communication is an abstract of a thesis submitted by J. R. Marshall in partial fulfilment of the requirements for the degree of Master of Science in Chemistry at the University of Illinois.

[3] (a) Willstatter and Waldschmidt-Leitz, *Ber.*, 54, 113 (1912); (b) Willstatter and Hatt, *ibid.*, 45, 1471 (1921).

black, twenty-four hours. Other hydrocarbons were reduced under conditions comparable with those cited.

The benzene hydrocarbons have also been reduced by means of colloidal platinum. Skita[4,5] and his associates reduced several, of which may be mentioned as examples, 1 g. of toluene in 120 cc. of acetic acid with 0.41 g. of colloidal platinum in three and one-half hours; 10 g. of xylene in 80 cc. of acetic acid with 1.5 g. of platinum in three to four hours, using in this instance, however, **3** atmospheres' pressure and 80° temperature.

The use of platinum-oxide platinum black has proved to be of value and to be a catalyst far more effective than those mentioned. Although the investigation is not entirely complete, publication of the results at hand is offered since, in an article recently published, Kuhn[6] has noted in the course of an investigation on the addition reactions of conjugated systems that certain compounds such as diphenylbutadiene were reduced by platinum-oxide platinum black not merely to diphenyl substituted saturated hydrocarbons, but even further until the benzene nuclei were saturated. Thus the completely hydrogenated derivatives of diphenylbutane, diphenylhexane and diphenyloctane were prepared. Though alcohol has usually proved to be the most satisfactory solvent for reductions with platinum-oxide black, with ethyl acetate as the second most desirable, in the case of the aromatic hydrocarbons neither is as suitable as glacial acetic acid. The temperature was in practically all cases that of the room and the pressure was varied from two to three atmospheres. The following table indicates how readily various hydrocarbons may be reduced in practically quantitative yields with a small amount of catalyst.

The first seven compounds and the last two in the table could be reduced to completion with 0.2 g. of catalyst. The heavier molecules, however (in general those with more than one phenyl group), required several additions of 0.2 g. of catalyst to obtain complete reduction within a required time.

A few experiments were made with benzene, toluene and xylene, increasing the amount of catalyst and, as might be expected, the time of reduction was very materially decreased. In addition it might be stated that fluorene and α,α-diphenylpropane resisted all attempts at reduction by a similar procedure. It is the opinion of the authors that this difficulty was probably due to slight impurities, even though special precautions were taken to remove them. In general, the rate of reaction of these aromatic compounds seemed to be very dependent on the purity of the compounds and reagents Presence of traces of impurities frequently diminished the rate of reduction markedly.

Skita[4,5] fractionated very carefully 9 g. of reduced m-xylene. From this

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[4] Skita and Meyer, *Ber.*, 45,3589 (1912).

[5] Skita and Schneck, *Ber.*, 55,144 (1922).

[6] Kuhn and Winterstern, *Helv. Chim. Acta,* 11, 123 (1928).

TABLE I

REDUCTION OF AROMATIC COMPOUNDS IN 50 CC. OF GLACIAL ACETIC ACID AT 25–30° TEMPERATURE AND 2–3 ATMOSPHERES' PRESSURE

Compound used	B. p. or m. p., °C.		Amount of substance, g.	Amount of catalyst, g.	Time, hrs.
Benzene	79.5–80		15.6 (0.2 mole)	0.2	2.0
Toluene	110–111		18.4 (0.2 mole)	.2	2.75
Ethylbenzene	136–136 8		21.2 (0.2 mole)	.2	7.5
m-Xylene	139–140		21.2 (0.2 mole)	.2	21.5
Mixed xytenes	138–145		21.2 (0.2 mole)	.2	26.0
Mesitylene	164.5–166		12 (0.1 mole)	.2	8.5
Cymene	175–176.2		13.4 (0.1 mole)	.2	7.5
Diphenylmethane		27 (m. p.)	16.8 (0.1 mole)	.2	7 0
Triphenylmethane[a]		92.2–92.5 (m. p.)	8.74 (0.033 mole)	4 X 0.2	480
α,α-Diphenylethane	147 (15 mm.)		18.2 (0.1 mole)	3 × 0.2	26.5
Dibenzyl		52.5–53 (m. p.)	18.2 (0.1 mole)	3 X 0.2	37.0
Phenylacetic acid		76 (m. p.)	13.6 (0.1 mole)	.2	5.5
β-Phenylpropionic acid		48 (m. p.)	15.0 (0.1 mole)	.2	6 0

Compound obtained	B. p., °C.	n_D	d	Ref.
Cyclohexane	79–79.5 (752 mm.)	1.4242/20°	0.7769/20°	7, 3, 4
Methylcyclohexane	100–100 2 (742 mm.)	1.4198/20°	.7687/20°	7, 4
Ethylcyclohexane	129.8–130 (743 mm.)	1.4278/25°	.7899/25°	8
m-Dimethylcyclohexane	118.5–119 (747 mm.)	1.4230/25°	.773/25°	3b, 9, 10
Mixed dimethylcyclohexanes	118–123 (743 mm.)	....	....	..
Trimethylcyclohexane	135.5–136 (743 mm.)	1.4257/25°	.8250/25°	9
1-Methyl-4-*iso*propylcyclohexane	63 (22 mm)	1.4370/25°	.8061/25°	9
Dicyclohexylmethane	110–110.5 (18 mm.)	1.4875/20°	.8884/20°	11
Tricyclohexylmethane	163.2 (4 mm.)	1.5264/20°	.9644/20°	12, 13
α,α-Dicyclohexylethane	112 (7 mm.)	1.4887/25°	.9070/25°	7, 14
α,β-Dicyclohexylethane	147–148.5 (12 mm.)	1 4760/18°	.8774/18°	4
Cyctohexylacetic acid	110–112 (3 mm)	1.4558/30°	1 007/30°	16
β-Cyclohexylpropionic acid	112–114 (4 mm.)	1.4596/25°	1.0178/25°	15, 17

[a] Temp., 60° C.; 100 cc. of acetic acid.

(7) Ipat'ev, ***Ber.***, 40, 1281 (1907); (8) Sabatier and Senderens, ***Compt. rend.***, 132, 566 (1901); (9) Skita and Schneck, ***Ber.***, 55, 144 (1922); (10) Skita, Z. ***angew. Chem.***, 34, 230 (1901); (11) Sabatier and Senderens, ***Compt. rend.***, 132, 210 (1901); (12) Ipat'ev and Dolgov, ***Compt. rend.***, 183,304 (1926); (13) Godchot, Marcel, ***Compt. rend.***, 147, 1057 (1918); (14) Sabatier and M. Murat, ***Compt. rend.***, 154, 1771 (1923); (15) Zelinsky, ***Ber.***, 41, 2676 (1908); (16) Treudler and Damond, ***Compt. rend.***, 141, 594 (1915); (17) Ipat'ev, ***Ber.***, 41,1003 (1908).

he reports that he was able to obtain two constant boiling fractions, one at 119° and the other at 121.5°, which he assumed to be the *trans* and cis forms, respectively. In the reduction with platinum-oxide platinum black the product, even though available in much larger quantities than reported by Skita, could not be fractionated into two constant boiling compounds. It appears that the largest proportion of the product was probably the *trans* form. In the same way, at least the greater proportion of the reduction product of cymene was a single compound.

Experimental

Platinum Black.—The platinum oxide was prepared from C. P. chloroplatinic acid in the manner described previously.[18] The apparatus was the same as has been used in the previous investigations.

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[18] Adams and Shriner, THIS JOURNAL, 45,2171 (1923); *Org. Syn.*, 8, 92 (1925).

Purification of Substances to be Reduced.—Commercial C. P. products were obtained and further purified. Thiophene-free benzene, toluene, ethylbenzene, xylene. mesitylene, cymene and diphenylmethane were refluxed for three hours over sodium and then distilled. Only the constant boiling fraction was used for the reduction. Triphenylmethane, α,α-diphenylethane, dibenzyl, phenylacetic acid and β-phenylpropionic acid were crystallized alternately from alcohol and glacial acetic acid. After several recrystallizations the compounds were used for reduction.

Method of Isolation of Products.—After filtration and evaporation of the solvent, the reduced compounds, with the exception of the two acids, were treated several times with a mixture of 10 cc. of concd. nitric acid and 25 cc. of sulfuric acid at 0–5° for five to ten minutes. After each treatment the compound was washed with water. When the acid mixture no longer turned yellow, the compound was considered to be pure and was washed, dried and distilled.

The cyclohexylacetic acid and the β-cyclohexylpropionic acid were merely distilled from the acetic acid in order to purify them.

Summary

It has been found that platinum-oxide platinum black is an excellent catalyst in the reduction with hydrogen of various types of aromatic hydrocarbons in glacial acetic acid as a solvent.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA]

THE EFFECT OF THE CYANIDE GROUP ON THE BASICITY OF ALIPHATIC AMINES AS DETERMINED IN WATER AND ALCOHOL SOLUTIONS

BY T. D. STEWART AND VIVIEN COOK

RECEIVED APRIL 16, 1928 PUBLISHED JULY 6, 1928

Stewart and Aston[1] studied the influence of alkoxyl substitution upon the basicity of tertiary aliphatic amines, using derivatives of the type $ROCH_2N(C_2H_5)_2$. They found that methoxy, ethoxy and isobutoxy substitution lowered the base strength and gave to the basic dissociation constants of the amino ethers the values 3.6×10^{-9}, 1.8×10^{-8} and 4×10^{-7}, respectively. The comparisons were made colorimetrically in alcohol, using methylaniline and benzylamine as standards. By assuming that the relative base strengths in water and alcohol solution would be the same, the above figures were assigned as for an aqueous solution. The work of Goldschmidt and Mathiesen[2] indicates that in general amines are stronger bases in alcohol than in water, but with notable exceptions, so that comparisons of basicity in alcohol cannot be considered to offer a similar comparison in water. The above values, then, must be considered not as absolute but as relative to themselves and to methylaniline in alcohol solution only. It is, nevertheless, apparent that alkoxyl sub-

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[1] Stewart and Aston, THIS JOURNAL, 48, 1642 (1926).

[2] Goldschmidt and Mathiesen, *Z. physik. Chem.*, **119**, 439 (1926).

stitution upon the α-carbon of an amine causes a marked decrease in the tendency of the nitrogen atom to attach a proton, and particularly interesting to observe that the effects of different alkoxyl groups are considerably different in magnitude.

The present paper deals with the effect upon the base strength of substituting a cyanide group for a hydrogen atom upon a carbon in the a-position to the nitrogen in methyldiethylamine, triethylamine, benzyldiethylamine and isopropyldiethylamine. The comparisons are made both in alcohol and water solutions in the first and third cases, but only in alcohol in the other two because of the rapid decomposition of these bases in aqueous acid.

Experimental Results

The electrometric titrations of α-diethylamino-acetonitrile and of α-diethylaminophenylacetonitrile were carried out in water as described in the Experimental Part. The results indicate basic dissociation constants,

TABLE I

THE ELECTROMETRIC TITRATION OF SOLUTIONS OF α-DIETHYLAMINO-ACETONITRILE IN EXCESS OF 0.1 *N* HYDROCHLORIC ACID WITH 0.1 *N* SODIUM HYDROXIDE

Part A

Expt	Sample, equiv.	Total add, cc. of 0.1 *N*	Temp., °C.	Concn. of amino salt at the true end-point, equiv./L.
1	0.003976	45.49	22.8	0.07777
2	,003597	45.56	22.6	.06405
3	.004135	45.13	22.5	.0837

Part B

Expt.	Percentage titration of salt by NaOH	Voltage, from plot	$H^+ \times 10^{-3}$, equiv./L.	$K_B \times 10^{10}$
1	0	0.481	3.353	.66
	25	.535	.399	.75
	50	.561	.1438	.69
2	0	.489	2.401	1.07
	25	.545	.2647	1.13
	50	.573	.0886	1.13
3	0	.488	2.462	1.31
	25	.550	.2218	1.35
	50	.575	.0810	1.23
				Av. 1.03

TABLE II

THE ELECTROMETRIC TITRATION OF SOLUTIONS OF α-DIETHYLAMINOPHENYLACETONITRILE IN EXCESS OF 0.1 N HYDROCHLORIC ACID WITH 0.1 *N* SODIUM HYDROXIDE

Part A

Expt.	Sample, equiv.	Total acid, cc. of 0.1 *N*	Elapsed time before titration, min.	Weak base found, eqmv.	Temp., °C.
1	0.00275	36.17	35	0.00240	22.5
2	.002785	36.03	25	.00238	22.8
3	.002875	36.05	120	.001225	22.5

TABLE II (*Concluded*)

Part B

· Approximate Solubility of Free Base, 0.00176 Equiv./L.

Expt.	0 1 *N* NaOH, cc.	Total vol cc.	Salt present (approx.), equiv./l.	Voltage	(H^+), equiv /l	Cation, equiv /l.	$K_B \times 10^{11}$
1	9 58	45.75	0 0496	0.4477	0,01234	0.0373	1.72
1	16 05	52.22	.0328	.4559	00896	.0239	1 52
1	25 38	61 55	0126	4812	.00331	.00932	1 60
2	8 9 6	44.99	.0515	4491	.01175	0398	1 92
2	15.98	52 01	.0308	.4618	.00714	.0237	1 89
2	24 09	60.12	.0132	.4811	.00335	0099	1.68
							Av. 1 72

K_B, of 1.0×10^{-10} and 1.7×10^{-11}, respectively, and are summarized in Tables I and II and Fig. 1. The method of calculation is described in the later section.

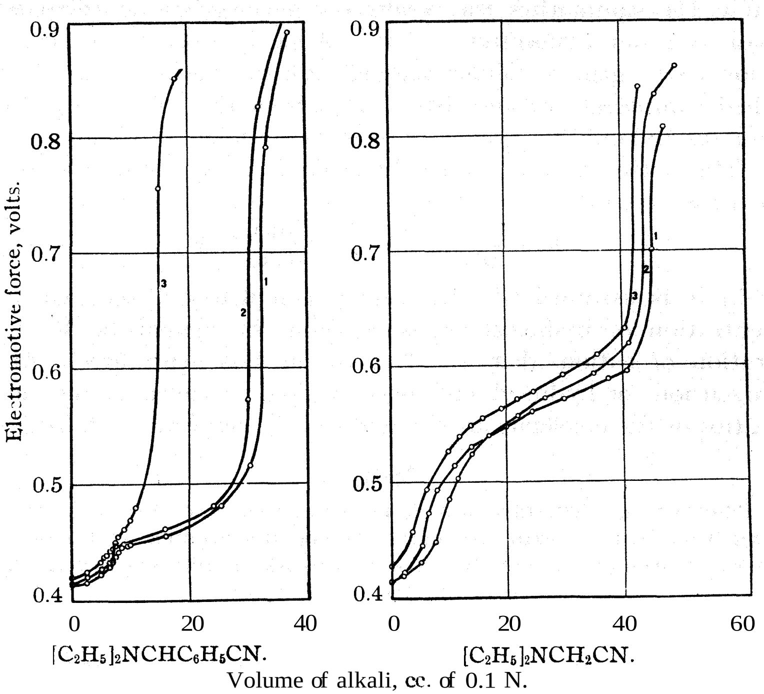

Fig. 1.—Titration curves of salts of α-aminonitriles in water.

In each of the three titrations of a-diethylamino-acetonitrile (Table I, Part B) consistent values of K_B are obtained, but the three do not agree well among themselves, perhaps due to constant small errors in the electrode condition. Still greater difficulty was experienced in attempting to get reproducible results when the base was titrated directly with acid, probably due to poisoning of the electrodes in the alkaline solution. The numerical average given may be considered accurate within 30%.

Since the α-diethylaminophenylacetonitrile is sparingly soluble in water and upon titration of its acid solution started to precipitate before the excess acid was neutralized, the inflection point of the titration curve did not signify the point of equivalency of acid and base present. Moreover, the substance decomposes more or less rapidly in dilute acid, presumably according to the equation

$$C_6H_5CHCNN(C_2H_5)_2 + H_2O \longrightarrow C_6H_5CHOHCN + (C_2H_5)_2NH$$

The net result is the transformation of a weak base to a stronger base, so that the concentration of the salt present (Table II, Part B, Col. 4) **was** corrected for this reaction (see Experimental Part). Curve III, Fig. 1, for this substance was for an acid solution which had stood for two hours before titration. The weak base had almost disappeared.

Table III summarizes the results of the colorimetric comparison in alcohol at room temperature. An alcoholic hydrogen chloride solution of known strength, containing the indicator in question, was added to a weighed sample of the pure base. Details of the color comparison are given later and only the average of several determinations is given in Table III. The ratios of the various basic dissociation constants are taken from the expression

$$K = \frac{(\text{Cation})}{(\text{Base})}(\text{OH}^-) = \frac{(\text{Salt})}{(\text{Base})}(\text{OH}^-)$$

wherein it is assumed that the acid is completely dissociated and the concentration of hydrogen ion is negligible in comparison to the concentration of cation, that is, all of the acid is neutralized. At equal hydrogen ion (or hydroxyl ion) concentration, as shown by the indicator, the ratios of the constants are the ratios of the respective salt/base ratios.

TABLE III

THE PERCENTAGE TITRATIONS OF SOME α-DIETHYLAMINO NITRILES, *m*-CHLOROANILINE AND ANILINE WITH ALCOHOLIC HYDROGEN CHLORIDE AT CORRESPONDING INDICATOR COLORS, AND THE RELATIVE STRENGTHS OR THE RESPECTIVE BASES IN ABSOLUTE ALCOHOL SOLUTIONS

Part A

	Methyl red and propyl red				Methyl red	
m-Chloro aniline (K_C)	a-Diethylamino-propionitrile (K_P)		a-Diethylamino-acetonitrile (K_A)		a-Diethylamino-phenylacetonitrile (K_D)	
%	%	K_P/K_C	%	K_A/K_C	%	K_C/K_D
40	58	2.07	56	1.91	11	5.4
50	66	1.94	64	1.78	13	6.7
60	72	1.72	72	1.72	16	7.8
70	80	1.72	80	1.72	18	10.6
80	87.5	1.75	87.5	1.75	25	12.0
90	..	..	..	..	41	12.9
		Av. 1.8		Av. 1.8		Av. 9.2

TABLE III (Concluded)

Part B			Part C		
	Propyl red		Methyl red and thymol blue		
m-Chloro-aniline (K_C)	a-Diethylamino-phenylacetonitrile (K_D)		a-Diethylamino-acetonitrile (K_A)	Aniline (K_N)	
%	%	K_C/K_D	%	%	K_N/K_A
50	14.5	5.9	40	92	17.3
60	17.0	7.3	50	95	19
70	21.5	8.5	60	97.2	..
80	31	8.9			
		Av. 7.7			Av. 18

The trend in the ratio of the constants in the case of the phenylated derivative may be due to experimental error, although there is no suggestion in the actual data of an uncertainty of this magnitude.

The fact that the trend is less marked in the experiment using Propyl Red than it is in those with Methyl Red, suggests some specific action of the base upon the indicator, or it may involve the assumptions used in the comparison of the constants.[3] It is doubtful whether the numerical average should be taken rather than an extrapolation toward higher fractional neutralization. Since the averages agree in the two series better than the extrapolations, they are taken as more nearly approaching the correct value and a final value of 8.5 assumed for the ratio of the constants of m-chloro-aniline to a-diethylaminophenylacetonitrile in alcohol. It is believed that this is correct within 20%.

Table IV gives a résumé of the results. The values for aniline and m-chloro-aniline in water are taken from Landolt-Bornstein's "Physikalische-Tabellen." K_B is the basic dissociation constant in water, K_A, the acidic dissociation constant of the cation, obtained for water solution from the relation $K_A = K_W/K_B$, where $K_W = 1.0 \times 10^{-14}$. K_A in alcohol solution is taken in the case of aniline, methylaniline and *m*-chloro-aniline from the work of Goldschmidt and Mathiesen,[2] and in the other cases calculated from these and from the above determined ratios.[4]

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[3] Goldschmidt and Mathiesen, ref. 2, give the dissociation constant of *m*-chloro-anilonium ion ($ClC_6H_4NH_3^+$) in alcohol as 6.1×10^{-5}, and of anilonium ion ($C_6H_5NH_3^+$) as 2×10^{-6}. A solution of aniline hydrochloride which is 0.05 M would then contain about 3×10^{-4} *N* hydrogen ion, since hydrogen chloride is a strong acid, even in alcohol. A solution of chloro-aniline and its hydrochloride, in equivalent amounts, would contain about 6×10^{-5} *N* hydrogen ion, and at the same point our data show aniline to be about 98% titrated, whereas calculated from the above figures it should be 97%. We are, then, in substantial agreement and are apparently justified in the assumption of our simplified formula.

[4] In addition to the results of Table IV, we have made measurements on a base prepared from acetone, and which is presumably α-diethylamino-*iso*butyronitrile. It had the correct equivalent weight and is a new preparation so far as we know. The yield was small and the preparation has not been duplicated, hence we have not detailed the results at this time. In alcohol solution the substance titrated precisely as does aniline. If this is true, it means that whereas the introduction of one methyl

TABLE IV

BASIC AND ACIDIC DISSOCIATION CONSTANTS OF SOME AMINE BASES AND SALTS IN WATER AND IN ALCOHOL

	Water solution			Alcohol solution	
Base	K_B	K_A	Ratios of the basic constants	K_A	Ratios of the constants
a-Diethylaminophenylacetonitrile	1.7×10^{-11}	5.9×10^{-4}	...	5.2×10^{-4}	....
m-Chloro-aniline	3.4×10^{-11}	2.9×10^{-4}	2	6.1×10^{-5}	8.5
a-Diethylamino-acetonitrile	1.0×10^{-10}	1.0×10^{-4}	2.9	3.4×10^{-5}	1.7
a-Diethylaminopropionitrile	....	....	...	3.4×10^{-5}	1.0
Aniline	4.6×10^{-10}	2.2×10^{-5}	4.6	2×10^{-6}	17
Methyl aniline	....	....	...	1.3×10^{-5}	0.154
a-Diethylamino-methyl methyl ether	....	....	...	9.2×10^{-7}	14.1
a-Diethylamino-methyl ethyl ether	....	....	...	1.84×10^{-7}	5.0
a-Diethylamino-methyl isobutyl ether	....	....	...	8.27×10^{-9}	22.2
Methyldiethylamine	2.7×10^{-4}	3.7×10^{-11}	...	....	....

Discussion of Results

We may record in Table V for reference[5] the dissociation constants in water of the parent compounds of the cyano and alkoxyl amines and the data for a similar series of substitutions in acetic acid.

TABLE V

BASIC AND ACIDIC DISSOCIATION CONSTANTS IN WATER

Bases	K_B	Acids	K_A
Methyldiethylamine	2.7×10^{-4}	Acetic	1.8×10^{-5}
Diethylbenzylamine	3.6×10^{-5}	Phenylacetic	5.3×10^{-5}
Triethylamine	6.4×10^{-4}	Cyanoacetic	3.7×10^{-3}
		Methoxyacetic	3.3×10^{-4}
		Ethoxyacetic	2.3×10^{-4}

From a comparison of Tables IV and V, using either the ratios of the dissociation constants or the logarithms of such ratios, it is seen that the cyano and alkoxyl groups substituted in amines reduce the basicity to a much greater extent than they increase the strength of acetic acid when substituted upon the a-carbon atom. The two systems are not strictly comparable, since that of the amines is a 1,3-substitution from the affected atom (nitrogen) whereas in acids the substitution is 1,4. The effect of substituting a methyl or phenyl group in a cyano-amine is the same as for the same substitution in the simple amine. The logarithm of the dissociation constant of methyldiethylamine (in water) is decreased

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group into the acetonitrile derivative causes no change in the base strength, a second methyl group produces a 17–18 fold increase in base strength. Mr. A. J. Alstrom, to whom we are indebted for this provisional result, is repeating the preparation.

[5] Landolt-Börnstein, "Physikalische-Chemische Tabellen," Berlin, 1923.

about 0.85 by phenyl substitution in the α-position, and about 6.4 by cyano substitution. Similarly substitution of hydrogen by phenyl in diethylamino-acetonitrile decreases the logarithm of the dissociation constant by 0.77. The increase of the logarithm of the dissociation constant of acetic acid is 0.47 for phenyl substitution, 2.32 for cyano substitution and 1.27 for methoxy substitution. Methoxy substitution in the amines likewise produces a smaller effect than cyano substitution, at least in alcohol solution. From the data now available, it would not be safe to assume that the effect of change of solvent from water to alcohol would produce in the amino nitriles and in the amino ethers the same change or even a similar change in the basic dissociation constants of the respective bases. It is, however, probable that the two classes of amines closely maintain in water the same relative basicities as in alcohol.

It so happens that the bases studied here maintain the same order in base strength in alcohol and in water, although the ratios of the dissociation constants differ widely in the two solvents. The series of bases studied by Goldschmidt and Mathiesen[2] differed even in order. The reasons for this will not be discussed fully at this time. It is evident, however, that in the expression

$$Kg = \frac{(\text{Cation})}{(\text{Base})}(\text{OH}^-)$$

the parentheses denote the activities of the respective substances. Since normally it is the concentration and not the activity that is measured, and since in the present work solutions of equal hydrogen ion activity are compared, we may substitute for the above activities the product of the concentration by a factor γ and write for two different bases in a given solvent

$$\frac{K'_B}{K''_B} = \frac{\dfrac{\gamma_1 C'_{\text{Cation}}}{\gamma_2 C'_{\text{Base}}}}{\dfrac{\gamma_3 C''_{\text{Cation}}}{\gamma_4 C''_{\text{Base}}}}$$

A similar expression could be written for a second solvent. It is then seen that the ratio of the constants, K'_B and K''_B, as calculated only from the concentrations, can be the same in two solvents only in case the ratio of the four γ factors remains constant with change of solvent. The γ factors involve deviations from the laws of perfect solutions and may, in addition, not be constant with respect to changes in concentration. It is not surprising that numerical constancy of the above ratios is not found. The question is further complicated by the assumption of infinitely dilute solutions in each solvent as the standard state of a given molecular species in that solvent. There would be a difference in the energy contents of the hypothetical molal solution of a given solute in two different solvents which should be included in a strict comparison of the basic dissociation constants of a substance in those solvents.

Finally, if a base is composed of two or more tautomers, the net base strength is determined in part by the relative amounts of the tautomers present. A change of solvent may change these relative proportions and in a manner unrelated to the relative base strengths of the individual tautomers. Then the comparison of a base which may tautomerize with one which may not, in different solvents, might lead to results which would be difficult of interpretation in terms of their respective structures.

Experimental Part

Preparation of Materials.—The following amino nitriles were prepared using the method of Knoevenagel and Mercklin.[6]

a-Diethylamino-acetonitrile from formaldehyde, sodium bisulfite, diethylamine and potassium cyanide; colorless oil, soluble in water; b. p. 35–40° (6 mm.) and 62–63° (14 mm.); yield, 85% based on diethylamine.

a-Diethylaminopropionitrile from acetaldehyde and other reagents as above; colorless oil, soluble in water; rapidly hydrolyzes in aqueous acid; b. p. 47–49° (7 mm.) and 67–68' (17 mm.); yield, 65% based on diethylamine.

a-Diethylaminophenylacetonitrile from benzaldehyde and other reagents as above; slightly soluble in water, soluble in dilute acid, usually light yellow or greenish yellow after distillation; b. p. 112° (7 mm.) and 130–131° (11 mm.); yield, 83% based on diethylamine. The base decomposes more or less rapidly in acid solution, most rapidly in dilute acid, but even then the reaction requires some hours. It may be dissolved in acid and be reprecipitated with base unchanged. The equivalent weight may be accurately determined by dissolving a weighed sample in a known excess of 0.1 *N* acid and back-titrating immediately with 0.1 N base, using the difference between the precipitation end-point and the phenolphthalein end-point as a measure of the base present. The latter end-point should coincide with that of an equal amount of acid to which no base has been added.

α-Diethylamino-*iso*butyronitrile, from acetone and the other reagents as above. The yield was very poor and the preparation could not be duplicated after several trials; b. p. 75–77° (23 mm.); equivalent weight to methyl orange titration, 140 g.; colorless oil, soluble in water, rapidly hydrolyzed in aqueous acid.

Aniline.—A redistilled sample of a commercial preparation was used. It was colorless and remained so, in the dark, for several days.

***m*-Chloro-aniline.**—A redistilled sample of Kahlbaum's preparation was used. It distilled within a range of one degree and was colorless.

Alcoholic Hydrogen Chloride was prepared by generating hydrogen chloride from pure concentrated hydrochloric and sulfuric acids, drying the gas by passage through sulfuric acid and collecting it in cooled commercial absolute alcohol of good grade. It was then diluted to the desired normality with the same alcohol and the indicator added to the stock solution in the following concentrations, respectively: methyl red, 0.0083 g. per liter; propyl red, 0.012 g. per liter; thymol blue (acid), 10 cc. of a saturated solution in alcohol, per liter. The normality of the alcoholic acid was determined by diluting a measured volume of the solution with water and titrating with standard alkali, using the contained indicator. One series of experiments was made using 0.1 N acid and several using about 0.05 *N* acid.

Solubility of a-Diethylaminophenylacetonitrile in Water.—This was determined at 20° as follows. A 0.4580-g. sample (0.002349 equiv.) was dissolved in 30.0 cc. of 0.1 N

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[6] Knoevenagel and Mercklin, Ber., 37, 4087 (1904).

acid and 2.00 cc. portions of this solution were added to known volumes of water. Excess akali in known volume was then added to the mixture and the presence or absence of a turbidity noted. In one experiment, a final volume of 97.0 cc. allowed no turbidity; in another a final volume of 91 cc. allowed a very slight turbidity which cleared on the addition of 1.0 cc. of water. Since a high degree of accuracy was not desired, this volume of 92.0 cc. was taken as accurate and represents a solubility of 0.00176 ± 2% equivalents per liter. At 30° the solubility is about 0.00185 ± 2% equivalents per liter.

Electrometric Titration Procedure.—The side arm of an ordinary decinormal potassium chloride calomel electrode was dipped directly into the solution prepared for the titration. In this was immersed an apron type foil platinum electrode. No attempt was made to exclude liquid junction potentials because of other uncertainties involving poisoning of the electrode which could be of much greater magnitude. A Leeds and Northrup type K potentiometer, a calibrated standard cell and electrolytic hydrogen generator completed the equipment. The hydrogen electrode was first brought in equilibrium with a known amount of 0.1 *N* standard acid and then an amount of organic base added which was not quite equivalent to this acid. The solution was then titrated with 0.1 N alkali as usual.

The titration curves are given in Fig. 1 and the data for the calculations given in Tables I and II (see previous section). The hydrogen ion concentration was calculated from the equation

$$\log \frac{1}{(H^+)} = \frac{E - 0.3358}{0.00019844T}$$

In the case of a-diethylamino-acetonitrile, the constant of hydrolysis of the salt and the basic dissociation constant of the base were calculated from the expressions

$$K_H = \frac{(H^+)^2}{(\text{concn. of salt}) - (H^+)};\quad K_B = \frac{K_W}{(K_H)}$$

The concentration of salt was determined from the total volume (volume of acid plus volume of alkali) at the true end-point, and the amount of base used. The other calculations were based on the simplified expression

$$K_B = \frac{(\text{Salt})\ K_W}{(\text{Base})\ (H^+)}$$

In the case of the phenylacetonitrile derivative the last equation given was used. The concentration of the base was constant and equal to that in a saturated solution; that of the salt (cation) was calculated from: (e) total volume of the solution and (b) total equivalents of salt present (base used minus base decomposed minus salt neutralized and hydrolyzed). The amount of base decomposed was given by the difference between the acid started with and acid found, as shown by the second inflection of the titration curve. Most of the reaction of decomposition took place before the back-titration started and used up acid by the formation of a strong base, presumably diethylamine.

Colorimetric Determination of Relative Base Strengths in Alcohol.—A wedge type colorimeter was used. The two wedges were fitted with the stock alcoholic acid–indicator solution, and one of them was then made alkaline with a few drops of diethylamine. They were each mounted separately on movable frames provided with a scale reading from 0 to 100. The comparator cup was of such dimensions as to give the same depth of solution as that provided by the wedges when their combined scale readings were 100. Careful calibration of the colorimeter was not necessary because it was used in a purely empirical way. A daylight lamp furnished illumination, reflected from a frosted glass background. Manipulation of the wedges permitted variation of the color shades and intensity, and the recorded scale readings allowed reproduction at will of any previously used color standard. In practice it was found that the alkaline wedge could be shifted appreciably without sensible alterations of the color shade. Readings of the acid wedge scale only were used.

The organic bases to be compared were weighed into a small flask provided with glass tubing attachments similar to those of a wash bottle. The stock acid–indicator solution was added in desired quantity from a buret the tip of which passed through the stopper of the flask. At any given time some of the solution could be forced over into the comparator cup, the color comparison made, withdrawn back into the flask, more acid added and the operation repeated until the possible range of color comparison was covered. Small amounts of water caused no appreciable change in the color of the solutions, and in the system employed there was no exposure of the solution to the air except through calcium chloride filled tubes, and except that the comparator cup had a small opening for the insertion of a glass tube through which the liquid was introduced and withdrawn. The acid wedge reading was plotted for each base against its percentage titration and smooth curves were drawn through the points. A given wedge reading then represented a corresponding hydrogen ion activity for each of the various solutions. A summary of the data is given in Table III. By the above method, using the same stock solution for all the bases, the comparisons are made at equal cation, hydrogen ion and anion concentrations (assuming complete ionization of acid and salts). The ratio of the dissociation constants is then very closely the inverse ratio of the concentrations of the free bases under these conditions. Moreover, the total ionic strength of the solution changes but very little during the whole course of the titration.

Summary

The basic dissociation constants of a-diethylamino-acetonitrile and of a-diethylaminophenylacetonitrile in water are 1.0×10^{-10} and 1.7×10^{-11}, respectively. In alcohol solution, the acidic dissociation constants of their salts (chlorides) are 3.4×10^{-5} and 5.2×10^{-4}, respectively, while those of a-diethylaminopropionitrile and of α-diethyl*iso*butyronitrile in alcohol are 3.4×10^{-5} and 2×10^{-6}, respectively. The base strengths of some

amino ethers in alcohol have been recalculated. Some of the factors which determine the apparent change in relative base strength with change of solvent are discussed.

BERKELEY, CALIFORNIA

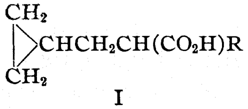
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

CYCLOPROPYLMETHYL ALKYL ACETIC ACIDS AND THEIR BACTERICIDAL ACTION TOWARD B. LEPRAE. XIII[1]

BY J. A. ARVIN[2] AND ROGER ADAMS

RECEIVED APRIL 17, 1928 PUBLISHED JULY 6, 1928

The various synthetic acids which have been studied for their bactericidal action have so far contained either a five or six membered ring. The present investigation has covered the synthesis of a series of acids containing a three-membered ring, namely, the cyclopropylmethyl alkyl acetic acids, (I) where the R varies from n-amyl to n-myristyl. These acids are of interest because they lead to the possibility of determining whether the significant factor for the bactericidal action in the many acids that have been studied is the character of the ring or is the molecular weight of the whole molecule, or merely that part of the molecule outside of the ring structure.



$(CH_2)_2>CHCH_2CH(CO_2H)R$

I

In Table I are given the bacteriological results.

TABLE I

CYCLOPROPYLMETHYL ALKYL ACETIC ACIDS, $C_3H_5CH_2CH(CO_2H)R$

	Dilutions of sodium salt in thousands																	
R =	10	20	30	40	50	60	70	80	90	100	111	125	133	143	153	167	176	185	200
n-C_5H_{11}	+	+	+	+	+	+	+	+	+	+									
n-C_6H_{13}	+	+	+	+	+	+	+	+	+	+									
n-C_7H_{15}	−	+	+	+	+	+	+	+	+	+									
n-C_8H_{17}	−	−			+			+		+									
n-C_9H_{19}	−	−			−			−		+									
n-$C_{10}H_{21}$										−	−	−	−	−	+	+	+	+	+
n-$C_{11}H_{23}$										−	−	−	−	−	±	±	−	*	+
n-$C_{12}H_{25}$										−	−	±	−	+	+	+	+	+	+
n-$C_{14}H_{29}$										+	+	+	+	+	+	+	+	+	+

It is noticeable that practically no bactericidal effect appears until the R group is n-octyl or larger. The two most effective acids were those containing the decyl and the undecyl groups. It appears, then, that in this as in other series, at least sixteen carbon atoms in the molecule must

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[1] Paper XII in this series, THIS JOURNAL, 50, 1790 (1928).

[2] This communication is an abstract of a portion of a thesis submitted by J. A. Arvin in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.

be present before the bactericidal effect approaches the maximum. In Table II are the most effective acids of four series.

TABLE II

COMPARISON OF BACTERIOLOGICAL RESULTS OF VARIOUS COMPOUNDS

General formula $R'CH(CO_2H)R$	R =	R_1	Max. effective dil. in thousands	Empirical formula
$C_3H_5CH_2CH(CO_2H)R$	n-$C_{10}H_{21}$	C_4H_7	143	$C_{16}H_{30}O_2$
	n-$C_{11}H_{23}$	C_4H_7	153	$C_{17}H_{32}O_2$
$C_5H_9(CH_2)_2CH(CO_2H)R$	n-C_7H_{15}	C_7H_{13}	160	$C_{16}H_{30}O_2$
	n-C_8H_{17}	C_7H_{13}	170	$C_{17}H_{32}O_2$
$C_5H_9CH(CO_2H)R$	n-$C_{10}H_{21}$	C_5H_9	143	$C_{17}H_{32}O_2$
	n-$C_{11}H_{23}$	C_5H_9	153	$C_{18}H_{34}O_2$
$C_6H_{11}CH(CO_2H)R$	n-C_9H_{19}	C_6H_{11}	176	$C_{17}H_{32}O_2$
	n-$C_{10}H_{21}$	C_6H_{11}	176	$C_{18}H_{34}O_2$
$C_6H_{11}(CH_2)_2CH(CO_2H)R$	n-C_7H_{15}	C_8H_{15}	220	$C_{17}H_{32}O_2$
	n-C_8H_{17}	C_8H_{15}	320	$C_{18}H_{34}O_2$

It appears that there is no marked difference between the molecules containing different rings provided the molecular weight of the whole molecule is sufficiently large. It is interesting to note also that in those compounds of proper molecular weight, there seems to be a greater bactericidal effect where the two groups which are substituted in the acetic acid have approximately the same number of carbon atoms.

The acids were prepared by condensing cyclopropylmethyl bromide with malonic ester. The diethyl cyclopropylmethyl malonate was then condensed with the various alkyl bromides, the esters were saponified and carbon dioxide was eliminated.

Experimental

Cyclopropylmethyl Bromide.—This was made by the method of J. von Braun.[3] The last step in the procedure was not described in detail and was observed by the authors to require rather definite conditions if the best results were to be obtained.

In a 500-cc. Claisen flask, 135 g. of phosphorus tribromide was converted to pentabromide by the slow addition of 80 g. of bromine. The mixture was cooled during the addition and then allowed to stand for a few hours. The side arm of the Claisen flask was bent downward and extended through the neck well into the bulb of a 500-cc. distilling flask used as a receiver. The side arm of this receiving flask was also bent downward and connected in the same way to another distilling flask. The phosphorus pentabromide was heated in an oil-bath at 85–90° for a few minutes and then 79 g. of molten cyclopropylmethyl benzamide was added. When the contents of the flask were homogeneous, the system was evacuated and the receiving flasks were cooled by ice and salt mixtures. The reaction mixture was distilled until the temperature of the distilling vapors reached 150° at 18 mm. The distillate was poured into ice water and allowed to stand at 0–5° with occasional stirring for two hours. The product was separated, the aqueous layer extracted with a little ether and the whole washed with water. The crude material made in this way from three runs was fractionated and 87–91 g. (46–48%) of cyclopropylmethyl bromide was obtained: b. p. 104–110°.

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[3] J. von Braun. Ann., 445, 201 (1925).

Diethyl Cyclopropylmethyl Malonate.—Cyclopropylmethyl bromide was condensed with malonic ester in the usual way, though the mixture was heated for forty hours before the reaction was complete. The yields were 66–70% of the theoretical.

Diethyl Cyclopropylmethyl Alkyl Malonates.—These were prepared by a method previously described, by the condensation of alkyl bromides with diethyl cyclopropylmethyl malonate.[4] The yields were 60–66% of the theoretical.

Cyclopropylmethyl Alkyl Acetic Acids.—These were prepared from the malonic acids by a method previously described.' The yields were 86–94% of the theoretical.

TABLE III

DIETHYL CYCLOPROPYLMETHYL ALKYL MALONATES, $C_3H_5CH_2C(CO_2C_2H_5)_2R$

R =	B. p., °C.	n_D^{20}	d_4^{20}	Calcd., %		Found, %	
				C	H	C	H
n-C_5H_{11}	122–125 (1.7 mm.)	1.4459	0.9770	67.56	9.93	67.02	9.73
n-C_6H_{13}	139–142 (2.9 mm.)	1.4470	.9685	68.40	10.14	67.98	10.08
n-C_7H_{15}	146–149 (2.7 mm.)	1.4481	.9613	69.17	10.33	68.71	10.22
n-C_8H_{17}	149–154 (2.3 mm.)	1.4491	.9559	69.88	10.50	69.70	10.41
n-C_9H_{19}	165–168 (2.5 mm.)	1.4503	.9512	70.53	10.67	70.73	10.76
n-$C_{10}H_{21}$	162–166 (1.9 mm.)	1.4510	.9460	71.13	10.81	70.93	10.80
n-$C_{11}H_{23}$	186–189 (3 mm.)	1.4519	.9419	71.68	10.95	71.52	10.85
n-$C_{12}H_{25}$	183–187 (2 mm.)	1.4526	.9395	72.19	11.07	71.71	10.97
n-$C_{14}H_{29}$	192–195 (1.9 mm.)	1.4530	.9377	73.11	11.29	73.37	11.01
H	129–133 (18 mm.)	1.4363	1.0216	61.61	8.58	61.03	8.32

TABLE IV

CYCLOPROPYLMETHYL ALKYL ACETIC ACIDS, $C_3H_5CH_2CH(CO_2H)R$

R =	M. p., °C.	B. p., °C.	n_D^{20}	d_4^{20}	Calcd., %		Found. %	
					C	H	C	H
n-C_5H_{11}	...	112–115 (1.4 mm.)	1.4469	0.9375	71.68	10.95	71.37	10.91
n-C_6H_{13}	...	130–132 (1.8 mm.)	1.4498	.9253	72.66	11.19	72.46	11.03
n-C_7H_{15}	...	136–139 (2 mm.)	1.4509	.9236	73.52	11.40	73.33	11.39
n-C_8H_{17}	...	146–149 (2.1 mm.)	1.4529	.9142	74.27	11.58	74.11	11.52
n-C_9H_{19}	...	162–164 (2.3 mm.)	1.4545	.9105	74.93	11.75	74.70	11.66
n-$C_{10}H_{21}$	...	176–178 (2.7 mm.)	1.4553	.9064	75.51	11.89	75.23	12.04
n-$C_{11}H_{23}$	27–28	186–189 (3 mm.)	....	....	76.05	12.03	75.72	11.93
n-$C_{12}H_{25}$	29–30	191–195 (3 mm.)	....	....	76.52	12.14	76.39	12.00
n-$C_{14}H_{29}$	35–37	176–179 (1.3 mm.)	....	....	77.34	12.39	76.76	12.19

Summary

A series of cyclopropylniethyl acetic acids has been prepared and tested for bactericidal action toward B. Leprae.

No appreciable bactericidal effect appeared until the alkyl group was n-octyl or larger, thus indicating as in previous researches that molecular weight of the whole molecule plays an important role. No marked difference was found between molecules containing 5-, 6- or 3-membered rings provided the molecular weight was approximately the same.

URBANA, ILLINOIS

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[4] Adams, Stanley and Stearns, THIS JOURNAL, 50,1475 (1928).

[150TH CONTRIBUTION FROM THE COLOR AND FARM WASTE DIVISION, BUREAU OF CHEMISTRY AND SOILS, DEPARTMENT OF AGRICULTURE]

THE CHEMISTRY OF LIGNIN.
II. FRACTIONAL EXTRACTION OF LIGNIN FROM CORN COBS

BY MAX PHILLIPS

RECEIVED APRIL 20, 1928 PUBLISHED JULY 6, 1928

In a previous communication,[1] a description was given of a lignin fraction obtained by treating corn cobs with alcoholic sodium hydroxide solution at room temperature. The analytical data presented agreed with those required for the dissected formula $C_{37}H_{33}O_9(OH)_4(OCH_3)_3$. The yield of this fraction amounted to 3.49% of the weight of the corn cobs treated. This yield represents only a part of the total lignin in corn cobs as determined for example by the Dore[2] modification of the Konig and Becker[3] method. The question arose whether all the lignin could be removed by prolonged and repeated extraction with alcoholic sodium hydroxide solution. If all the lignin were similarly combined with the carbohydrates, such a result might reasonably be expected. It was found, however, that only a part of the total lignin could be obtained even after exhaustive extraction with this reagent. The residual lignin could be obtained only by subjecting the extracted corn cobs to the action of sodium hydroxide solution at successively higher-temperatures.

The experimental procedure employed consisted in subjecting corn cobs that had previously been extracted with a 1:1 alcohol–benzene solution to exhaustive extraction with alcoholic sodium hydroxide solution at room temperature until a test sample upon removal of the alcohol and subsequent acidulation no longer gave any precipitate of lignin. The residual material, which still contained some combined lignin, was successively extracted with a 2% aqueous sodium hydroxide solution at 100° until the extract was free from lignin. The residue from this treatment was similarly extracted with a 2% aqueous sodium hydroxide solution at 135° and finally with a 4% sodium hydroxide solution at 180°. The residue obtained from the final treatment was entirely free from lignin.

Among chemists who have accepted the view that lignin is chemically combined with the cellulose or with other carbohydrate material, much difference of opinion prevails regarding the manner in which this combination occurs. Erdmann[4] and Lange[5] assume that an ester-like union exists

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[1] Phillips, THIS JOURNAL, 49, 2037 (1927).

[2] Dore, *J. Ind. Eng. Chem.*, 12, 984 (1920).

[3] Konig and Becker, "Veroffentlichungen der Landwirtschaftskammer fur die Provinz Westfalen," Heft 26, 1918, and E. Becker, *Dissertation*, Münster, 1914, *Z. angew. Chem.*, 32, 155 (1919).

[4] Erdmann, *Ann.*, 138, 1 (1866); *Ann. Supplement*, V, 223 (1867).

[5] Lange, *Z. physiol. Chem.*, 14, 15, 283 (1889).

between an acid group in the lignin and an hydroxyl of the carbohydrate. On the other hand Hoppe-Seyler,[6] Grafe,[7] and Mehta[8] are inclined to the view that there exists an ether-like linkage between the lignin and the cellulose or other carbohydrate, Data obtained on the fractional extraction of the lignin from corn cobs indicate that the lignin is dissimilarly combined with the carbohydrates. The assumption that *all* of the lignin is combined with the carbohydrates either as an ester or an ether is unwarranted as far as the lignin from corn cobs is concerned. It is believed that both types of linkage are present, which explanation would account for the fact that only a part of the lignin may be removed from corn cobs with alcoholic sodium hydroxide solution even after exhaustive extraction. The analyses made on the lignin fractions do not justify the conclusion that there is more than one kind of lignin present in corn cobs. There is apparently no alkali lignin present in corn cobs in the free state, for extraction with a solvent such as a 2:1 acetone–ethanol solution, which is an excellent solvent for free alkali lignin, fails to yield any lignin.

Experimental

Five hundred grams of ground corn cobs which had previously been extracted with boiling 1:1 alcohol–benzene solution was digested at room temperature with 1000 cc. of alcoholic sodium hydroxide solution (20 g. of sodium hydroxide, 400 cc. of water and 600 cc. of 95% ethanol) for forty-eight hours. The yellow liquor was decanted, the cobs were pressed and the liquor was combined with that obtained by decantation. This solution was neutralized with hydrochloric acid and the alcohol was removed by distillation under reduced pressure. After the residual solution had been made distinctly acid with hydrochloric acid, the precipitated lignin was filtered off, washed free from hydrochloric acid and dried at 80°. This digestion with alcoholic sodium hydroxide solution and subsequent isolation of the lignin was continued until no more lignin was obtained. Six extractions were required. The six lignin fractions were combined and purified by dissolving in 2:1 acetone–alcohol solution (200 cc. of acetone, 100 cc. of 95% ethanol) filtering and pouring the filtrate into 1.5 liters of boiling water containing 50 cc. of concentrated hydrochloric acid. This was allowed to cool to room temperature, filtered, washed with water until the washings gave no test for chlorine with silver nitrate and dried at 80°. A light yellow, amorphous powder was obtained (Fraction "A," Table I).

The residue from the digestion with alcoholic sodium hydroxide solution was refluxed with 2% aqueous sodium hydroxide solution for lour hours. It was then filtered, the filtrate acidified with hydrochloric acid and the lignin filtered off. The refluxing with 2% aqueous sodium hydroxide solution was continued until no more lignin was obtained. The several lignin fractions were combined and purified by dissolving in acetone and alcohol as already described (Fraction "B," Table I).

The residue obtained after the extraction of lignin fraction "B" was digested with a 2% aqueous sodium hydroxide solution for four hours in an autoclave at 135°. The alkaline liquor was filtered off and the digestion with 2% sodium hydroxide was repeated

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[6] Hoppe-Seyler, Z. *physiol. Chem.*, **13,** 84 (1888).

[7] Grafe, *Monatsh.*, 25,987 (1904).

[8] Mehta, *Biochem.* J., 19, 958 (1925).

until no more lignin was obtained. The lignin was isolated from the alkaline solution and purified from acetone and alcohol as already described (Fraction "C," Table I).

The residue from the foregoing treatment was heated for two hours with 4% aqueous sodium hydroxide in an autoclave at 180°. The alkaline extract was acidified with hydrochloric acid and the precipitated lignin was filtered off. The residue from this operation when similarly treated gave no lignin. The cellulose residue was nearly colorless and gave no color reaction with phloroglucinol and hydrochloric acid. When it was bleached with sodium hypochlorite, a pure white product was obtained. The yield of cellulose amounted to 35% of the weight of the moisture free corn cobs.

The results of this experiment are given in Table I.

TABLE I

LIGNIN FRACTIONS EXTRACTED FROM CORN COBS

Lignin fraction	Lignin (calcd. on corn cobs treated), %	Total lignin, %	Ash in lignin, %	Methoxy (calcd. on ash-free lignin), %	Pentosans in lignin Before purification with acetone and alcohol, %	Pentosans in lignin After purification with acetone and alcohol, %	Cellulose (calcd. on corn cobs treated). %
A[a]	4.4	48.4	0.37	16.45	0	0	35.8
B[b]	3.7	40.7	0.43	15.31	2.16	0	
C[c]	0.84	9.2	.19	15.05	0.79	0	
D[d]	.14	1.5	. .	7.50[e]	. .	.	

[a] "A"—Corn cobs extracted with 2% alcoholic sodium hydroxide at room temperature.

[b] "B"—Residue from "A" refluxed with 2% aqueous sodium hydroxide solution.

[c] "C"—Residue from "B" heated with 2% aqueous sodium hydroxide at 135°.

[d] "D"—Residue from "C" heated with 4% aqueous sodium hydroxide at 180°.

[e] No ash determined in this lignin fraction.

The percentage of methoxyl in the various lignin fractions was determined by the method of Zeisel and Fanto.[9] The pentosans in the lignin fractions were determined by the A. O. A. C. method.[10]

Table I shows that 48.4% of the total lignin in the corn cobs was obtained in the first fraction, 40.7% in the second, 9.2% in the third and 1.5% in the fourth. All of the lignin fractions after purification with alcohol and acetone were free from pentosans. Fraction "A" contained no pentosans or furfural yielding compounds even before purification, owing to the insolubility of the pentosans in the alcoholic sodium hydroxide solution. The statements in the literature that pentosan or some furfural yielding body forms an integral part of the lignin molecule must be considered as erroneous, especially as applied to the lignin from corn cobs. Attention is called particularly to the progressive decrease in the percentage of methoxyl in the lignin fraction with the increase in the temperature used for the extraction of the lignin.

[9] Houben-Weyl, "Die Methoden der organischen Chemie," Vol. III, Georg Thieme, Leipzig, 1923, p. 144.

[10] "Official and Tentative Methods of Analysis of the Association of Official Agricultural Chemists," A. O. A. C., Washington, D. C.

Carbon and hydrogen determinations of the four lignin fractions gave the following results.

Anal. (Fraction A.) Subs., 0.1534, 0.1215: CO_2, 0.3517, 0.2783; H_2O, 0.0666, 0.0529. Found: C, 62.52, 62.46; H, 4.86, 4.87.

Anal. (Fraction *B.*) Subs., 0.0890, 0.0948: CO_2, 0.2043, 0.2171; H_2O, 0.0390, 0.0438. Found: C, 62.60, 62.45; H, 4.90, 5.17.

Anal. (Fraction *C.*) Subs., 0.1112, 0.0974: CO_2, 0.2614, 0.2298; H_2O, 0.0543, 0.0469. Found: C, 64.10, 64.34; H, 5.46, 5.39.

Anal. (Fraction D.) Subs., 0.0857, 0.1039: CO_2, 0.2139, 0.2597; H_2O, 0.0487, 0.0603. Found: C, 68.06, 68.16; H, 6.36, 6.49.

Summary

Lignin was fractionally extracted from corn cobs by a 2% alcoholic sodium hydroxide solution at room temperature, by 2% aqueous sodium hydroxide at 100° and at 135°, and finally by 4% aqueous sodium hydroxide at 180". Each method of extraction was continued until no further lignin was obtained, before the next method in the series was employed. The results justify the conclusion that the lignin in corn cobs is unequally combined with the carbohydrates, part of it being loosely bound, possibly in the form of an ester, and the remainder being more firmly held, probably in the form of an ether-like combination.

WASHINGTON, D. C.

[149TH CONTRIBUTION FROM THE COLOR AND FARM WASTE DIVISION, BUREAU OF CHEMISTRY AND SOILS, U. S. DEPARTMENT OF AGRICULTURE]

THE TAUTOMERISM OF BRILLIANT CRESYL BLUE

BY WALTER C. HOLMES

RECEIVED APRIL 21, 1928 PUBLISHED JULY 6, 1928

Brilliant cresyl blue is an oxazine dye having metachromatic properties which finds important application in biological staining. The stain sold by the National Aniline and Chemical Company is the dimethyl homolog of the dye illustrated under No. 877 in the Colour Index.

With variation in concentration in aqueous solutions this dye undergoes a striking modification in color of the same type that all metachromatic dyes and the majority of aminated triphenylmethane and quinone-imide coloring matters in general undergo.[1] In relatively concentrated aqueous solutions it is present principally in a violet form, with maximum absorption at about 575mμ. The dilution of these solutions is accompanied by a progressive transition to a second dye form, which is blue, with maximum absorption at about 625mμ. Representative absorption curves are recorded in Fig. 1.

Considerable evidence has been obtained which indicates that color modification of this type does not arise from electrolytic or hydrolytic

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[1] Holmes, Ind. *Eng. Chem.*, *16*, 35 (1924).

dissociation, solvation or alteration in the state of molecular aggregation of the solute. It constitutes evidence of tautomerism in the dye, in which the modification in the dye molecule is probably the result of a rearrangement of affinities, brought about by the interplay of residual affinities of solute and solvent.[2,3]

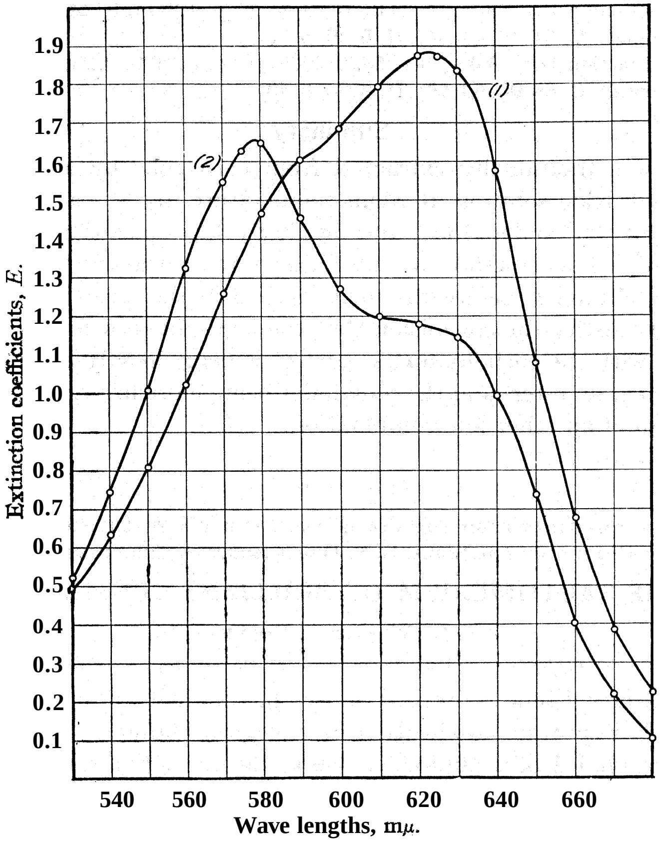

Fig. 1.—Brilliant cresyl blue. (1) Approximately 40 mg. of dye per liter of distilled water in a 1-cm. layer. (2) Approximately 1000 mg. of dye per liter of distilled water in a 0.0432-cm. layer.

Means have been found of obtaining the violet form of brilliant cresyl blue in a medium in which its properties may be investigated to better advantage than is possible in aqueous solutions. The writer is indebted to Dr. Marian Irwin of the Rockefeller Institute for suggestions which led to this discovery.

Holmes, THIS JOURNAL, 46, 2118 (1924).

[3] Holmes, *Am. Dyestuff Reporter*, 16,429 (1927).

A 0.1% solution of the dye is prepared in a $M/15$ acetate buffer solution of 0.6 M sodium chloride content, having a PH value of 3.42. (The solution should be distinctly acid, but the precise degree of acidity is relatively immaterial.) The solution is shaken thoroughly with an equal volume of chloroform and the chloroform is diluted 1:5 to obtain a suitable intensity of color for spectrophotometric measurements in 1-centimeter cells. The absorption curve of such a solution is recorded in Fig. 2, Curve 1.

In this solution most of the dye is present in its violet form. The curve gives evidence, however, of a small proportion of dye in its blue form. The modification of this solution upon saturation with ammonia is illustrated by Fig. 2, Curve 2.

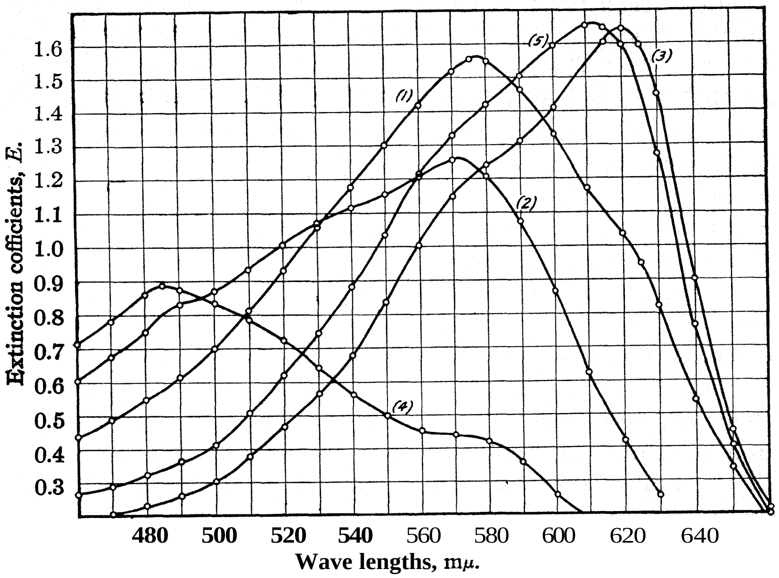

Fig. 2.—Brilliant cresyl blue.

By direct solution of the solid dye in chloroform a solution which gives the absorption represented by Fig. 2, Curve 3, may be obtained. In this solution the greater part of the dye is present in its blue form, although there is definite evidence of the presence of a small proportion of the violet form. The modification of this solution upon saturation with ammonia is recorded in Fig. 2, Curve 4, and the subsequent modification of the ammoniacal solution upon the addition of 2% glacial acetic acid is shown in Fig. 2, Curve 5.

The principal interest of these data lies in the evidence which they supply respecting the relative reactivity of the various forms of the dye.

The saturation of the solution of the violet form of the dye with ammonia results in only a minor degree of conversion to the orange dye-base (see Curves 1 and 2, Fig. *2)*. The actual degree of conversion of violet dye to base is much less than the apparent degree, owing to the presence in the original solution of appreciable quantities of the blue form of the dye, which undergoes complete conversion to base. On the other hand, the saturation of the solution of the blue form of the dye with ammonia results in its immediate and complete conversion to the dye-base (see Curves **3** and 4, Fig. *2)*. The resulting solution still contains the dye originally present in the violet form, apparently in an unaltered state. The blue form of the dye is very reactive to alkali, whereas the violet form of the dye is highly inactive.

When the blue form of the dye is converted to dye-base and the dye is subsequently regenerated, the absorption curve of the recovered dye does not coincide in spectral location with that of the original dye (see Curves **3** and 5, Fig. *2)*. The recovered dye is not brilliant cresyl blue but its monomethyl homolog, as indicated by the agreement between its absorption and that of the monomethyl homolog prepared by direct synthesis at this Laboratory. It is well known that various quinone-imide dyes, such as methylene blue, are so susceptible to alkaline oxidation that their conversion to the dye-base may be attended by the loss of an alkyl substituent group. The blue form of brilliant cresyl blue is so readily oxidized in ammoniacal chloroform solutions that the reaction is practically instantaneous.

The orange dye-base is readily and completely converted into the dye by acids (see Curves 4 and 5, Fig. 2). The dye-base is so reactive, in fact, that the mere exposure of its unprotected chloroform solutions to air results in a comparatively rapid conversion into dye carbonate.

Both the orange dye-base and the blue form of the dye, accordingly, are highly reactive, whereas the violet form of the dye is relatively inert.

In accordance with the hypothesis recently advanced by the writer[4] to account for the tautomerism observed with variation in concentration of aminated dyes in aqueous solution, the transition concerned is one between structure of addition product type, in which the amino nitrogen atom involved is essentially trivalent, and structure of the ammonium salt type in which it is pentavalent. In the instance of brilliant cresyl blue the two color forms may be represented in the following manner

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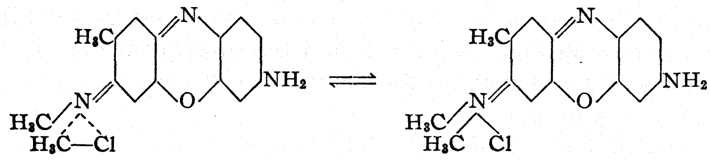

II

(violet) (blue)

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[4] **Holmes, Stain *Technology*, 1, 116 (1926).**

This hypothesis was based upon color considerations and apparently affords a thoroughly adequate explanation of the observed differences in color in tautonieric forms of aminated dyes. Direct evidence of structure of the type illustrated in Formula I is lacking, although a closely analogous structure has been demonstrated in the complexes which basic dyes form with cyclic derivatives containing phenolic groups.[5]

A compound of the structural type represented by Formula I would be expected to be relatively inert. The writer's hypothesis, accordingly, supplies an explanation of the observed lack of chemical reactivity in the violet form of brilliant cresyl blue, and this inactivity, in turn, supports the validity of the hypothesis.

Summary

The violet and blue forms of brilliant cresyl blue, which exist in tautomeric equilibrium in aqueous solutions of the dye, have been isolated. The former tautomer is chemically inert whereas the latter is reactive. These facts are held to support the author's hypothesis that the tautomerism is one between structure of addition product type and structure of ammonium salt type.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF CORNELL COLLEGE]

THE WURTZ REACTION. FACTORS INVOLVED IN THE PREPARATION OF OCTANE

BY HARRY F. LEWIS, ROBERT HENDRICKS AND G. ROBERT YOHE

RECEIVED APRIL 23, 1928 PUBLISHED JULY 6, 1928

The work herein described is concerned with an attempt to determine the factors which govern the successful carrying out of a Wurtz reaction. The preparation of octane from butyl bromide offers such an opportunity.

The preparation of 2,5-dimethylhexane from *iso*butyl iodide and sodium as described by Würtz[1] opened up to the organic chemist a valuable method for the preparation of the higher aliphatic hydrocarbons. Fittig and others soon adapted the reaction for use in the synthesis of mixed aromatic aliphatic and higher aromatic hydrocarbons.

Schorlemmer,[2] using butyl iodide and sodium, was the first to use the reaction in the preparation of normal octane. He compared his product with those octanes formed through the hydrogenation of methylhexylcarbinol and suberic acid and proved their identity.

The mechanism of the Wurtz-Fittig reaction has received much study

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[5] Holmes and Hann (awaiting publication). This paper will probably be published in the October, 1928, issue of *Stain* Technology.

[1] Wurtz, *Ann.*, 96, 365 (1855).

[2] Schorlemmer, Ann., 161, 280 (1872).

within the last few years and a good picture of the situation will be found in a recent article by Bachmann and Clarke.[3]

Discussion of Experimental Work

In order to determine the importance of the various factors which govern the formation of octane, a number of variables have been studied in connection with a standard procedure; these include the relative masses of sodium and butyl bromide, the amount of solvent (diethyl ether), temperature, time, area and diameter of the sodium, dryness of reagents, agitation, influence of methyl cyanide and the method of recovery of octane from the reaction mass.

As the result of this study, a method has been developed for the preparation of large amounts of octane, with yields of 65–70% based upon butyl bromide. Octane thus prepared has the following physical constants: b. p., 124.2–124.8°; $n_D^{20} = 1.3961$; $d_4^{20} = 0.7044$.

The data tabulated on the following pages indicate that: 1. optimum yields of octane are obtained when the sodium is used in excess; the excess need not be greater than 50 mole per cent. This holds for sodium used either as 2 mm. wire, shot or thin shavings.

2. A volume of ether two and a half times the volume of butyl bromide is necessary for keeping the reaction mixture sufficiently fluid to agitate. More is unnecessary and less may result in a loss of octane due to local overheating.

3. Low temperatures appear to favor the production of octane; higher temperatures give greater quantities of unsaturated hydrocarbons. At 0° high yields of octane result. At this temperature the blue intermediate compound is not formed. An accurate temperature study is hard to make without changing more than one variable at a time. An attempt was made to use the higher ethers as solvents, but was not successful because of the difficulty of separating those ethers from the octane. It should be stated here that the ethers up to the iso-amyl ether are stable to the action of sodium for several hours at the reflux temperature.

4. Each set of operating conditions has a maximum time for optimum yield. Too long operation may even cause a loss of octane for there is some evidence that octane is slowly acted upon by sodium at its reflux temperature.

5. The finer the sodium wire, and consequently the greater the area, the more rapid is the formation of octane. Wire finer than 0.5 mm. is difficult to prepare with the ordinary sodium press. Wire of 2 mm. diameter is easily prepared and satisfactory for most uses.

6. Traces of water present in the reaction mixture cut down the yields far more than would be predicted on the basis of the primary reaction

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[3] Bachmann and Clarke, THIS JOURNAL, 49, 2089 (1927).

between sodium and water. On the other hand, ether prepared by washing with water, drying over phosphorus pentoxide and distilling over sodium does not yield as much octane as does ether dried over calcium chloride and distilled over sodium.

7. Agitation speeds up materially the octane-producing reaction.

8. Methyl cyanide has no positive action in the formation of octane. In fact, octane was not obtained from the reaction mixture containing five drops of the cyanide. This is somewhat different from the experience of Michael.[4] In the preparation of butyl and *iso*-amyl benzene on the other hand, methyl cyanide has no effect on the yield of hydrocarbon.

9. Small amounts of octane are easily recovered from the reaction mixture by distillation at the conclusion of the experiment. Larger amounts are best obtained after the sodium is first destroyed, either with dilute alcohol or with water, as recommended by Bartow and Sellards.[5]

Chemicals Used

Butyl Bromide.—Butyl bromide was prepared from *n*-butanol according to the method described in "Organic Syntheses," Vol. I, p. 5; $d_4^{20} = 1.2740$; $n_D^{20} = 1.4381$.

Sodium.—J. T. Baker metal, used as **2** mm. wire.

Diethyl Ether.—U. S. P. dried over calcium chloride and distilled and kept over sodium.

Procedure

The solvent ether, **50** cc. (**0.472** mole), is placed in a 500-cc. round-bottomed flask equipped with a double neck addition tube and a reflux condenser, and the sodium, **6.9** g. (**0.3** mole), added. The butyl bromide, **21.9** cc. (**0.202** mole), is run in over a period of two minutes. In a short time, the mixture is at the reflux temperature where it is maintained during the required time. If the mixture is to be agitated, a special three-necked addition tube bearing a mercury seal replaces the two-necked tube. At the end of the time set for the reaction, the condenser is turned down and volatile materials distilled. These are separated by fractional distillation, two fractionations being sufficient. The fraction coming over between **110** and 130° is collected as crude octane and the octane content estimated by the refractive index. Reference is made to an octane–butyl bromide refractive index curve drawn from values obtained on mixtures of known composition and tested in an Abbé refractometer, using the sodium light and at a tempera-

TABLE I

PHYSICAL CONSTANTS OR MIXTURES OF OCTANE AND BUTYL BROMIDE

Octane, %	Butyl bromide, %	Density, 20°	Refractive index. 20° (sodium light)
100.00	...	0.7044	1.3961
95.07	4.93	.7239	1.4000
83.35	16.65	.7607	1.4011
51.91	48.09	.8940	1.4091
32.00	68.00	1.0064	1.4189
15.41	84.59	1,1229	1.4276
6.53	93.47	1.2058	1.4330
...	100.00	1.2740	1.4381

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[4] Michael, **Am. Chem. J.**, **25**,419 (1901).

[5] Bartow and Sellards, THIS JOURNAL, 27, **371** (1905).

ture of 20°. When the reaction is carried on for two and a half hours, a yield of octane of 70% is consistently obtained.

Experimental Data

1. Variation in Sodium–Butyl Bromide: Ratio

Concentration in moles					
Sodium	Butyl bromide	Ether	Time, hours	Yield. % octane	Notes
0.1	0.202	0.472	2.5	18.4	
.3	.202	.472	2.5	71.3	
.3	.202	.472	2.5	71.5	
.35	.202	.472	2.5	72.2	
.5	.202	.472	2.5	66.5	
.6	.202	.472	2.5	73.0	

2. Time–Yield Relation

0.3	0.202	0.472	0.5	14.7	Diameter wire, 2 mm.
.3	202	.472	1.75	41.5	
.3	.202	.472	2.5	71.3	
.3	.202	.472	0.5	27.3	Diameter wire, 1 mm.
.3	2 0	4 7	1.0	62.4	
.3	.202	.472	1.5	66.8	
.3	.202	.472	0.5	66.4	Diameter wire, 0.5 mm.
.3	202	.472	1.0	75.3	
.3	.202	.472	2.0	73.6	
.55	.330	.472	1.0	36.6	Sodium as shot
.55	330	.472	2.5	73.2	
.55	.330	.472	5.0	71.8	
.55	.330	.472	10.0	69.4	
.55	.330	.472	24.0	70.0	

3. Size of the Sodium Wire

0.3	0.202	0.472	0.5	71.3	0.5 mm. sodium wire
.3	.202	.472	.5	41.5	1.0 mm. sodium wire
.3	.202	.472	.5	14.7	2.0 mm. sodium wire

4. Influence of Water on Yield

0.27	0.180	0.236	0.5	47.4	No water
.27	.180	.236	.5	37.6	0.1 cc. water
.27	.180	.236	.5	30.3	.5 cc. water
.27	.180	,236	.5	4.1	1.0 cc. water
.27	.180	.236	.5	3.5	2.0 cc. water

5. Agitation of the Reaction Mixture

0 3	0 24	0.36	2.5	22.6	No agitation
.3	24	.36	5.0	44.5	No agitation
.3	24	.36	2.5	41.4	Agitation
.3	.24	36	5 0	72 8	Agitation

6. Influence of Methyl Cyanide

0.3	0.202	0 472	0 5	13.6	
.3	.202	.472	.5	16.7	
.3	.202	.472	.5	. .	Five drops methyl cyanide
.3	.202	.472	.5	. .	Five drops methyl cyanide

Separation of Octane from Reaction Mixture.—No great difference is noted in the yield of octane in runs which have come to an end, when the octane is recovered by distillation on the one hand and by destruction of excess sodium by water and separation of the water insoluble layer on the other. The latter method is much safer when working with large quantities of materials. It has been the experience in this Laboratory that a rapid evolution of octane may occur in the distillation process when the temperature of the sodium mass reaches a certain point. Under such conditions fires may be expected.

Discussion

Constant yields of octane have not been obtained when the solvent ether is completely omitted from the reaction mixture. At times, however, 70% yields of octane have been reached by adding the butyl bromide slowly to the sodium in the standard set-up or by adding sodium in small amounts to the bromide and allowing the mixture to reflux. When the apparatus is fixed for distilling rather than for refluxing, octane mixed with some unchanged bromide may be distilled from the sodium as fast as butyl bromide is added. The octane yield under these conditions is between 50 and 70%.

Large quantities of octane may be prepared in the following way. Twenty moles (1480 g.) of ether, dried over calcium chloride and distilled over sodium, is placed in a five liter round-bottomed flask equipped with an addition tube, a four foot reflux condenser and an agitator. Sodium cut thin with a sodium knife is added to the amount of 12.1 moles (278 g.) and then 8.3 moles (1137 g.) of dry butyl bromide run in over fifteen minutes. The mixture is refluxed with agitation for ten hours and then the excess sodium destroyed by slowly adding water to the contents of the flask. The layers are separated; the ether layer is dried with calcium chloride and fractionally distilled.

Fractions are collected up to 55, 55–110, 110–130, 130–180, 180–210, 210–250 and 250–300°. After a second fractionation, a yield of 450 cc. of octane is obtained. This is 68% on the basis of butyl bromide. The ether recovery is better than 75%.

Butene is also formed and this is recovered by bubbling the reaction gases through bromine. Dibromobutane is recovered; this boils between 160 and 170° and has a refractive index of 1.5151 at 20°. A typical run gave 26 g. of dibromobutane. The literature gives 166° for 1,2-dibromobutane.

A saturated hydrocarbon boiling at 295–300° is recovered to the extent of about one gram. This may be a hexadecane. Three grams of another saturated hydrocarbon, boiling point 210–215°, is also found. The dodecanes boil at that point.

Sodium bromide is recovered from the aqueous layer by crystallization.

The recovery is practically quantitative and the quality of the product satisfactory for use in making butyl bromide.

Conclusions

1. A study has been made of the factors influencing the formation of octane from butyl bromide by the Wurtz reaction.
2. Based upon this study, a method has been developed for the formation of octane in rather large amounts and with yields of 65–70% based upon butyl bromide.
3. Butene and at least two higher saturated hydrocarbons are also formed. The boiling points of the hydrocarbons suggest dodecane and hexadecane.

MOUNT VERNON, IOWA

[CONTRIBUTION FROM THE LABORATORY OF FOODS AND SANITATION, UNIVERSITY OF WISCONSIN]

CAROTIN: A PIGMENT OF HONEY[1]

BY H. A. SCHUETTE AND PHYLLIS A. BOTT

RECEIVED APRIL 23, 1928 PUBLISHED JULY 6, 1928

Color and quality in honey have from time immemorial borne an inverse relationship to each other in the minds of the average consumer, the more deeply pigmented honeys, as a rule, commanding a lesser price. As a result of this, the practice of designating its color has become universal in the grading of honey to the end that certain loosely defined names for these colors have come into use. It is only within recent years, however, that these colors have been defined with the aid of a spectrophotometer.[2]

Since these color designations are but an attempt to describe the pigmentation of a particular honey, and since this pigmentation is due wholly if not in part to red, orange or yellow coloring matters, it seemed but reasonable to assume that the latter are of the carotinoid type. To harmonize this assumption with factual evidence was the purpose of the study herein recorded.

Experimental

A highly pigmented buckwheat honey, described in trade parlance as amber colored, was selected for study since it seemed to offer the greater promise for the recovery of the necessary quantity of pigment for identification.

Attempts at removal of the coloring matter by precipitation with those clarifying agents which are commonly used in "purifying" a sugar con-

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[1] Constructed from a thesis submitted by Miss Bott to the Faculty of the Graduate School of the University of Wisconsin in partial fulfilment of the requirements for the degree of Master of Science, June, 1924.

[2] E. L. Sechrist, U. S. Dept. Agr., *Dept. Circ.* 364, 1925, p. 3.

taining solution preliminary to analysis, followed by drying and extraction of the resulting precipitate, were abandoned after repeated trials during the course of which numerous variables centering around the dilution of the honey, the nature of the precipitant and the character of the solvent were introduced. Clarification was never complete because of the colloidal nature of the non-sugars; the extraction of the coloring matter from the dried precipitate was not quantitative because of what appeared to be a physico-chemical combination between pigment and sugars or albuminous matter of the honey; and finally the pigment in part was invariably lost by oxidation because the whole operation is time consuming.

An adaptation, with slight modifications to suit the material in question, of the method developed by Palmer and Eckles[3] for the extraction of carotin from blood serum proved to be successful in this case. The procedure is as follows.

One kg. of honey was intimately mixed with an equal weight of plaster of Paris in an ordinary one-gallon ice-cream freezer. To the resulting plastic mass 150 cc. of 95% ethyl alcohol was added and, when this had been thoroughly incorporated in the mass, 500 cc. of petroleum ether (b. p. 60–70°). The contents of the freezer were then stirred for about twenty minutes, the solvent was removed and the extraction continued with successive, but smaller, quantities of the ether until fresh portions were no longer colored. Approximately 800 cc. of solvent was used per kilo of honey.

The residue from 15 kg. of honey represented a yield of 0.01% of a crude pigment which in petroleum ether solution was of a yellowish-orange color and in carbon disulfide an intense orange-red. The colors of these solutions were similar to those prepared from the carotin which had been extracted from carrots by the procedure of Euler and Nordenson.[4]

Purification of the crude carotin was effected by fractional precipitation with absolute ethyl alcohol from carbon disulfide solution. The pigment so obtained was subsequently qualitatively identified[5] as carotin by its resistance to the action of alkalies. by the fact that it was not adsorbed from carbon disulfide solution by finely divided calcium carbonate, and that with ferric chloride it produced a green coloration but none that was characteristic with concentrated sulfuric acid.

Final proof of identity was established by a determination of its adsorption spectrum in carbon disulfide solution. By means of a Hilger constant deviation prism spectroscope illuminated by an iron arc, spectrophotographs were made of solutions of the carotin when placed in I-inch cells provided with quartz ends. Carotin solutions[4] prepared from the pigments of carrots served as controls. It was observed that absorption of light occurred in the region of 4700–5250 Å. and that a portion of the visible violet rays and all of the rays in the region of the ultraviolet were absorbed. This is a characteristic function of carotin.

Summary

It has been shown that at least one of the pigments of buckwheat honey can be isolated with petroleum ether in the presence of ethyl alcohol

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[3] Palmer and Eckles, J. *Biol. Chem.*, 17,224 (1914).

[4] Euler and Nordenson, *Z. physiol. Chem.*, 56,223 (1908).

[5] Ref. 3, p. 225.

and calcium sulfate (plaster of Paris), a method applied by Palmer in the removal of pigments from blood serum, and that this pigment is carotin.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OR THE UNIVERSITY OF NORTH CAROLINA]

PARA-CYMENE STUDIES.

X. PARA-CYMYLENE-2,5-DIAMINE AND CERTAIN NEW DYES

BY ALVIN S. WHEELER AND R. W. BOST[1]

RECEIVED APRIL 25, 1928 PUBLISHED JULY 6, 1928

Of the four possible p-cymylenediamines two are known, the 2,6-diamine described by Alfthan[2] and the 2,5-diamine, the latter only in the form of its hydrochloride as described by Liebermann and Ilinski.[3] The free base was apparently isolated by Kehrmann and Messinger[4] for they state that it was so easily oxidized in the air that it could only be kept as the hydrochloride. Wallach and Schrader[5] prepared the diacetate, melting at 260°. Wheeler and Brooks[6] obtained the same diacetate on reducing 2-acetoamido-5-nitrocymene,followed by acetylation. A method superior to all others was found in the reduction of an azo derivative of 2-aminocymene, a method first used by Martius and Griess.[7] The aminocymene was coupled with diazotized sulfanilic acid, the resulting dye being reduced with stannous chloride. A poor yield is obtained if aniline is substituted for sulfanilic acid.

We locate the second amino group in position 5 for several reasons. This position is para to the amino group already present and is the point where coupling should take place according to analogous reactions. Secondly, the melting point of the diacetate is 260°, which is the same as that of the diacetate obtained from the reduction product of thymoquinonedioxime. Further proof was obtained by converting the diamine into thymoquinone, melting at 45° and described by Carstanjen,[8] and its monoxime, melting at 154–6°, and finally into hydrothymoquinone, melting at 139.5°.

p-Cymylene-2,5-diamine is so unstable in the air that no description of it has appeared in the literature. We isolated it in an atmosphere of nitrogen and at reduced pressure in a specially constructed apparatus.

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[1] An abstract of a thesis submitted in June, 1928, to the Faculty of the University of North Carolina by R. W. Bost in candidacy for the degree of Doctor of Philosophy

[2] Alfthan, *Ber.*, 53, 86 (1920).

[3] Liebermann and Ilinski, *Ber.*, 18, 3200 (1885).

[4] Kehrmann and Messinger, *Ber.*, 23, 3562 (1890).

[5] Wallach and Schrader, Ann., 279, 375 (1894).

[6] Wheeler and Brooks, THIS JOURNAL, 49,2834 (1927).

[7] Martius and Griess, *Chem. Zentr.*, 1866, 136.

[8] Carstanjen, J. *prakt. Chem.*, [2] 3, 53 (1871).

It is a light yellow solid which on exposure to the air changes color within a few minutes, passing through deep red and green to blue. Oxidizing agents readily convert it into the quinone, ferric chloride in the cold giving a quantitative yield in less than fifteen minutes. Neither *p*-phenylenediamine nor *p*-toluylenediamine is oxidized to a quinone under like conditions. The diamine forms salts with great readiness, the picrate and benzoate forming almost instantaneously, whereas an ether solution of aniline, o-toluidine or aminocymene gives no apparent reaction with benzoic acid in twenty-four hours.

The diamine was characterized by its conversion into the following new compounds: 2,5-*bis*-(thioureido)-1-methyl-4-*iso*propylbenzene, 2,5-diureido-1-methyl-4-*iso*propylbenzene and p-aminocymyloxamido acid.

Two series of dyes were prepared: first, a group of diazo dyes by coupling with certain naphthols and amino acids; second, a group of azine dyes of the Eurhodine class. The first group gave blue, yellow and red colors while the second gave brown and purple shades. The dye obtained with 2-naphthol colors wool a blackish violet, whereas the thionaphthol dyes wool a light buff; thus the sulfur shows a strong hypsochromic effect. The dye obtained with the naphthol disulfonic acid possesses a very high tinctorial power and the dye-bath exhausts completely.

The isopropyl group in the diamine is very sensitive, for in bromination and nitration reactions it is largely destroyed.

Experimental Part

Reduction of 5-(4-Sulfobenzeneazo)-carvacrylamine Hydrochloride.—This compound was prepared as described by Wheeler and Cutlar,[9] who coupled 2-aminocymene with diazotized sulfanilic acid. Its reduction was carried out as follows: 47 g. of the hydrochloride was slowly added to a boiling solution of 75 g. of stannous chloride, 65 cc. of concd. hydrochloric acid and 500 cc. of water. When the last trace of color had disappeared, the solution was cooled and treated with an excess of sodium hydroxide. The diamine was extracted with ether and converted into the hydrochloride by passing hydrogen chloride gas into the solution; yield, 26 g. or 77.9% of the theoretical.

_p_-Cymylene-2,5-diamine, $C_6H_2CH_3C_3H_7(NH_2)_2$.—The free base was isolated by distillation in an atmosphere of nitrogen and at reduced pressure in an apparatus shown in the accompanying diagram. The air in the system ABIDJR was displaced by nitrogen from a cylinder connected with A. Stopcock B was then turned so that the nitrogen displaced the air in the system ABGC. An aqueous solution of the diamine and 200 cc. of ether was admitted through buret E into funnel G and the solution saturated with nitrogen. In the meantime the system IDJR was evacuated by a pump connected to R. A 15% solution of sodium hydroxide was added to the diamine salt solution in G through buret E until the phenolphthalein present showed excess thereof. The stream of nitrogen passing through the solution served to stir the diamine so that it readily dissolved in the ether layer. The water layer was drawn off through F. The path of the nitrogen stream was changed so as to pass from A through C into G. Stopcock B was opened into the evacuated system IDJR, whereupon the ether solution was drawn from G into flask I. A gentle stream of nitrogen was then passed through the

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[9] Wheeler and Cutlar, THIS JOURNAL, 49, 2819 (1927).

system ABIDJR and the ether distilled off spontaneously from flask I at a pressure around 120 mm. A light yellow solid remained in the flask into which 200 cc. of methyl alcohol, previously saturated with nitrogen, was admitted in a manner similar to that in which the ether was admitted. The alcohol took up the few droplets of moisture present and also dissolved the diamine. The alcohol was distilled at 120–130 mm. and a temperature around 30°. The diamine remained as a yellow, solid mass, apparently consisting of needles though not well defined.

The diamine in I was dissolved in ether saturated with nitrogen and admitted through the same channel as the alcohol. A partial vacuum was produced in G by evacuating the system ACGBIDJR. C was closed and a rapid stream of nitrogen was passed through ABIDJR until the pressure was one atmosphere. D was closed and B opened into the partial vacuum G whereupon the ether solution of the diamine in I was drawn over into G. Nitrogen was then bubbled through ABGC and the diamine precipitated by the addition of petroleum ether to G through buret E. Then F was connected with L by rubber tubing and the finely divided precipitate of the diamine filtered by suction into the nitrogen filled desiccator P.

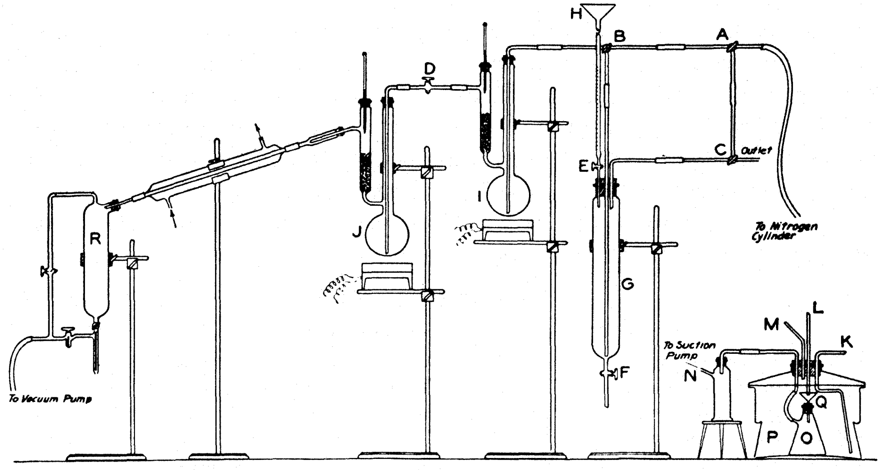

Fig. 1.—Apparatus.

Dibenzoate, $C_6H_2CH_3C_3H_7(NHCOC_6H_5)_2$.—The benzoate was prepared in the usual way in alkaline solution with benzoyl chloride. The product was recrystallized from hot alcohol giving fine, white needles, soluble in acetone and alcohol; m. p. 280°; yield, quantitative.

Anal. Subs., 0.2082: 7.27 cc. of 0.1524 N HCl required for NH_3. Calcd. for $C_{24}H_{24}N_2O_2$: N_2, 7.52. Found: 7.45.

Quinones

The 2,5-cymo-*p*-quinone, its oxime and the corresponding hydroquinone were prepared for orientation purposes. They have been described by Carstanjen.[8]

2,5-Cymo-*p*-quinone.—Four g. of the diamine salt was dissolved in 200 cc. of 2% acetic acid. To this solution was added 5 g. of chromic acid in 200 cc. of water. After stirring for thirty minutes, the brownish black precipitate was filtered off, dried and purified by sublimation to give long, slender, glistening yellow needles; m. p. 45.5°.

Its **monoxime** was prepared by heating the quinone with hydroxylamine hydrochloride for five hours on the water-bath. The product was recrystallized by dissolving in ether and adding petroleum ether, yielding fine, brownish-yellow needles, m. p. 154–156°.

2,5-Cymo-*p*-hydroquinone.—The quinone was dissolved in the least possible amount of acetone and a 2% solution of titanium chloride added until reduction was complete. The product was extracted with ether; fine, white needles; m. p. 139".

Salts

The salts indicated in the table were made by mixing the constituents in the cold. To obtain the hydrochloride dry hydrogen chloride was passed into an ether solution of the diamine. For the hydrobromide and nitrate the corresponding acids were used with gentle heating. These three salts were recrystallized from absolute alcohol. The other salts were prepared by mixing ether solutions of the constituents and washing the salt with ether. All are soluble in water, alcohol and acetone but difficultly soluble in ether. Analyses were made by titrating with sodium hydroxide, using phenolphthalein as indicator.

TABLE I

DATA ON THE SALTS

Salt	Crystal form	M. p., ° C.	Analysis, acid Calcd., %	Found, %
Hydrochloride (di)	Fine granules	323 (decomp.)	30.75	30.77
Hydrobromide (di)	Microscopic needles	330 (decomp.)	49.63	49.13
Nitrate (di)	Microscopic needles	196 (decomp.)	43.42	43.13
Chloro-acetate (mono)	Microscopic needles	144	36.53	36.65
Dichloro-acetate (di)	Microscopic needles	165	61.10	60.70
Trichloro-acetate (di)	Granular	171	66.56	67.08
Bromo-acetate (mono)	Needles	148 (decomp.)	45.85	44.32
Benzene sulfonate (di)	Granular	Decomp.	69.28	69.22
Benzoate (mono)	Microscopic needles	145	42.65	42.53
o-Chlorobenzoate (mono)	Microscopic needles	161	48.81	49.10
3,5-Dinitrobenzoate (mono)	Granular	199 (decomp.)	56.37	56.67
2,4,6-Trinitrobenzoate (mono)	Needles	130 (decomp.)	61.05	60.85
Picrate (di)	Needles	207 (decomp.)	18.10	17.93

Condensation Products

2,5-Bis-(thio-ureido)-1-methyl-4-*iso*propylbenzene, $C_{10}H_{12}(NHCSNH_2)_2$.—A solution of 2.0 g. of the diamine salt was poured into a solution of 1.64 g. of potassium sulfocyanate. The solution was evaporated to dryness and the residue kept on the steam-bath for two hours. The material was then washed several times with boiling water, filtered and recrystallized from hot methyl alcohol; white, granular substance; m. p. 235–237°. It is soluble in alcohol but insoluble in water, ether and benzene; yield, 1.2 g.

And. Subs., 0.2024: 18.69 cc. of 0.1524 N HCl required for NH_3. Calcd. for $C_{12}H_{18}N_4S_2$: N2, 19.85. Found: 19.70.

2,5-Diureido-1-methyl-4-*iso*propylbenzene, $C_{10}H_{12}(NHCONH_2)_2$.—To a solution of 0.5 g. of the diamine salt dissolved in 10 cc. of water was added dropwise a solution of 1 g. of potassium cyanate in 5 cc. of water. The mixture was heated on the steam-bath for one hour, the product filtered off, washed with hot water, then with alcohol and finally with ether. It consisted of a white powder insoluble in water and rather difficultly soluble in alcohol and ether. It did not melt under 350°; yield, 0.6 g.

Anal. Subs., 0.1076: 11.37 cc. of 0.1524 *N* HCl required for NH_3. Calcd. for $C_{12}H_{18}O_2N_4$: N_2, 22.39. Found: 22.54.

p-Aminocymyloxamido Acid, $C_{12}H_{16}O_3N_2$.—1.44 g. of the diamine salt was dissolved in 50 cc. of water and the base set free by the addition of sodium hydroxide. The diamine was shaken out with ether and the ether solution carefully dried. To this solution was added an ether solution of 0.55 g. of anhydrous oxalic acid. A precipitate formed immediately but the mixture was refluxed for two hours, the ether distilled off and replaced with 75 cc. of absolute alcohol and then refluxed for fifteen hours. The crystals melt at 210–211°. The product is rather soluble in water but difficultly soluble in alcohol and ether; yield, 0.21 g. The success of the reaction depends upon having the ether solution of the diamine dry before adding the oxalic acid.

Anal. Subs., 0.2040: 11.10 cc. of 0.1524 N HCl required for NH_3. Calcd. for $C_{12}H_{16}O_3N_2$: N_2, 11.86. Found: 11.60.

Diazo Dyes

These dyes were prepared by diazotizing p-cymylene-2,5-diamine at 0°, adding the phenol dissolved in alkali, precipitating the dye with acetic acid and recrystallizing the product from a suitable solvent.

TABLE II

DISAZO DYE DATA

No.	Coupler	Solvent	Formula	Calcd., %	Found. %	M. P.. °C.
1	Resorcinol	Dilute alcohol	$C_{22}H_{22}O_4N_4$	N, 13.72	13.43	168–170
2	2-Naphthol	Benzene	$C_{30}H_{26}O_2N_4$	N, 11.81	11.34	295–298 (dec.)
3	Sulfanilic acid	Alcohol	$C_{22}H_{26}O_6N_6S_2Cl_2$	S, 10.59	10.19	100 (dec.)
4	2-Naphthol-3,6-disulfonic acid	Methyl alcohol	$C_{30}H_{20}O_{14}N_4S_4Na_6$	S, 13.84	12.42	Above 340
5	Naphthionic acid	Alcohol	$C_{30}H_{28}O_6N_6S_2$	S, 10.13	10.33	270–272 (dec.)
6	2-Thionaphthol	Carbon tetrachloride	$C_{30}H_{26}N_4S_2$	S, 12.66	13.07	138–140

TABLE III

DYEING COLORS

The amount of dye used was 4% of the weight of the fiber

No.	Wool	Silk	Cotton	Behavior with sulfuric acid Cold	Hot	Dilute
1	Chestnut brown	Deep chestnut brown	Pale salmon	Brown	Deep brown	Pale brown
2	Dull violet black	Blackish-purple	Dusky violet blue	Light blue	Dark brown	Brown
3	Pale orange yellow	Pale orange yellow	Pale orange yellow	Pale brown	Dark brown	Brown
4	Diamine azo blue	Diamine azo blue	Light Windsor blue	Dark violet	Reddish-brown	Pale brown
5	Dragon's blood red	Dragon's blood red	Salmon	Cherry red	Reddish-brown	Brown
6	Light buff	Warm buff	White	Pale straw	Greenish yellow	Greenish brown

Azine (Eurhodine) Dyes

Three Eurhodine dyes were prepared by dissolving the nitroso compound in 100 cc. of hot methyl alcohol and adding to this solution the diamine salt dissolved in 50 cc. of methyl alcohol. The mixture was refluxed for thirty minutes when the alcohol was distilled off and replaced with water. The dye was set free on the addition of weak ammonia. The product was recrystallized from dilute alcohol.

TABLE IV

AZINE (EURHODINE) DYES

	1	2
Intermediate	*p*-Nitrosodimethylaniline	*p*-Nitrosophenol
Solvent	Dilute alcohol	Dilute alcohol
Crystal color	Blue black	Dark brown
Formula	$C_{18}H_{22}N_4$	$C_{16}H_{17}ON_3$
M. p., ° C.	300 (dec.)	200–206 (dec.)
N, calcd., %	19.04	15.73
N, found, %	18.96	15.91
Color on wool	Purplish black	Dusky brown
Color on silk	Purplish black	Dusky brown
Color on cotton	Plumbeous	Pale purple drab

Summary

1. *p*-Cymylenediamine prepared by reducing the dye obtained by coupling 2-amino-*p*-cymene with diazotized sulfanilic acid is shown to be the 2,5-diamine.
2. A series of thirteen salts with inorganic and organic acids was prepared.
3. Condensation products were obtained with potassium sulfocyanate, potassium cpanate and oxalic acid.
4. A series of disazo dyes was prepared by coupling the diamine with certain naphthols and amino acids.
5. Two azine dyes of the Eurhodine class were prepared.

CHAPEL HILL, NORTH CAROLINA

[CONTRIBUTION FROM THE FOOD RESEARCH DIVISION, BUREAU OF CHEMISTRY AND SOILS, DEPARTMENT OF AGRICULTURE]

THE ACIDS OF MAPLE SIRUP

BY E. K. NELSON

RECEIVED APRIL 26, 1928 PUBLISHED JULY 6, 1928

It has long been known that *l*-malic acid is the chief acid in maple products. In an examination of maple sugar "sand," the deposit of the calcium salts of organic acids which forms in the evaporating kettles, v. Lippmann[1] found, in addition to much l-malic acid, considerable d-tartaric acid and a small quantity of tricarballylic acid. E. O. v. Lippmann gives very little information regarding his methods of separating these acids. He states, however, that tricarballylic acid was extracted from the acid mixture by means of ether. A sample of maple sugar sand, obtained in Vermont, was examined in the Food Research Laboratory. In addition to *l*-malic a number of acids not mentioned by E. O. v. Lippmann were identified, but only a trace of tartaric acid and of tricarballylic acid was found.

The material used in the investigation reported in this paper consisted of two 10-gallon lots of maple sirup, one from a producer in Vermont, and the other from a producer at Belleville, Michigan. Both manufacturers were reliable, and the sirups were guaranteed to be genuine and free from adulteration.

The alkalinity of the ash in the Vermont sirup was equivalent to 140 cc. of $N/10$ acid per 100 cc., and in the Michigan sirup it was equivalent to 103 cc. of $N/10$ acid per 100 cc.

The free acidity in the Vermont sirup was 4 cc. of $N/10$ acid per 100 cc.; in the Michigan sirup it was 4.5 cc. of $N/10$ acid per 100 cc. Most of the organic acids in maple sirup are, therefore, in the form of salts.

The general course of procedure consisted of three steps: (1) extracting the ether soluble acids after the addition of a quantity of hydrochloric acid equivalent to the alkalinity of the ash; (2) distilling volatile acids in a vacuum pan and precipitating the non-volatile acids as lead salts; (3) recovering the acids, and esterifying and fractionating the esters.

Experimental

Thirty-eight liters of each sirup were acidified with a quantity of hydrochloric acid equivalent to the alkalinity of the ash, diluted with an equal volume of water and twice shaken out with ether in 4-liter lots. The ether was concentrated on the steam-bath, and the concentrated ether solution was reserved until the entire quantity of sirup had been extracted. The ether extracts were shaken with a dilute solution of sodium bicarbonate to remove ether soluble acids, and the ether solution was reserved for a later investigation of the flavoring substances of maple sirup. The bicarbonate solution was acidified and the acids were recovered by extraction with ether. The residue from the

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[1] E. O. v. Lippmann, *Ber.*, 47, 3094 (1914).

ether, sharp in odor and dark in color, was dissolved in boiling water and filtered with a little norite.

On standing, the concentrated solution formed crystals. Of this sparingly soluble acid, 0.22 g. was obtained from the Vermont sirup and 0.24 g. from the Michigan sirup. It was unsaturated to potassium permanganate and melted at 286° in a sealed tube. An optical crystallographic examination[2] confirmed its identity with fumaric acid. The further concentration of the filtrate from fumaric acid yielded a small quantity of an unidentified acid having a high melting point but different in optical properties from fumaric acid and not corresponding to aconitic, tricarballylic or succinic acid.

An examination for succinic acid by optical methods established its presence in very small quantity in the Michigan sirup. Proof of its presence in the Vermont sirup was lacking.

After extraction with ether, the solution was concentrated in a vacuum pan to a thick sirup, and the distillates, neutralized with caustic soda, were evaporated to dryness. The residue of sodium salts was dissolved in water, an excess of sulfuric acid was added and the volatile acids were distilled. The distillate was exactly neutralized with barium hydroxide, concentrated to small volume and fractionally crystallized.

The total weight of barium salts from the Vermont sirup was 26.4 g. and from the Michigan sirup, 15.7 g.

The barium salt of volatile acids from the Vermont sirup yielded the following fractions: 1, 4.45 g. = 60.18% of barium (calcd. for barium formate, barium = 60.35%); 2, 2.47 g. = 58.60% of barium; 3, 3.97 g. = 57.09% of barium; 4, 9.23 g. = 56.52% of barium; 5, 4.40 g. = 54.63% of barium (calcd. for barium acetate, barium = 53.72%).

After the formic acid was removed from Fraction 5, the silver salt was prepared and analyzed. It gave 64.01% of silver (calcd. for silver acetate, 64.45%). Optical examination showed that Fraction 1 was pure barium formate and the barium salts were a mixture of nearly equal parts of barium formate and barium acetate.

The barium salts of the volatile acids from Michigan sirup yielded the following fractions: 1, 3.74 g. = 60.58% of barium; 2, 4.98 g. = 59.45% of barium; 3, 2.48 g. = 56.28% of barium; 4, 7.03 g. = 55.95% of barium.

The formic acid was removed from Fraction 4 by potassium permanganate and the silver salt was prepared and found to contain 64.25% silver (calcd. for silver acetate, 64.45% of silver). Fraction 1 was found on optical examination to be nearly pure barium formate, and calculation showed the barium salts to be a mixture of 11.3 g. of barium formate and 6.9 g. of barium acetate.

The concentrated sirup, from which the volatile acids had been distilled, was diluted with water and precipitated with a moderate excess of lead subacetate. The lead precipitate was filtered and washed. Carbon dioxide was passed through its suspension in water to break up lead sugar compounds, after which it was again filtered, dried and weighed. It was then decomposed with an excess of sulfuric acid and the lead sulfate was removed by filtration.

The sulfuric acid was determined in an aliquot of the measured filtrate and its equivalent of barium hydroxide was added to remove it. After filtering barium sulfate, the solution of acids was evaporated to dryness on' the steam-bath. The organic acids were refluxed for five hours with 500 cc. of absolute alcohol containing 2.5% of hydrochloric acid and, after the alcohol was distilled off, this operation was repeated with a fresh portion of alcoholic hydrochloric acid.

The esters, after removal of the alcohol, were dissolved in ether. The ether solu-

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[2] The optical examinations were kindly made by G. L. Keenan of the Food, Drug and Insecticide Administration.

tion was washed with dilute sodium hydroxide solution until neutral, dried with anhydrous sodium sulfate and evaporated, leaving the crude esters. The esters were then fractionated at **10** mm.

The crude esters from the Vermont sirup weighed **70** g. and after three distillations gave the following fractions: **1,** 115–125°, **0.3 g.; 2,** 125–130°, **52.3** g., α_D = **−11.62"; 3,** 130–135°, **1.7** g.; **4,** 135–145°, **1.8** g.; **5,** 145–165°, **0.4** g.; **6,** 165–170°, **4.8** g.; total, **61.3 g.**

The hydrazides were prepared from these fractions, **0.7** g. of ester, **5** cc. of absolute alcohol and **1** cc. of hydrazine hydrate (42%) being used. Fraction **1** afforded a hydrazide melting at 173–175°, identified as *l*-malic hydrazide. Fraction **2** gave a hydrazide melting at **177–179°,** *l*-malic hydrazide. Nothing but *l*-malic hydrazide in impure form was obtained from Fractions **3** and **4,** whereas Fractions **5** and 6 gave citric trihydrazide, identified by its melting in the hydrated form at 105–107° and in its anhydrous form at **147°** and also by optical crystallographic comparison with pure citric trihydrazide.

Michigan sirup afforded **53.5** g. of crude esters, yielding the following fractions on being distilled twice at **10** mm.: **1,** 125–130°, **41.4** g.; **2, 130–140°, 2.1** g.; **3,** 140–150°, 0.5 g.; **4,** 150–165°, 1.3 g.; **5,** 165–170°, **4.7** g.; total, **50.0** g.

Fractions **1,2** and **3** afforded *l*-malic hydrazide and Fraction **5** gave citric hydrazide, melting (hydrated form) at 105–107°. The identity of the fractions was further checked by optical crystallographic examination.

Fraction **4** was tested for tartaric acid in the following manner. The fraction was saponified with alcoholic potassium hydroxide, made acid with acetic acid and diluted to **150** cc. Then **0.25** g. of ammonium I-tartrate and an excess of calcium acetate were added, the mixture being well stirred. It was allowed to stand for some time but no precipitate of calcium racemate was obtained, establishing the absence of d-tartaric acid.

The approximate quantities of the respective acids in these maple sirups, calculated in grams per liter, are as follows.

Acids	Formic	Acetic	*l*-Malic	Citric	Fumaric	Succinic
Vermont, g.	0.134	0.150	1.04	0.095	0.0056	None identified
Michigan, g.	.121	.085	0.81	.11	.0063	Small quantity present

Summary

The acids in maple sirup from two localities were investigated. In addition to malic acid, which predominates, formic, acetic and citric acids were identified. Also, a small quantity of fumaric acid and a trace of succinic acid were found. There was evidence of the presence of a small quantity of an unidentified acid having a high melting point. Neither d-tartaric acid nor tricarballylic acid could be found.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE FOOD RESEARCH DIVISION, BUREAU OF CHEMISTRY AND SOILS, DEPARTMENT OF AGRICULTURE]

THE FLAVOR OF MAPLE SIRUP

BY E. K. NELSON

RECEIVED APRIL 26, 1928 PUBLISHED JULY 6, 1928

The pleasant and characteristic flavor of maple sirup and maple sugar has been imitated by mixtures of such things as lovage, fenugreek, hickory bark, vanillin and coumarin. The true character of the Aavor seems never to have been investigated. The investigation reported in this paper was undertaken with the object of throwing some light on the nature of maple flavor.

Experimental

The first attempt to isolate the flavoring material was by the barium process devised by Sale and Wilson[1] of the Food, Drug and Insecticide Administration, a process which consists in removing most of the sugar by means of barium hydroxide. Five liters of Vermont sirup were treated. The product, a concentrated solution of the flavoring material containing sugar and coloring matter, was thoroughly extracted with ether. The ether solution was shaken out with dilute ammonia, 1:10, and then the ammonia solution was acidified and extracted with ether. After the ether had been carefully evaporated, the residue was stirred with 100 cc. of water and 25 cc. of 10% lead acetate solution and filtered, and the filtrate was extracted with ether. On evaporation of the ether, a reddish oil remained which did not crystallize. It has a sharp, acid odor. It was therefore dissolved in dilute sodium carbonate and extracted with ether. The ether residue had a peculiar (phenolic?) odor, and with ferric chloride gave a green color reaction. Vanillin was not identified.

The ether solution left after extraction with dilute ammonia was evaporated, the residue was dissolved in water, lead acetate solution added and the mixture filtered. The filtrate was extracted with ether and the ether was evaporated. The residue became partly crystalline. The crystals were separated on a porous plate and recrystallized from ethyl acetate. White, spindle-shaped crystals, which gradually turned brown in the air, were obtained. The substance melted exactly at 212° but darkened at a lower temperature. It was insoluble in water but dissolved in sodium hydroxide solution and, on shaking, this solution became red.

The substance reduced copper acetate and silver nitrate solutions; on boiling it with ferric chloride a pungent, chlorine-like odor was evolved, and a crystalline substance condensed in the upper part of the tube. These reactions indicate a quinone derivative. Hydrophlorone, which melts at 212°, was prepared and compared crystallographically with the unknown material, but the two were found to be different.

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[1] United States Patent 1,642,789.

An optical examination[2] showed that the material consisted of spindle-shaped crystals with straight extinction and invariably showing n = 1.560 (approximately) lengthwise, the n crosswise being higher than 1.690.

The oil absorbed by the porous plate was recovered. Most of it was soluble in water to a clear, yellow solution. Ferric chloride turned it red and caused turbidity. Nothing definite was obtained from it.

As it was assumed that the barium treatment may have caused changes in the flavoring substances of maple, a direct extraction of 1 gallon of sirup with ether was undertaken. The ether extract was washed with water, concentrated in a still, and finally evaporated in a vacuum desiccator. The residue was small and had an intense odor of maple. When it was dissolved in dilute sodium hydroxide, the maple odor disappeared, and acidifying the solution did not restore it. This shows that the flavoring material is very sensitive to caustic alkalies.

It was found that the flavor of maple sirup can be removed with norite. One liter of sirup diluted with 1 liter of water was stirred for twenty minutes with 50 g. of norite and filtered. The norite was washed with three 100-cc. portions of water, drained on a Biichner funnel and exhausted with ether in a Soxhlet extractor. On evaporating the ether a red oil remained in which the maple flavor was indistinct. The sirup filtered from the norite, however, had lost its maple flavor. Evidently the flavor, although adsorbed by the norite, had either not been recovered from it or had become changed and lost its identity.

These preliminary experiments having shown that a direct ether extraction is perhaps the best method of isolating the flavoring material, which is a very unstable substance, the use of fixed caustic alkalies and adsorbents was avoided in the further study of the problem.

In the investigation of the organic acids[3] of maple sirup, ether extractions were made and the ether solutions, after being washed with dilute sodium bicarbonate for the recovery of ether soluble acids, were reserved for the investigation of the flavor. These solutions, which represent the ether extracts from **38** liters of Vermont maple sirup and from an equal quantity of Michigan sirup, were shaken with a strong solution of sodium bisulfite and kept in an ice box with occasional shaking for twenty-four hours. The bisulfite solutions were separated and acidified with dilute sulfuric acid, and a stream of carbon dioxide was allowed to bubble through for some time to remove the sulfur dioxide. They were then extracted with ether and the ether carefully evaporated. The residues were boiled out several times with petroleum ether and after this was evaporated the residues had a distinct vanillin-like odor.

The substance obtained from the Vermont sirup showed a tendency to crystallize, but was not sufficiently pure for examination, though it gave a blue color reaction with ferric chloride.

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[2] Optical examinations were kindly made by G. L. Keenan of the Food, Drug and Insecticide Administration.

[3] Reported in a previous paper on "The Acids of Maple Sirup," THIS JOURNAL, *50, 2006* **(1928).**

The substance from the Michigan sirup, however, was obtained in crystalline form. The entire quantity of material was only 127 mg., of which one-half was dissolved by petroleum ether. The substance gave a blue color reaction with ferric chloride and responded to the resorcinol and phloroglucin tests for vanillin. It crystallized from petroleum ether in plates instead of needles. Crystallographic examination showed that it was neither vanillin nor the ethyl homolog of vanillin. It melted at 74–76°. The odor was intense and very much like that of vanillin.

On boiling with dilute ferric chloride and cooling, a crystalline precipitate corresponding to dehydrodivanillin was obtained. This crystallized in tufts and was found to be different from dehydrodivanillin in optical properties.

The residues left after boiling with petroleum ether were not crystalline and had an odor like maple. The residue insoluble in petroleum ether from the Michigan sirup had a particularly agreeable odor, somewhat like heliotrope (piperonal).

After extraction with bisulfite the ether solutions were shaken out twice with ammonium hydroxide, 1:10, 50 cc. being used for each extraction. The dilute ammonia solutions were separated, poured into dilute sulfuric acid and shaken with ether.

On careful evaporation of the ether, reddish-yellow residues, which were resinous and had an intense odor of maple, remained. The residue from Vermont sirup weighed 0.4 g. and that from Michigan sirup, 0.5 g.

All efforts to induce crystallization failed. Methylation and acetylization also failed to afford crystalline derivatives. A hydro-alcoholic solution treated with a few drops of dilute ferric chloride was colored red, which changed to greenish yellow. The substance changed easily to a darker colored resin, at the same time losing its characteristic maple odor. This change seems to take place to some extent on evaporating its etheral solutions, but whether it is owing to polymerization or oxidation is undetermined.

Boiling with ferric chloride failed to give a volatile, quinone-like substance such as was observed in the crystalline material isolated from the products of the experiment in which the Sale-Wilson process was used.

The maple flavor, therefore, appears to depend to a great extent on an unstable, phenolic substance, or substances, the exact nature of which remains undetermined. It seems a reasonable hypothesis, however, that it may be related to the vanillin-like substance associated with it, and possibly also to the phlorone-like substance which gave a volatile, pungent, crystalline derivative on boiling with ferric chloride. That it may be closely allied with the vanillin-like substance is indicated by the fact that the latter appears to be more unstable than vanillin, easily turning yellow in the air and on heating.

The ether solution remaining after the removal of acids, aldehydes and phenols was evaporated. The residue was very small and did not have a maple odor. It was reddish and became partly crystalline. Recrystallized from alcohol, spindle-shaped crystals which melted at 210–212° were formed. It was thought that this must be the same as the quinone-like substance previously obtained, but when it was boiled with ferric chloride no pungent, volatile substance resulted. On boiling it with ferric chloride a faint odor of vanillin was observed. The residue from the Vermont sirup contained a small quantity of a saponifiable oil. This was not found in the corresponding residue from the Michigan sirup, and it is very probably an oil used in the kettles to stop foaming.

Conclusion

Investigation of the flavor of maple sirup showed that it depends to a great extent on an unstable phenolic substance which is associated with a crystalline aldehyde melting at 74–76' and similar in odor and properties to vanillin. Maple sirup may contain minute quantities of other aldehydic substances which influence the flavor.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE FOOD RESEARCH DIVISION, BUREAU OF CHEMISTRY AND SOILS, UNITED STATES DEPARTMENT OF AGRICULTURE]

THE ACIDS OF FIGS

BY E. K. NELSON

RECEIVED APRIL 26, 1928 PUBLISHED JULY 6, 1928

No record has been found in the literature regarding the identity of the acids of figs. Bigelow and Dunbar[1] in their review of the literature on fruit acids do not mention the fig. Condit and Creuss[2] state that fresh Kadota figs contain from 19 to 24% of sugar and from 0.1 to 0.44% of acid, calculated as citric.

In an investigation of sour figs and figs affected with internal rot, B. J. Howard, of this Bureau, collected samples of normal and diseased figs near Fresno, California, during the summer of 1927. They included Adriatic "black necks," normal Adriatics, Calimyrna figs affected with internal rot and normal Calimyrnas. Part of these samples, when dried, afforded the material for an investigation of the acids in figs.

Experimental

Approximately two kilograms of each kind of figs was ground to a paste. The paste was disintegrated in 1 gallon of water at 60°, digested on a steam-bath for an hour, diluted with an equal volume of alcohol and strained through a linen bag. The residue was pressed dry, soaked in hot dilute alcohol and re-pressed. The fig extract was concentrated to a sirup in a vacuum pan, the distillate being collected for the determination of volatile acids. After being diluted with water and acidified with sulfuric acid, the sirup was extracted with ether to recover ether soluble acids. Only fig fat and small quantities of stearic and oleic acids were found in this ether extract.

The diluted sirup was then precipitated with a moderate excess of lead subacetate. After filtration, the lead precipitate was suspended in water and a stream of carbon dioxide was allowed to bubble through it for some time in order to break up lead sugar compounds. After it was filtered and washed, the lead precipitate was decomposed with sulfuric acid and the excess of acid was removed with the equivalent quantity of barium hydroxide. The acid solution was evaporated to dryness on the steam-bath

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[1] Bigelow and Dunbar, *J. Ind. Eng. Chem.*, 9, 767 (1912).

[2] Condit and Creuss, Calif. Agr. Expt. Sta., Bull., 436, 1-45 (1927).

and esterified by being refluxed for five hours with absolute alcohol containing 2.5% of hydrochloric acid. After distilling off the alcohol, the esterification process was repeated. The crude esters, in ether solution, were washed with sodium hydroxide solution, the ether was evaporated and the esters, after being weighed, were subjected to fractional distillation at 10 mm.

The hydrazides prepared from the fractions were used for the identification of the respective acids.

The barium salt of the volatile acids from 2282 g. of Adriatic black necks weighed 15.71 g. It was fractionally crystallized and the barium in each fraction was determined. Fraction 1 contained 53.9% of barium; Fraction 2, 53.89%; Fraction 3, 53.95%; and Fraction 4, 53.87%; calcd. for barium acetate, barium = 53.72%. The volatile acid is therefore acetic acid. No ether soluble acids other than small quantities of stearic and oleic from the fig fat were identified.

The crude ester of the non-volatile acid, 9.75 g., when distilled at 10 mm. at 170–171° afforded 8.1 g. of pure ester. It had the boiling point of triethyl citrate and gave the characteristic hydrazide, melting at 104–106° in its hydrated form and at 147° when seeded and in the anhydrous form.

In the tests with normal Adriatic figs, 1925 g. of fruit yielded 1.11 g. of barium salt of volatile acids, corresponding to 0.27 g. of acetic acid per kilo. The silver salt was analyzed and 64.44% of silver was found; calcd. for silver acetate, 64.45%. The ethyl citrate, boiling at 170–171° at 10 mm., weighed 8.93 g., corresponding to 3.2 g. of citric acid per kilo, and afforded the characteristic hydrazide.

Two kilos of Calimyrna figs affected with internal rot yielded 2.4 g. of the barium salt of volatile acids, corresponding to 0.56 g. of acetic acid per kilo. It was shown to be acetic acid by the analysis of the silver salt (64.15% of silver). From the ester of the non-volatile acids a small quantity was obtained distilling under 170° at 10 mm., and from the hydrazide of this, several times recrystallized, a small quantity of malic acid hydrazide which melted at 177–179° was separated; a mixture of this with pure malic hydrazide showed no lower melting point. The main portion of the ester, 9.51 g., distilled at 170–171°, corresponding to 3.3 g. citric acid per kilo and affording the characteristic hydrazide.

Normal Calimyrnas, 2.066 kilos, afforded 1.15 g. of the barium salt of volatile acids, corresponding to 0.26 g. of acetic acid per kilo. The silver salt contained 64.6% of silver.

In the esters of the non-volatile acids, a small quantity of malic acid was identified by the hydrazide. Nine and five-tenths grams boiling at 170–171° at 10 mm. corresponded to citric acid, 3.5 g. per kilo.

Conclusion

Acetic and citric acids were found in Adriatic figs, and acetic, citric and a small quantity of malic acids were identified in Calimyrna figs.

It was found that Adriatic black neck figs contained more than 10 times as much free acetic acid as the normal Adriatic figs. Less citric acid was found than in the normal figs.

Normal Calimyrna figs contained 0.26 g. per kilo of free acetic acid and 3.5 g. of citric acid, besides a small quantity of malic acid.

In Calimyrna figs affected with internal rot the free acetic acid amounted to 0.56 g. per kilo, and the citric acid amounted to 3.3 g. per kilo.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE LOUISIANA STATE UNIVERSITY]

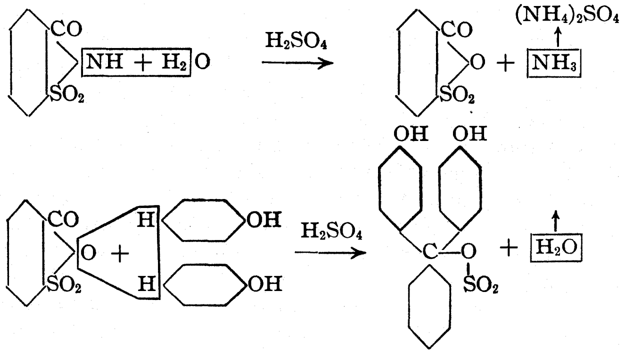
A NEW METHOD FOR THE PREPARATION OF PHENOLSULFONEPHTHALEIN AND BROMOSULFONEPHTHALEIN

BY R. FREAS AND E. A. PROVING

RECEIVED APRIL 27, 1928 PUBLISHED JULY 6, 1928

Introduction

The method used today for the preparation of phenolsulfonephthalein remains in principle the same as that originally employed by Sohon. An observation made by one of us in this Laboratory that saccharin, heated with phenol and sulfuric acid, gave fair quantities of phenol red led to the present study. This reaction probably proceeds according to the following equations



Experimental

Preliminary work indicated the importance of a study of the effect of temperature, which seemed quite a critical factor. High temperatures up to 180° yielded a dye in good quantity, but it was very dark in color, quite readily assumed a tarry condition and was precipitated with difficulty from solution. Lower temperatures gave far superior products but lower percentage yields.

The effect of temperature was studied by heating ten grams of saccharin with phenol and sulfuric acid for seventeen hours at temperatures ranging from 116 to 135°. The results of five such runs are tabulated in Table I.

TABLE I

EXPERIMENTAL RESULTS

Temp., °C.	Molar ratios, phenol	Saccharin to sulfuric acid	Yield, % of theoretical	Quality of product
116	1:4.9	1:3.9	1.0	Excellent
120	1:4.9	1:3.9	1.0	Excellent
125	1:4.9	1:3.9	1.5	Excellent
130	1:4.9	1:3.9	4.6	Fair
135	1:4.9	1:3.9	10.9	Poor

It appears that increase in temperature increases the yield progressively but with accompanying deterioration of the product. The maximum temperature yielding a good product was found to be 125°.

The dye obtained by heating from 130° upwards to 150° was increasingly worse. When isolated it was very dark and inclined to be tarry, rather than the bright red, dry product sought. Examination of some of those samples obtained at temperatures above 135° gave us reason to believe that considerable sulfonation had occurred. They exhibited the typical phenol red color changes but were not tested for their PH range.

The next factor studied was the effect of time upon yield. The optimum temperature which gave a dye of good quality, as previously determined, was 125°, for which reason this was chosen as the constant temperature for the following four runs.

The quantities of the reagents were the same as those used in the study of temperature effect, that is, 10 g. of saccharin in the molar ratio of 1:4.9 of phenol, and 1:3.9 of sulfuric acid. The results for four different intervals of time expressed in per cent. of theoretical yield are tabulated below.

TABLE II

VARIATION OF YIELD WITH TIME

Time in hours	17	35	48	86
Theoretical yield, %	1.5	12.9	24.8	27.0

These results indicate that the best yields may be expected when the experiment reaction mixture is heated for at least forty-eight hours.

Variations of the proportions of saccharin to phenol was next tried. In the five tests, the mixtures were heated for eighty-six hours at a constant temperature of 125". The molar ratio of saccharin to sulfuric acid was 1:3.9 in each case. The five runs are tabulated below.

TABLE III

VARIATION OF YIELD WITH VARIOUS PROPORTIONS OF SACCHARIN

Molar ratio of saccharin to phenol	1:2	1:4	1:4.9	1:5.3	1:9.7
Theoretical yield, %	1.7	10.0	27.0	22.5	20.0

These yields point to a desirable molar ratio of about 1:5.

The next study considered the proper proportions of saccharin to sulfuric acid. The molar ratio of saccharin to phenol previously employed, 1:4.9, was used and the heating was conducted for eighty-six hours at 125°. The variation in the molar ratio of saccharin to acid is tabulated below.

TABLE IV

RESULTS WITH VARIOUS PROPORTIONS OF SULFURIC ACID

Molar ratio of saccharin to sulfuric acid	1:2.5	1:3 9	1:6.4
Theoretical yield, %	10.4	24.8	2.0

The molar ratio of 1:3.9 seemed to be the most desirable.

A study of Tables I, II, III and IV led to the belief that the following are the optimum conditions: time, 48 hours; temperature, 120°; molar ratios, saccharin 1, phenol 5, sulfuric acid, 4.

Certain metal sulfates were next tested as to their catalytic power of accelerating the reaction. To each of a number of test-tubes was added 1 *g.* of the metal salt along with the proportions of reagents just given. These tubes were again heated at 120° for forty-eight hours. A check tube containing no added metal sulfate was included for comparison of color development. This was the means of judging the efficiency as a catalyst of the added salt. The findings are tabulated below.

TABLE V

RESULTS WITH METALLIC SULFATES

Metal sulfate, 1 g.	Intensity of color development as compared to check tube containing no metal salt	Metal sulfate, 1 g.	Intensity of color development as compared to check tube containing no metal salt
Copper	Slight decrease	Cerium	Decrease
Zinc	Slight decrease	Cobalt	Decrease
Mercuric	No difference	Ferric	Marked decrease
Aluminum	Decrease	Manganese	Marked decrease
Chromium	Decrease	Nickel	Marked decrease
Bismuth	Decrease	Silver	No color at all
Thorium	Decrease		

Observations on color intensity were first made on the melt in tubes immediately after heating. These melts were then dissolved, neutralized and diluted, and comparisons of color made with the check tube. In no case was any catalytic action observed.

Experiments were conducted on the effect of various other substances ordinarily used as condensing agents, as possible substitutes for the sulfuric acid. There is always a danger of sulfonation when sulfuric acid is used, which makes necessary a lower temperature with consequent lowering of yield.

The first experiment consisted of heating the optimum proportions of saccharin and phenol with the condensing agents, with the inclusion of one blank. The substances tested were: anhydrous aluminum chloride, anhydrous zinc chloride, anhydrous ferric chloride and phosphoric acid (85%). In all cases the development of color was slight after the tubes were heated for seventeen hours at 120° except with the check tube containing sulfuric acid, in which the deep red color developed as usual. The superiority of sulfuric acid as condensing agent was obvious.

The second experiment consisted of heating saccharin, phenol and sulfuric acid together in tubes with the addition of the four condensing agents used in the last test. Comparison with the fifth check tube again showed no improvement due to the extra condensing agent.

A method based upon the foregoing studies which gives the best yield of the highest quality product is given in detail below.

Procedure

A small balloon flask is charged with 10 g. of saccharin, 25 g. of phenol and 21 g. (12 cc.) of ordinary concentrated sulfuric acid. The contents are warmed until all of the solid is dissolved, then heated in an electric oven at 120° for forty-eight hours. An extra day of heating will increase the yield somewhat. The deep red, tarry looking reaction product is treated while still hot with warm water until solution is nearly complete. Sodium carbonate (a 30% solution is convenient) is added to neutrality, the change of color is the best guide, and the contents are subjected to steam distillation until all traces of phenol are removed. The solution is made faintly acid with hydrochloric acid and allowed to stand. The precipitated dye is filtered off with suction, washed with a minimum of ice water and dried. The dye should be of a bright reb color and but slightly soluble in water.

A few comments on the method outlined adove may be added. Sodium carbonate solution is used in the neutralization of the sulfuric acid present because it will not bind any considerable quantity of phenol, the latter seeming to prevent the dye from precipitating finally as a fine red powder.

Repeated solution of crude products in sodium carbonate and reprecipitation by addition of hydrochloric acid almost to the neutral point rendered the final product a much brighter red and much easier to precipitate.

The vreparation of **tetrabromophenolsulfonephthalein** offered no difficulty. The method used is given here in brief.

Five grams of phenol red was dissolved in 100 cc. of absolute alcohol and the cooled solution was treated with the calculated quantity of bromine. It was found desirable to use a calibrated 10cc. buret to deliver the bromine, basing the weight upon the accurately determined density at room temperature. Mechanical stirring during the slow addition of the bromine and for a short time after the addition was complete was sufficient to complete reaction.

The brom phenol blue was recovered by diluting, dissolving the dye in sodium carbonate solution and finally precipitating it with hydrochloric acid.

Conclusions

A simple method for making phenol red has been given. The product is obtained from cheap materials and after the simplest of manipulative operations.

The preparation of brom phenol blue from phenol red is described and offers no new procedure.

The products obtained checked perfectly with the PH ranges given in the literature for those substances. They were both further tested by the absorption spectrometric method and were pronounced very pure.

The application of the above method of preparation was found practicable in the condensation of many other phenols yielding useful sulfonethaleins and work is now in progress on a simple method of preparation for each of those used in colorimetric hydrogen ion estimation.

BATON ROUGE, LOUISIANA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

THE ACTION OF THIOCYANOGEN UPON O,N-DISUBSTITUTED HYDROXYLAMINES AND PRIMARY AMINES[1]

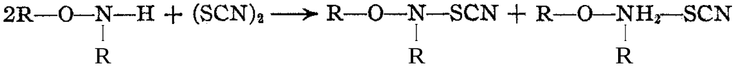
BY LAUDER W. JONES AND ELMER E. FLECK

RECEIVED MAY 12, 1928 PUBLISHED JULY 6, 1928

The action of thiocyanogen upon amines has been investigated by Soderback[2] and by Lecher, Wittwer and Speer.[3] Soderback studied the reaction with phenyl-, diphenyl- and dimethylphenylamine and, in each case, found that the thiocyanogen group entered the benzene ring para to the amino group. Lecher, Wittwer and Speer showed that in the case of the products formed with ammonia and with diethylamine, the thiocyanogen group attaches itself directly to the nitrogen atom. The purpose of this work was to extend the study of these reactions of thiocyanogen by investigation of the behavior of thiocyanogen with O,N-disubstituted hydroxylamines and with certain primary amines.

O,N-Disubstituted N-Thiocyanohydroxylamines

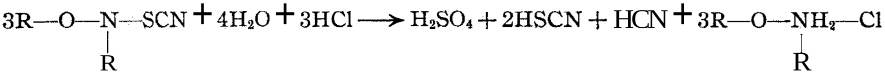
The action of thiocyanogen on O,N-disubstituted hydroxylamines corresponded to the action of thiocyanogen upon ammonia and diethylamine. Hydroxylamines with ethyl and benzyl groups were used for this purpose. They reacted with thiocyanogen as follows



$$2R{-}O{-}\underset{\substack{|\\ R}}{N}{-}H + (SCN)_2 \longrightarrow R{-}O{-}\underset{\substack{|\\ R}}{N}{-}SCN + R{-}O{-}\underset{\substack{|\\ R}}{NH_2}{-}SCN$$

The thiocyanohydroxylamines formed in this manner are not very stable compounds. O,N-diethyl-N-thiocyanohydroxylamine distilled from 45 to 46" at 2 mm. but decomposed rapidly when exposed to the air at room temperature. At 0° this substance showed no signs of decomposition after several hours. The corresponding O,N-dibenzyl compound was a white crystalline solid; m. p. 50–52°. At room temperature it could be kept for about forty-eight hours without signs of decomposition.

Hydrolysis of O,N-Disubstituted N-Thiocyanohydroxylamines.—The structure of these compounds was established by acid and by alkaline hydrolysis. Acid hydrolysis gave results which corresponded closely in form with those observed by Lecher, Wittwer and Speer in their investigations of similar amine derivatives.



$$3R{-}O{-}\underset{\substack{|\\ R}}{N}{-}SCN + 4H_2O + 3HCl \longrightarrow H_2SO_4 + 2HSCN + HCN + 3R{-}O{-}\underset{\substack{|\\ R}}{NH_2}{-}Cl$$

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[1] This paper is based upon a thesis submitted by Elmer E. Fleck to the Faculty of the Graduate School of Princeton University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Soderback, *Ann.*, 419, 270 (1919).

[3] Lecher, Wittwer and Speer, *Ber.*, **56B,** 1104 (1923).

Bjerrum and Kirschner[4] have shown that the first step in the hydrolysis of thiocyanogen proceeded as follows

$$(SCN)_2 + HOH \longrightarrow HSCN + HOSCN$$

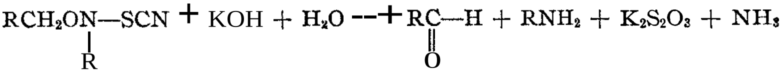
The hypothiocyanic acid then underwent auto-oxidation according to the following reaction

$$3HOSCN + HOH \longrightarrow 2HSCN + HCN + H_2SO_4$$

Since thiocyanic, hydrocyanic and sulfuric acids were also obtained by the hydrolysis of O,N-disubstituted N-thiocyanohydroxylamines, it seemed certain that the first step in the latter hydrolysis must yield O,N-disubstituted hydroxylamine and hypothiocyanic acid. The production of hypothiocyanic acid indicates that the thiocyan group in O,N-disubstituted N-thiocyanohydroxylamine may be regarded as "positive," since it reacts in a manner similar to the "positive" halogen of the halogen amines[5]

$$R_2NCl + HOH \longrightarrow R_2NH + HOCl$$

On the other hand, alkaline hydrolysis of O,N-disubstituted N-thiocyanohydroxylamines gave products quite unlike those obtained in the alkaline hydrolysis of diethylthiocyanamine. Thus, the alkaline hydrolysis of the hydroxylamine derivatives proceeds according to the following reaction



$$RCH_2O\underset{\displaystyle R}{\underset{|}{N}}{-}SCN + KOH + H_2O \longrightarrow R\underset{\displaystyle O}{\underset{\|}{C}}{-}H + RNH_2 + K_2S_2O_3 + NH_3$$

while the alkaline hydrolysis of diethylthiocyanamine gave the following results[3]

$$(C_2H_5)_2N{-}SCN + KOH + H_2O \longrightarrow (C_2H_5)_2NH + KOCN + S$$

The presence of ammonia among the products of hydrolysis of hydroxylamine derivative may be explained by hydrolysis of potassium cyanate. The formation of potassium thiosulfate instead of sulfur may be explained since it has been shown by Lecher and co-workers that sulfur and potassium hydroxide react even in the cold to give thiosulfate and polysulfide. Taking into account these variations in the two reactions, it can be shown that the hydrolysis of O,N-disubstituted N-thiocyanohydroxylamines not only agrees with the theory of Lecher, Wittwer and Speer, but serves to support the mechanism of the hydrolysis advanced by them for thiocyanamine. They postulate, first, the formation of N,N-diethylthiohydroxylamine and then a chain splitting to give diethylamine and sulfur. If a similar reaction occurs in the case of O,N-disubstituted N-thiocyanohydroxylamine, the O,N-disubstituted thiohydroxylamine formed during the first step

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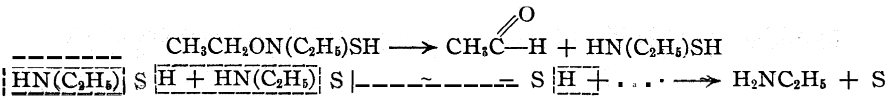
[4] Bjerrum and Kirschner, "Die Rhodanide des Goldes und das freie Rhodan," Kopenhagen, 1918.

[5] Seliwanow, *Ber.*, **25**, 2621 (1892), Berg, *Ann. chim.*, [7] **3**, 341 (1894); W. A. Noyes, THIS JOURNAL, 23, 460 (1901); Stieglitz, *ibid.*, **23**, 797 (1901); Jones, *ibid.*, **36**, 1268 (1914).

of the hydrolysis would certainly be unstable by virtue of the linking of the ethoxy group and the group SH to the same nitrogen atom. Since the ethoxy group is already in the state of oxidation comparable to an aldehyde,[6] it separates as aldehyde, leaving N-ethylthiohydroxylamine, and this, in turn, decomposes to give sulfur and ethylamine in accordance with the explanation of Lecher, Wittwer and Speer.

$$CH_3CH_2ON(C_2H_5)SCN + KOH \longrightarrow CH_3CH_2ON(C_2H_5)SH + KOCN$$



$$CH_3CH_2ON(C_2H_5)SH \longrightarrow CH_3C(=O)-H + HN(C_2H_5)SH$$

$$\boxed{HN(C_2H_5)}S\ \boxed{H + HN(C_2H_5)}S \cdots S\boxed{H} + \cdots \longrightarrow H_2NC_2H_5 + S$$

In order to show that the formation of aldehyde could not be accounted for by the action of alkali upon the disubstituted hydroxylamine under the conditions of the experiment, sealed tubes containing the disubstituted hydroxylamine and 2% potassium hydroxide were heated at temperatures varying from 100 to 180° for periods of eight hours. In the case of O,N-diethylhydroxylamine no acetaldehyde or ethylamine could be detected below 150°. At 180° considerable quantities of acetaldehyde and ethylamine were formed. O,N-dibenzylhydroxylamine was not affected at 100°, but at 150° almost complete decomposition into benzaldehyde and benzylamine occurred.

Thiocyanamines

The only mention of the action of thiocyanogen upon primary amines,[7] other than the case of aniline already cited, was made by Söderbäck.[2] He stated that such reactions lead only to ill-defined products. In the present work, benzylamine and triphenylmethylamine were found to react with thiocyanogen to produce the corresponding thiocyanamine. The reaction proceeded as follows

$$2RNH_2 + (SCN)_2 \longrightarrow RNHSCN + RNH_3SCN$$

Pure triphenylmethylthiocyanamine was isolated by the action of triphenylmethylamine with thiocyanogen. Triphenylmethylthiocyanamine is a white, crystalline solid; m. p. 142°. It may be allowed to stand at room temperature for a week without serious decomposition. Benzylthiocyanamine, formed by the action of benzylamine with thiocyanogen, could not be isolated in the pure condition. It could neither be crystallized nor distilled. Analysis for nitrogen and sulfur gave values too low by 1–2% for benzylthiocyanamine, but its reactions with acids confirmed its structure.

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[6] Nef, *Ann.*, 280,328 (1894); Jones, THIS JOURNAL, *36,* 1285 (1914).

[7] Attention was directed to this type of reaction by what seemed to be a decomposition of O,N-dibenzyl-N-thiocyanohydroxylamine into benzaldehyde and benzylthiocyanamine. When O,N-dibenzyl-N-thiocyanohydroxylamine was first made considerable difficulty was experienced in crystallizing it. The oil possessed an odor not unlike that of benzaldehyde. Accordingly an attempt was made to prepare benzylthiocyanamine from benzylamine and thiocyanogen in order that the products of this suspected decomposition might be studied.

The reaction of thiocyanogen with primary amines to form thiocyanamines is of particular interest because it corresponds to the production of a monohalogen amine by the action of the halogen upon the amine in an inert solvent.

Action of Acids upon Thiocyanamines.—If the thiocyanamines are related to the monohalogen amines in this fashion, they should react with acids according to the following equation

$$RNHSCN + 2HX \longrightarrow RNH_3X + XSCN$$

The corresponding reaction of the monohalogen amines may be represented[8]

$$RNHX + 2HX' \longrightarrow RNH_3X' + X—X'$$

Thiocyanamines were found to undergo this reaction. When triphenylmethylthiocyanamine was dissolved in dry ether and treated with hydrochloric acid gas, triphenylmethylammonium chloride was precipitated. The ether filtrate, separated from the salt, was evaporated in a current of air and a heavy oil, which possessed a pungent odor, remained. This oil may be the monomolecular form of chlorothiocyanogen which Kaufmann and Lecher[10] have been seeking, as it evaporated slowly and gave an intense red color when treated with a solution of ferric chloride.

Picric acid also reacts with triphenylmethylthiocyanamine to give triphenylmethylammonium picrate, but in this case the second product of the reaction is a yellow, amorphous substance which did not melt but gradually decomposed when heated.

Benzylthiocyanamine reacted similarly with hydrochloric and picric acids. The hydrochloride and the picrate were formed, respectively. In both these reactions the yellow, amorphous substance referred to above was obtained.

Rearrangement of Triphenylmethylthiocyanamine.—Further evidence that the thiocyanamines are related to the monohalogen amines may be had from the fact that triphenylmethylthiocyanamine undergoes the Stieglitz rearrangement.[11] Stieglitz and co-workers have succeeded in causing triphenylmethylbromo-amine, triphenylmethylhydroxylamine, triphenylmethylazide and *bis*-triphenylmethylhydrazine to rearrange; they obtained phenylimidobenzophenone from the rearrangement products. According to the theory advanced by Stieglitz, rearrangement in compounds of this type will be brought about by a reagent which removes a molecule of hydrobromic acid, water, nitrogen or ammonia, as the case may be, and gives rise to an intermediate, monovalent nitrogen compound. It is assumed that two electrons then shift from the methyl carbon atom

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[8] Berg, *Ann. chim.*, [7] 3, 338 (1894); Vosburgh, This Journal, 38, 2086 (1916).

[9] Kaufmann and Liepe, *Ber.*, 57B, 923 (1924); Kaufmann, *Ber.*, 60B, 58 (1927).

[10] Lecher and Joseph, *Ber.*, 59B, 2603 (1926).

[11] Stieglitz and Leech, This Journal, 36, 272 (1914); Vosburgh, *ibid.*, 38, 2081 (1916); Senior, *ibid.*, 38, 2718 (1916); Stieglitz and Senior, *ibid.*, 38, 2727 (1916); Stieglitz and Brown, *ibid.*, 44, 1270 (1922); Stieglitz, *ibid.*, 44, 1293 (1922).

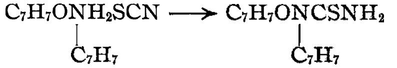
of the triphenylmethyl radical to the nitrogen atom, followed by a migration of a phenyl group from the carbon atom to the nitrogen atom; the final product of the rearrangement is phenylimidobenzophenone. This reaction may be represented in the case of triphenylmethylthiocyanamine as follows

$$(C_6H_5)_3CNHSCN \xrightarrow{—HSCN} (C_6H_5)_3C—N \longrightarrow (C_6H_5)_2C{=}N(C_6H_5)$$

Triphenylmethylthiocyanamine was found to undergo this rearrangement when it was mixed with calcium oxide and heated at a temperature between 440 and 450° for a very short time. The phenylimidobenzophenone produced by this rearrangement was identified by the products of its acid hydrolysis, namely, aniline and benzophenone.

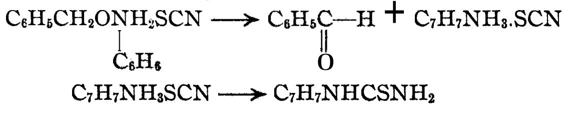
Attempts to use other reagents to produce this rearrangement did not succeed. Soda lime converted triphenylmethylthiocyanamine almost quantitatively into triphenylmethylamine. Mercuric oxide, lead oxide and sodium methylate were also tried.

Formation of Ureas from Substituted Ammonium **Thiocyanates.**—The O,N-dibenzylhydroxylammonium thiocyanate formed in the preparation of O,N-dibenzyl-N-thiocyanohydroxylamine was found to undergo two interesting transformations. When this salt was suspended in water and the water removed by evaporation, the usual transformaton occurred and α,α'-benzylbenzyloxythiourea was the product.



$$C_7H_7O\underset{\displaystyle C_7H_7}{\underset{|}{N}}H_2SCN \longrightarrow C_7H_7O\underset{\displaystyle C_7H_7}{\underset{|}{N}}CSNH_2$$

This compound was found to be the same as that prepared by evaporation of a suspension of O,N-dibenzylhydroxylamine hydrochloride and potassium thiocyanate; but when O,N-dibenzylhydroxylammonium thiocyanate was heated for fifteen minutes at 150° previous to its treatment with water, no α,α'-benzylbenzyloxythiourea could be obtained; the products isolated were benzylthiourea and benzaldehyde. The following reaction represents these changes



$$C_6H_5CH_2O\underset{\displaystyle C_6H_6}{\underset{|}{N}}H_2SCN \longrightarrow C_6H_5\underset{\displaystyle O}{\underset{\|}{C}}—H + C_7H_7NH_3.SCN$$

$$C_7H_7NH_3SCN \longrightarrow C_7H_7NHCSNH_2$$

Efforts to convert triphenylmethylammonium thiocyanate into the corresponding thiourea by this method failed. Heat brought about decomposition and evaporation with water caused hydrolysis of the salt. Triphenylmethylcarbinol was isolated from the products of hydrolysis.

Experimental Part

O,N-Diethyl-N-thiocyanohydroxylamine, $(C_2H_5O)(C_2H_5)NSCN$

Preparation of **O,N-Diethyl-N-thiocyanohydroxylamine.**—A suspension of 11.3 g. of lead thiocyanate in 50 cc. of absolute ether was treated with 4.8 g. of bromine. The mixture was shaken until the color of bromine disappeared and then filtered into an ice-cooled ether (50 cc.) solution of 9.2 g. of O,N-diethylhydroxylamine, prepared by the method of Hecker[12] as modified by Major and Fleck.[13] Reaction took place at once and 4.0 g. of O,N-diethylhydroxylammonium thiocyanate separated as an oil. The ether was removed rapidly by means of diminished pressure. During this operation the temperature of the flask was not allowed to rise above 0°. The oil which remained distilled at 45–46° under 2 mm. A liquid air trap interposed between the receiver and the oil pump greatly facilitated the maintenance of this pressure; yield, 40%.

Anal. Subs., 0.0988: $BaSO_4$, 0.1559. Subs., 0.0536: N_2, 9.0 cc. (20°, 759.6 mm.). Calcd. for $C_5H_{10}ON_2S$: S, 21.92; N, 19.15. Found: S, 21.87; N, 19.5.

Acid Hydrolysis of O,N-Diethyl-N-thiocyanohydroxylamine.—One g. of O,N-diethyl-N-thiocyanohydroxylamine was added to 100 cc. of ice-cooled 2% hydrochloric acid and the mixture kept in the ice box until the oil dissolved. The solution was then distilled and hydrocyanic acid and thiocyanic acid were found in the distillate. A test for sulfate was obtained from the residue of the distillation. The remainder of this residue was made alkaline and distilled. The distillate was extracted with benzene and treated with phenylisocyanate. The crystals which separated melted at 63°. When mixed with α-phenyl β,β'-ethylethoxyurea, $(C_2H_5O)(C_2H_5)N{\cdot}CONH(C_6H_5)$, prepared by the method of Jones and Major,[14] the melting point was unchanged.

Alkaline Hydrolysis of O,N-Diethyl-N-thiocyanohydroxylamine.—One g. of O,N-diethyl-N-thiocyanohydroxylamine was added to 100 cc. of an ice-cooled 2% solution of potassium hydroxide and the mixture allowed to stand in an ice box for two days. The solution was then distilled. The distillate contained acetaldehyde and ethylamine.

The residual liquid of this distillation contained no free sulfur but gave the ordinary tests for thiosulfate. To precipitate lead thiosulfate, calcium nitrate was added to the remainder of the residue, the solution filtered, the color of phenolphthalein in the filtrate discharged by acetic acid and the salt obtained by the addition of lead nitrate.

Anal. Subs., 0.1272: $PbSO_4$, 0.1220. Subs., 0.0606: 19.0 cc. of 0.01 N I_2 solution. Calcd. for PbS_2O_3: Pb, 64.99; S, 20.06. Found: Pb, 65.5; S, 20.0.

The distillate, which contained acetaldehyde and ethylamine, was acidified with hydrochloric acid and the acetaldehyde removed by distillation. This distillate was treated with an acetic acid solution of *p*-nitrophenylhydrazine. The yellow plates which separated melted at 127.5°. Mixing with acetaldehyde-*p*-nitrophenylhydrazone[15] did not alter this melting point. This established the formation of acetaldehyde.

The residual liquid, which contained the hydrochloride of ethylamine, was made alkaline and distilled. Addition of ethyl oxalate to a portion of the distillate yielded colorless needles which melted at 178°. The melting point was not changed when mixed with diethyloxamide.[16] This established the presence of ethylamine. The remainder of this distillate was acidified with hydrochloric acid and evaporated to dryness. Ammonium chloride was found to be present.[17]

O,N-Dibenzyl-N-thiocyanohydroxylamine, $(C_7H_7O)(C_7H_7)NSCN$

Preparation of O,N-Dibenzylcarbethoxyhydroxamic Ester.—To 59 g. of carbethoxy-

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[12] Hecker, *Am. Chem. J.*, 50, 451 (1913).

[13] Major and Fleck, THIS JOURNAL, 50, 1479 (1928).

[14] Jones and Major, *ibid.*, 49, 1538 (1927).

[15] Hyde, *Ber.*, 32, 1813 (1899).

[16] Schiff, *Ber.*, 17, 1034 (1884).

[17] Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, New York, Vol. II, p. 39.

hydroxamic acid, prepared by the method of **Jones**,[18] 151 g. of benzyl chloride and 66 g. of potassium hydroxide, dissolved in alcohol, were added. The solution grew warm at once and potassium chloride separated. After twenty-four hours, the mixture was refluxed for one hour, then cooled and filtered. The alcohol was distilled and the residue diluted with water and extracted with ether. The ether solution was washed with dilute sodium hydroxide to remove any O-benzylcarbethoxyhydroxamic ester. Five g. of this substance, b. p. 171–172° under 7 mm., was recovered. The neutral portion remaining with the ether was dried with sodium sulfate. Distillation of the ether left a colorless oil which was fractionated. The fraction boiling between 200 and 203" under 7 mm. was collected; yield, 90 g.

Anal. Subs., 0.2652: N_2, 11.3 cc. (21°, 761.2 mm.). Calcd. for $C_{17}H_{19}O_3N$: N, 4.91. Found: 4.95.

Preparation of **O,N-Dibenzylhydroxylamine.**—A solution of 63 g. of O,N-dibenzylcarbethoxyhydroxamic ester was added to 25 g. of sodium hydroxide dissolved in 200 cc. of 50% alcohol and the mixture refluxed for one hour. After distillation of the alcohol, the O,N-dibenzylhydroxylamine was extracted with ether and the extract dried with sodium sulfate. The colorless oil which remained after removal of the ether distilled at 145–146' under 3 mm.; yield, 41 g.

Preparation of **O,N-Dibenzyl-N-thiocyanohydroxylamine.**—A suspension of 8.0 g. of lead thiocyanate in 50 cc. of absolute ether was treated with 3.8 g. of bromine. The mixture was shaken until the color of bromine disappeared and then filtered into an ice-cooled solution of 10 g. of O,N-dibenzylhydroxylamine in ether. Reaction took place at once and 5.9 g. of O,N-dibenzylhydroxylammonium thiocyanate crystallized. This salt was collected on a filter and recrystallized by dissolving it in a large amount of absolute ether and evaporating the ether under diminished pressure; m. p. 91°.

Anal. Subs., 0.1190: $BaSO_4$, 0.0988. Subs., 0.1450: N_2, 13.4 cc. (25°, 753.0). Calcd. for $C_{15}H_{16}ON_2S$: S, 11.75; N, 10.33. Found: S, 11.43; N, 10.48.

The ether filtrate, separated from the salt, was evaporated under diminished pressure to 10 cc. The second crop of O,N-dibenzylhydroxylammonium thiocyanate which separated during this process was removed by filtration and the filtrate was kept under a high vacuum at room temperature for three hours. The product remained as an oil but it finally crystallized when cooled in ice. Scratching the side of the containing vessel greatly facilitated this crystallization. The crystals were triturated with 5 cc. of absolute alcohol, filtered and washed with a small amount of cold dry ether; m. p. 50–52°; yield, 47%.

Anal. Subs., 0.2098: $BaSO_4$, 0.1746. Subs., 0.1422: N_2, 12.6 cc. (18°, 752.7). Calcd. for $C_{15}H_{14}ON_2S$: S, 11.85; N, 10.37. Found: S, 11.4; N, 10.3.

Acid Hydrolysis of **O,N-Dibenzyl-N-thiocyanohydroxylamine.**—One g. of O,N-dibenzyl-N-thiocyanohydroxylamine was dissolved in 100 cc. of a solution of 2% hydrochloric acid in 75% alcohol. The mixture grew warm and was distilled at once. Hydrocyanic and thiocyanic acids were found in the distillate. When the residue from this distillation was cooled, O,N-dibenzylhydroxylamine hydrochloride precipitated. Evaporation of the filtrate, separated from the salt, yielded more of this salt. A total of 0.95 g. of O,N-dibenzylhydroxylamine hydrochloride was obtained from this hydrolysis. The base was freed with sodium hydroxide, extracted with benzene and treated with phenylisocyanate. The benzene was removed by a current of air and the product purified by dissolving in alcohol and precipitating with water; m. p. 107'. The melting point remained unaltered when mixed with α-phenyl-β,β'-benzylbenzyloxyurea.[19]

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[18] Jones, *Am.* Chem. J., **20**, 39 (1898).

[19] Beckmann, J. prakt. *Chem.*, [2] 56, 77 (1897).

Sulfate was found in the filtrate from which O,N-dibenzylhydroxylamine hydrochloride had been removed.

Alkaline Hydrolysis of **O,N-Dibenzyl-N-thiocyanohydroxylamine.**—One g. of O,N-dibenzyl-N-thiocyanhydroxylamine was refluxed with 100 cc. of a 2% solution of potassium hydroxide for half an hour. A reddish solid formed. The products of hydrolysis were separated by the method used in the case of the corresponding ethyl compound. Benzaldehyde was identified by conversion into benzalphenylhydrazone and determination of the melting point when mixed with benzalphenylhydrazone prepared by the method of Behrend and Leuchs.[20]

Benzylamine was identified by extraction of the free base with benzene and conversion into α,β-phenylbenzylurea; m. p. 165°. When mixed with a,@-phenylbenzylurea prepared by the method of Ley and Kraft,[21] the melting point was not lowered. Thiosulfate was shown to be present by the usual qualitative tests.

Alkaline Decomposition of O,N-Disubstituted Hydroxylamines

Decomposition of **O,N-diethylhydroxylamine.**—One g. of O,N-diethylhydroxylamine was heated in a sealed tube with 100 cc. of a 2% solution of potassium hydroxide for eight hours. The contents of the tube were then distilled and the distillate was tested for aldehyde with Schiff's reagent. A negative test was obtained from a tube heated at 100°. At 150" only a slight amount of aldehyde was found, while at 180° almost complete decomposition took place. The contents of the tube heated at 180° was acidified with hydrochloric acid and the acetaldehyde removed by distillation. Yellow plates m. p. 127.5°, separated when the distillate was treated with *p*-nitrophenylhydrazine. When mixed with acetaldehyde-p-nitrophenylhydrazone it melted at 127.5°.

The residual liquid from this distillation was made alkaline and the ethylamine removed by distillation. Treatment of this distillate with ethyl oxalate gave white needles; m. p. 178". Mixing with diethyloxamide produced no change in the melting point.

Decomposition of **O,N-Dibenzylhydroxylamine.**—One g. of O,N-dibenzylhydroxylamine was sealed in a tube with 100 cc. of a 2% solution of potassium hydroxide. This solution heated for eight hours at 100° showed no change. When it was heated at 150° for a similar time, almost complete decomposition ensued. The products of this decomposition were separated as in the case of the diethyl compound. Benzaldehyde was identified by conversion into benzalphenylhydrazone; m. p. 155°. When mixed with benzalphenylhydrazone[20] it melted at 155–156°.

The residual liquid, which contained benzylamine hydrochloride, was made alkaline, extracted with benzene and the benzene solution treated with phenylisocyanate. The white crystals which separated melted at 169°. A mixture with α,β-phenylbenzylurea[21] showed no lowering of melting point.

Triphenylmethylthiocyanamine, $(C_6H_5)_3CNHSCN$

Preparation of **Triphenylmethylthiocyanamine.**—A suspension of 6.6 g. of lead thiocyanate in 50 cc. of absolute ether was treated with 3.2 g. of bromine. The mixture was shaken until the color of bromine disappeared and then filtered into a solution of 10.4 g. of triphenylmethylamine in 150 cc. of dry ether. The amine was prepared by the method of Elbs,[22] as modified by Vosburgh.[23] Immediate reaction, accompanied by the separation of 5.6 g. of triphenylmethylammonium thiocyanate, took place. This salt was collected on a filter and recrystallized from benzene by addition of ligroin; m. p. 173°.

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[20] Behrend and Leuchs, Ann., 257, 227 (1890).

[21] Ley and Kraft, Ber., 40, 703 (1907).

[22] Elbs, Ber., 17, 702 (1884).

[23] Vosburgh, THIS JOURNAL, 38, 2085 (1916).

Anal. Subs., 0.1630: $BaSO_4$, 0.1174. Subs., 0.1596: N_2, 12.2 cc. (23°, 750.5). Calcd. for $C_{20}H_{18}N_2S$: S, 10.06; N, 8.80. Found: S, 9.89; N, 8.76.

The ether filtrate, separated from the salt, was evaporated to dryness. The sticky solid which resulted was triturated with 10 cc. of carbon tetrachloride and the solution filtered. Triphenylmethylthiocyanamine was recrystallized from absolute ether by addition of ligroin (b. p. 30–60°); m. p. 142°; yield, 55%.

Anal. Subs., 0.1378: $BaSO_4$, 0.1038. Subs., 0.1446: N_2, 11.7 cc. (26°, 743.9). Calcd. for $C_{20}H_{16}N_2S$: S, 10.13; N, 8.86. Found: S, 10.36; N, 9.05.

Rearrangement of Triphenylmethylthiocyanamine.—A mixture of 0.5 g. of triphenylmethylthiocyanamine and 1.0 g. of freshly ignited calcium oxide was heated in a dry 60cc. Pyrex Erlenmeyer flask immersed in a metal-bath at 440–450° for one minute. Considerable decomposition occurred at this temperature and the odor of ammonia was apparent. The product was dissolved in ether, the solution filtered from the lime and the ether filtrate refluxed with an excess of dilute hydrochloric acid for half an hour. The two layers were separated, the water solution was extracted three times with ether and each ether extract washed with dilute hydrochloric acid. The original ether solution was washed twice with dilute hydrochloric acid. The acid portions were united (A) as were also the ether portions (B).

The acid solution (A) was made strongly alkaline and distilled with steam into dilute hydrochloric acid. This solution was evaporated to dryness on a water-bath. The resulting solid, 0.042 g., was treated with a few drops of a strong solution of sodium hydroxide and the aniline extracted with benzene. Addition of a-naphthylisocyanate caused *sym.*-α-naphthylphenylurea to separate m. p. 221–223°. No lowering in melting point was observed when this product was mixed with *sym.*-α-naphthylphenylurea prepared by the method of Dixon.[24]

Most of the ether was distilled from the ether solution (B) and the remainder was distilled with steam. The distillate was extracted with ether and the ether removed *in vacuo.* By this method 0.082 g. of benzophenone, m. p. 25–30°, was obtained. This benzophenone was converted into the corresponding oxime by the method given in Mulliken;[25] m. p. 141–142°. The melting point was not changed when mixed with benzophenone-oxime prepared from pure benzophenone.

Benzylthiocyanamine, $C_6H_5CH_2NHSCN$

Preparation of Benzylthiocyanamine.—A suspension of 6.6 g. of lead thiocyanate in 25 cc. of absolute ether was treated with 3.2 g. of bromine. The mixture was shaken until the color of bromine disappeared and then filtered into a solution of 4.3 g. of benzylamine dissolved in 25 cc. of dry ether. Reaction took place at once and 3.5 g. of benzylammonium thiocyanate separated. This salt was recrystallized from ethyl acetate by addition of ligroin; m. p. 100–101'. No lowering of the melting point of this salt could be detected when it was mixed with benzylammonium thiocyanate prepared by the method of Dixon.[26]

The filtrate, separated from the salt, was evaporated under diminished pressure. When practically all of the ether was removed, the heavy oil was subjected to a high vacuum for five hours. Crystallization could not be brought about and complete decomposition accompanied any attempt to distil this oil. Analysis for nitrogen and sulfur gave results too low by 1–2% for the calculated values. Change of reaction

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[24] Dixon, *Proc. Chem. Soc.*, 16,208 (1900).

[25] Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, New York, Vol. I, p. 150.

[26] Dixon, J. Chem. *Soc.*, 59, 553 (1891).

solvent, washing the reaction products with ice water, etc., did not improve the purity of the benzylthiocyanamine materially.

Action of Acids upon Benzylthiocyanamine.—One g. of benzylthiocyanamine was dissolved in absolute ether and dry hydrochloric acid gas passed into the solution. Benzylammonium chloride separated at once along with a yellow, amorphous substance. The benzylammonium chloride was converted into α,β-phenylbenzylurea and identified by mixed melting point determinations.

One g. of benzylthiocyanamine was dissolved in absolute ether and an absolute ether solution of picric acid added. The reaction proceeded slowly but was complete within one hour. A yellow, amorphous substance also separated from the solution. The benzylammonium picrate was freed from this substance by recrystallization from ethyl acetate by addition of ligroin; m. p. 200–201°. Mixed melting points proved this compound to be identical with benzylamine picrate prepared by addition of an absolute ether solution of picric acid to an absolute ether solution of benzylamine.

α,α'-Benzylbenzyloxyureas, $(C_7H_7O)(C_7H_7)N\cdot CONH_2$

Preparation of α,α'-benzylbenzyloxyurea.—A solution containing 2 g. of O,N-dibenzylhydroxylamine hydrochloride and 0.7 g. of potassium cyanate in 50 cc. of water was evaporated to dryness. The heavy oil which resulted was dissolved in alcohol and precipitated with water. The urea formed as an oil which solidified in long needles after several days. It was recrystallized from ligroin; m. p. 98-99°; yield, 30%.

Anal. Subs., 0.1134: N_2, 10.6 cc. (21°, 741.8). Calcd. for $C_{15}H_{16}O_2N_2$: N, 10.93. Found: 10.6.

Preparation of α,α'-benzylbenzyloxythiourea, $(C_7H_7O)(C_7H_7)N\cdot CS\cdot NH_2$.—To prepare this thiourea, the calculated amount of O,N-dibenzylhydroxylamine hydrochloride and potassium thiocyanate, dissolved in water, was treated as outlined in the previous experiment. The thiourea crystallized in plates; m. p. 94–95"; yield, 24%.

Anal. Subs., 0.1132: N_2, 10.8 cc. (24°, 753.3). Calcd. for $C_{15}H_{16}ON_2S$: N, 10.63. Found: 10.88.

Formation of Ureas from Substituted Ammonium Thiocyanates.—Two g. of O,N-dibenzylhydroxylammonium thiocyanate was suspended in 50 cc. water and the suspension evaporated to dryness. The oil which remained was dissolved in alcohol and precipitated by water. The α,α'-benzylbenzyloxythiourea was recrystallized from ligroin; m. p. 94–95°; yield, 31%. The melting point was not changed when this substance was mixed with α,α'-benzylbenzyloxythiourea prepared from O,N-dibenzylhydroxylamine hydrochloride.

One-half g. of O,N-dibenzylhydroxylammonium thiocyanate was subjected to dry distillation. The pressure was maintained at 20 mm. and the temperature of the metal-bath surrounding the distilling flask was kept between 150 and 160°. The distillate contained benzaldehyde which was identified by conversion into benzalphenylhydrazone and determination of the melting point when mixed with synthetic benzalphenylhydrazone.

The residue from the above distillation was dissolved in alcohol and precipitated carefully with water. The resulting solid was recrystallized from a large amount of boiling water. The benzylthiourea prepared in this manner melted at 147–148°. When mixed with benzylthiourea, prepared by the method of Dixon,[26] no lowering of melting point could be detected.

Summary

1. O,N-diethyl-N-thiocyanohydroxylamine and O,N-dibenzyl-N-thiocyanohydroxylamine have been prepared by the action of thiocyanogen on

the corresponding O,N-disubstituted hydroxylamines. The structure of these compounds has been proven by hydrolysis.

2. O,N-dibenzylhydroxylammonium thiocyanate was found to transform into α,α'-benzylbenzyloxythiourea when a solution of it in water was evaporated. When O,N-dibenzylhydroxylammonium thiocyanate was heated in the absence of water, benzylthiourea and benzaldehyde were the products.

3. Triphenylmethylthiocyanamine and benzylthiocyanamine have been prepared by the action of thiocyanogen on triphenylmethylamine and benzylamine, respectively. These compounds have been shown to resemble monohalogen amines in their chemical behavior.

4. Triphenylmethylthiocyanamine was found to undergo the Stieglitz rearrangement when heated with calcium oxide. Phenylimidobenzophenone was shown to be a product of rearrangement.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE FOOD RESEARCH DIVISION, BUREAU OF CHEMISTRY AND SOILS, UNITED STATES DEPARTMENT OF AGRICULTURE]

THE ACIDS OF MAPLE SUGAR "SAND"

BY E. K. NELSON

RECEIVED MAY 14, 1928 PUBLISHED JULY 6, 1928

Maple sugar "sand" is the deposit of the calcium salts of organic acids, chiefly calcium malate, which forms in the evaporating kettle during the concentration of maple sap. The acids of maple sugar "sand" have been investigated by v. Lippmann,[1] who found, in addition to *l*-malic acid, considerable d-tartaric acid and a small quantity of tricarballylic acid. V. Lippmann gives very little information regarding his method of procedure in separating these acids except that tricarballylic acid was extracted from the acid mixture by means of ether.

Van Zoeren,[2] attempting to confirm v. Lippmann's results, obtained sufficient tartaric acid to identify microscopically as acid potassium salt but was unable to isolate tricarballylic acid.

An investigation of a sample of maple "sand was made in the Food Research Division. The volatile acids were identified as a mixture of formic and acetic acids. In addition to *l*-malic acid, fumaric, succinic and citric acids were separated in small quantities. Traces of d-tartaric acid and tricarballylic acid were identified by crystallographic[3] examination of the proper fractions, though it was impossible to separate these acids in a state of purity sufficient for the determination of melting points.

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[1] E. O. v. Lippmann, *Ber.*, 47, 3094 (1914).

[2] Van Zoeren, *Trans. Roy. Soc. Canada* (3) *13*, 222 (1919).

[3] Crystallographic examinations were made by G. L. Keenan of the Food, Drug and Insecticide Administration.

Experimental

Five kilos of maple sugar "sand" from Vermont were used in this investigation. The material contained a considerable quantity of inert matter (clay) and 51% of mineral constituents. To neutralize the alkalinity of the ash required 150 g. of sulfuric acid per kilo of "sand."

To each kilo of sand, suspended in water, 150 g. of sulfuric acid was added, and the mixture was stirred well and filtered from calcium sulfate and insoluble matter. The filtrate was concentrated in a vacuum pan, the distillate was neutralized with sodium hydroxide and evaporated to dryness and the residue was reserved for the separation of volatile acids.

The concentrated solution left after the distillation of volatile acids was thoroughly extracted with ether to remove ether soluble acids, after which the non-volatile acids not removed by the ether were precipitated with a moderate excess of lead subacetate. The precipitate of lead salts was decomposed with sulfuric acid, and the lead sulfate was removed by filtration.

The excess of sulfuric acid, determined in a small aliquot of the measured filtrate, was removed with its equivalent of barium hydroxide and the filtrate from the barium sulfate was evaporated to dryness and esterified by refluxing for five hours with absolute alcohol containing 2.5% of hydrochloric acid. The alcohol was evaporated and the esterification was repeated. After removal of the alcohol, the ester mixture was dissolved in ether and washed with sodium hydroxide solution until neutral. The crude esters left after evaporating the ether were then submitted to repeated fractional distillation at 10 mm.

Volatile Acids.—The residue of sodium salts of volatile acids from five kilos of "sand" was acidified with phosphoric acid and the volatile acids were distilled from the concentrated solution in a current of steam. The distillate was neutralized with barium hydroxide and evaporated to dryness, yielding 2.7 g. of barium salts. This was dissolved in water and made up to a volume of 250 cc. An aliquot was tested for formic acid. Mercuric chloride was reduced to mercurous chloride and potassium permanganate solution was reduced. Silver nitrate was instantly reduced to metallic silver.

An aliquot of 200 cc. was warmed and treated with potassium permanganate in slight excess, the excess being removed with sodium sulfite. The filtrate from manganese dioxide was concentrated and slightly acidified with nitric acid. When an excess of silver nitrate was added, a small quantity of silver salt was obtained. On further concentration a second small quantity of silver salt was separated. Fraction 1 contained 63.49% of silver, Fraction 2, 63.66% of silver; calculated for silver acetate, silver = 64.45%. When this fraction was boiled with sulfuric acid and alcohol, the characteristic odor of ethyl acetate was noted. The volatile acids consist, therefore, of formic and acetic acids, the former predominating.

Ether Soluble Acids.—The combined ether extracts from five kilos of "sand" were evaporated and the residue was fractionally crystallized from water. A difficultly soluble acid, amounting to 0.4 g., melted at 286° and corresponded in optical properties with fumaric acid.

About 0.3 g. of a rather sparingly soluble acid melted at 185°, a mixture with succinic acid showing no depression in melting point. Optical crystallographic examination confirmed its identity with succinic acid.

The more soluble fractions were carefully examined for tricarballylic acid. A few crystals of that acid were identified by optical methods but attempts to isolate the acid in order to obtain a melting point were unsuccessful. Some malic acid, which had been removed by the ether extraction, was found in the soluble fractions, and a little succinic acid, which had remained in solution, was separated, but nothing else was identified. A separation of the barium salts of the more soluble fractions by means of 67% alcohol, in which barium lactate is soluble, was made. The acid recovered from the soluble barium salt did not respond to the Germuth[4] test for lactic acid.

Non–Volatile Acids.—The crude esters from five kilos of "sand" were fractionated six times at 10 mm. and the following fractions were obtained: 1, 127–132° = 384 g. (α_D = −10.6"); 2, 150–160° = 0.9 g.; 3, 170–180° = 2.0 g.; 4, 180–205° = 0.7 g.; 5, 205–210° = 3.0 g.; 6, residue = 6.0 g.; total = 396.6 g.

The hydrazides were prepared from these fractions by adding 1 cc. of hydrazine hydrate to a mixture of 0.7 g. of the ester and 5 cc. of absolute alcohol.

Fraction 1 gave pure I-malic dihydrazide, melting at 179–180°.

Fraction 2 gave an immediate precipitate of a small quantity of hydrazide melting at 173–175" which was not *l*-malic hydrazide as a mixture with that substance gave a sharply depressed melting point. The quantity was very small and no identification was made. Optically it did not correspond with any of the hydrazides available.

On further standing, the filtrate from this fraction deposited a further quantity of hydrazide which did not have a sharp melting point and which could not be purified.

A portion of this fraction, which may contain ethyl tartrate, was saponified, acetic acid was added in slight excess and then 0.2 g. of ammonium I-tartrate and an excess of calcium acetate were added. A small precipitate came down after some time. This was dissolved in hydrochloric acid and a solution of calcium acetate and sodium acetate was added. The precipitate formed, which was very small, was identified by optical methods as calcium racemate, proving the presence of a trace of d-tartaric acid.

Fraction 3 gave an immediate precipitate of a small quantity of the unknown hydrazide melting at 173–175°. On standing overnight the main portion of the hydrazide separated from the filtrate which had been seeded with citric hydrazide, crystals having the appearance of citric trihydrazide forming in clusters on the sides of the tube. The substance melted at 103–105". A mixture with citric trihydrazide (hydrated form) showed no depression in melting point and optical crystallographic examination confirmed its identity.

Fractions 4 and 5 afforded a hydrazide melting at 176–178° and a mixture with malic hydrazide showed no depression. The finding of malic acid in this fraction is anomalous. These higher boiling fractions undoubtedly consist of ethyl acid malate as a result of the incomplete neutralization of a portion of the crude ester with sodium hydroxide.

On saponifying these fractions malic acid was obtained, its identity being proved by its decomposition on heating into maleic acid melting at 130°, and fumaric acid.

Conclusion

The acids of maple sugar "sand" were separated and identified. In addition to 1-malic acid, formic, acetic, fumaric, succinic and citric acids were found. There was evidence of the presence of traces of d-tartaric

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[4] Germuth, *Ind. Eng. Chem.*, 19,852 (1927).

and tricarballylic acids. A small quantity of an unknown acid represented by a hydrazide melting at 173–175° was found.

Washington, D. C.

[Contribution from the Havemeyer Chemical Laboratory, Columbia University, No. 5721

ALPHA-FURFURYL AMINES

By J. E. Zanetti and C. O. Beckmann

Received May 15, 1928 Published July 6, 1928

The furfuryl amines have been but little investigated. Wallach[1] was the first to prepare a-furfuryl amine by the reduction of a-furoylnitrile with zinc and sulfuric acid. Tafel[2] prepared it also by the reduction of phenylfurfurazide with sodium amalgam in alcohol solution and Goldschmidt[3] by the reduction of furfuraldoxime. Since then but little work has been done upon them[4] until recently Williams6 prepared the hydrochloride of di-a-furfuryl amine by reducing furfuraldoxime with palladinized animal charcoal and hydrogen.

One of the reasons which has held back synthetic work in this field has been the absence of a convenient method of preparing the 2-methyl halogen furans. Since one of us[6] developed recently a convenient method of preparing a-furfuryl bromide in its ether solution, the ordinary methods of preparing these amines have become applicable.

The synthesis of the mono-, di- and tri-α-furfuryl amines was accomplished by a method similar to that employed in preparing the benzyl amines,[7] namely, by adding a solution of α-furfuryl bromide in ether to absolute alcohol saturated with dry ammonia gas (for details see experimental part). On allowing to stand for several days, a mixture of the three amines was obtained which was then fractionated.

The yields were very poor and considerable amounts of tarry material were obtained. We have been able, however, to prepare the three amines in a pure condition and have identified them by preparing some of their derivatives.

The amines when freshly distilled are colorless, oily liquids with an ammoniacal odor but rapidly turn yellow. They do not crystallize even when cooled in liquid air, passing through stages of increasing thickening

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[1] Wallach, *Ber.*, 14, 752, 1058 (1881); *Ann.*, 214, 227 (1882); Ciamician and Dennsted, *Ber.*, 14, 1059, 1475 (1881).

[2] Tafel, *Ber.*, 20, 399 (1887).

[3] Goldschmidt, *Ber.*, 20, 730 (1887).

[4] Marquis, *Compt. rend.*, 136, 1454 (1903).

[5] Williams, *Ber.*, 60B, 2509 (1927).

[6] Zanetti, This Journal, 49, 1066 (1927).

[7] Mason, J. *Chem. Soc.*, 63, 1311 (1893); Limpricht, Ann., 144, 305 (1867); Cannizzaro, Ann. *Suppl.*, 4, 24 (1865).

until they finally solidify to a glassy mass with no trace of crystallization. They show the ordinary properties of amines, giving well defined salts and addition compounds with gold and platinum chlorides.

Williams[6] obtained the hydrochloride of di-a-furfuryl amine in what appears to us to be an impure condition. He gives a melting point of 170–172°, whereas we have prepared a product melting at 186–187°. The salt prepared by him was yellow in color whereas ours is pure white. Our chlorine determinations give us a higher chlorine content and a further determination of nitrogen leaves no doubt that our compound was quite pure. We had, moreover, no difficulty in preparing the gold and platinum chloride salts, whereas he states that his hydrochloride reduced the platinum chloride to platinum.

Since a-furfuryl amine has already received considerable attention, we have confined ourselves to the preparation of derivatives of the di- and tri-α-furfuryl amines and merely report the synthesis of the mono-a-furfuryl amine by the new method.

Experimental

Preparation of the Amines.—An ether solution of α-furfuryl bromide was prepared from 80 g. of a-furfuryl alcohol and 80 g. of phosphorus tribromide by the method of Zanetti. The best results were obtained when this was made in two parts. This ether solution was added in small portions with cooling to 1 liter of absolute alcohol saturated with ammonia at 0° (about 100–110 g. of NH_3). The mixture was allowed to stand in the cold for one week. The alcohol and excess ammonia were evaporated under reduced pressure and the residue, consisting of the amine hydrobromides and ammonium bromide and probably some α-furfuryl ethers, was treated with dilute sodium hydroxide in the cold. The mixture was extracted with ether, dried and distilled. α-Furfuryl amine distilled over at 144–146° at 760 mm. Distillation was continued under reduced pressure. During this distillation no attempt was made to separate the secondary and tertiary amines. The distillate, consisting of the two amines with some furfuryl ethers, was dissolved in anhydrous ethyl ether. Dry hydrogen chloride was passed through this solution to precipitate the amine hydrochlorides. These were filtered off and washed with ether; yield about 15 g.

The amine hydrochlorides were dissolved in water, dilute sodium hydroxide added in the cold, the mixture extracted with ether, dried and distilled. The amines were separated by fractional distillation under vacuum. Di-a-furfurylamine boils at 102–103° at 1 mm., tri-α-furfurylamine at 136–138' at 1 mm. The amines are colorless oils which turn yellow on standing. Analyses are recorded in Table I.

TABLE I

ANALYSES

	Amine Calcd.	Amine Found	Hydrochloride Calcd.	Hydrochloride Found	Chloroplatinate Calcd.	Chloroplatinate Found	Chloro-aurate Calcd.	Chloro-aurate Found
Difurfuryl amine	C, 67.80	67.35	Cl, 16.62	16.49	$C_{20}H_{24}O_4N_2PtCl_6$		$C_{10}H_{12}O_2NAuCl_4$	
$C_{10}H_{11}O_2N$		67.37		16.54	Pt, 25.55	25.45	Au, 38.11	37.99
	H, 6.21	6.38	N, 6.56	6.75				
		6.30	M. p., 186–187°					
Trifurfuryl amine	C, 70.04	69.83	Cl, 12.08	12.01	$C_{30}H_{32}O_6N_2PtCl_6$		$C_{15}H_{16}O_3NAuCl_4$	
$C_{15}H_{15}O_3N$		69.98		12.06	Pt, 21.20	21.18	Au, 33.00	33.24
	H, 5.84	6.04	N, 4.77	4.81				
		5.78	M. p., 156–157°					

Preparation of the hydrochlorides.—The amines were dissolved in anhydrous ethyl ether and dry hydrogen chloride was passed through the solution. White crystals precipitated; these were filtered off and washed with ether. They were recrystallized by dissolving in the least amount of absolute alcohol possible and precipitating with anhydrous ether. They are white crystalline compounds. Analyses are recorded in Table I.

Preparation of the **Chloroplatinates.**—The amines were dissolved in small amounts of concd. hydrochloric acid and the theoretical amount of chloroplatinic acid added. Upon stirring and scratching the glass dish, the chloroplatinates crystallized out. The chloroplatinate of the di-a-furfuryl amine crystallized in red crystals, while that of the tri-a-furfuryl amine formed orange crystals. Analyses are recorded in Table I.

Preparation of the **Chloro-aurate.**—The method is the same as for the chloroplatinates. Both chloro-aurates are yellow, crystalline solids.

Summary

1. The mono-, di- and tri-a-furfuryl amines have been prepared in a pure condition and their properties, as well as those of some of their salts, are reported.

NEW YORK CITY

[CONTRIBUTION NO. 44 FROM THE DEPARTMENT OF CHEMICAL RESEARCH, PARKE, DAVIS AND COMPANY]

NEW DERIVATIVES OF BARBITURIC ACID

BY ARTHUR W. DOX AND EDWARD G. JONES

RECEIVED MAY 16, 1928 PUBLISHED JULY 6, 1928

Although more than sixty 5,5-dialkyl and 5,5-arylalkyl derivatives of barbituric acid, exclusive of homologs with further substitution on the nitrogen or substitution of oxygen or halogen in one or both of the alkyls, have been described, their variations in hypnotic potency and type of action are sufficient to warrant the preparation of additional members of the series as new alkyl halides become available. Among the alcohols which until very recently have not been obtainable for the preparation of halides required for such syntheses are tetrahydrofurancarbinol and n-amyl alcohol. The present paper describes the preparation of certain 5,5-disubstituted barbituric acids containing a tetrahydrofuranmethyl or a n-amyl group.

Tetrahydrofuranmethyl Bromide.—The alcohol used was a pure preparation supplied by the Miner Laboratories of Chicago. Although this alcohol, in contrast to the non-hydrogenated furancarbinol, is quite stable under ordinary conditions of light, air and moisture, it was found to be unstable to mineral acids, in the presence of which it showed a strong tendency to form tarry products. For this reason the yields of bromide obtained by treatment with hydrobromic acid, with or without sulfuric acid, or with phosphorus tribromide were small. The best yield of bromide thus far obtained was only 25%. It is not improbable that the yield might be much improved by suitable modifications of the usual methods of preparing alkyl bromides. The product was a colorless liquid with the odor characteristic of alkyl bromides and a boiling point of 168–170° at 744 mm.

Anal. (Carius). Subs. 0.2561: AgBr, 0.2943. Calcd. for C_5H_9OBr: Br, 48.48. Found: 48.90.

Ethyl Ethyltetrahydrofuranmethylmalonate.—The ordinary malonic ester synthesis was performed, using molecular proportions of the bromide just described, ethyl ethylmalonate and sodium ethoxide in absolute alcohol. The product was a colorless, oily liquid with faint, fruity odor and boiled at 155–157° at 12 mm.

Anal. Subs., 0.1777: CO_2, 0.4104; H_2O, 0.1426. Calcd. for $C_{14}H_{24}O_5$: C, 61.76; H, 8.82. Found: C, 62.98; H, 8.98.

Ethyltetrahydrofuranmethylbarbituric Acid.—The well-known Fischer and Dilthey synthesis, whereby the ester is condensed with urea in the presence of sodium ethoxide in absolute alcohol under pressure, gave a 75% yield of the disubstituted barbituric acid, which after recrystallization from dilute alcohol melted at 190°. The melting point is very close to that of barbital (191°) but a mixed melting point of the two substances showed a depression of 41°. The substance is rather more soluble in water than barbital and crystallizes in flat needles of much the same appearance.

Anal. (Kjeldahl). Subs., 0.1765: cc. of 0.1 N acid, 14.92. Calcd. for $C_{11}H_{16}O_4N_2$: N, 11.67. Found: 11.80.

Ethyl *n*-Amylmalonate.—The n-amyl bromide required for this synthesis has already been described in the literature. We prepared it from n-amyl alcohol supplied by the Sharples Solvents Corporation, using the hydrobromic–sulfuric acid method and collecting the fraction boiling at 127–131°. The malonic ester synthesis was performed in the usual way. Disregarding intermediate fractions which were not subjected to further fractionation, we obtained a yield of 62% of ethyl a-amylmalonate boiling at 134–136° at 14 mm. The ester is a colorless, oily liquid with a faint, fruity odor.

Anal. Subs., 0.2115: CO_2, 0.4812; H_2O, 0.1822. Calcd. for $C_{12}H_{22}O_4$: C, 62.6; H, 9.5. Found: C, 62.05; H, 9.64.

***n*-Amylmalonamide.**—Like most mono-alkylated malonic esters where the alkyl is primary, the above ester forms an amide when shaken for several days with an excess of concentrated aqueous ammonia. The amide crystallizes from dilute alcohol in very small needles which mat together on the filter into a felt. It is practically insoluble in water and in ether, readily soluble in alcohol and melts at 206°.

Anal. (Kjeldahl). Subs., 0.1799: cc. of 0.1 N acid, 20.70. Calcd. for $C_8H_{16}O_2N_2$: N. 16.28. Found: 16.11.

***n*-Amylchloromalonamide.**—This derivative was of particular interest to the writers because it represents the missing member in an homologous series on which some interesting observations had been made on sweet and bitter taste.[1] n-Amylmalonamide was dissolved in glacial acetic acid and a slow current of chlorine passed in until the solvent had taken on a yellow color. The solvent was then removed by distillation under diminished pressure and the residue treated with water. The white crystals which separated were then washed with water and recrystallized from dilute alcohol. The product resembles in appearance the non-chlorinated amide, but melts at 134–135° and has an intensely sweet taste. A 0.005% aqueous solution showed the same degree of sweetness as a 2% sucrose solution.

Anal. (Carius). Subs., 0.1841: AgCl, 0.1286. (Kjeldahl.) Subs., 0.1793, 0.1949: cc. of 0.1 N acid, 17.21, 18.81. Calcd. for $C_8H_{15}O_2N_2Cl$: Cl, 17.19; N, 13.56. Found: Cl, 17.27; N, 13.44, 13.51.

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[1] Dox and Houston, THIS JOURNAL, 46, 1278 (1924).

In one preparation in which chlorine was passed in for several hours the product melted at 106° and contained 22.25% of chlorine. Evidently a partial chlorination of the a-carbon of the amyl group had also occurred. The product had, however, approximately the same degree of sweetness as the pure substance on which the correct analysis was obtained.

n-Amylbarbituric Acid.—This was prepared by condensation of ethyl n-amylmalonate with urea in the presence of sodium ethoxide. After recrystallization from dilute alcohol it was obtained in flat, needle-shaped crystals melting at 215°.

Anal. Subs., 0.2027, 0.2086: cc. of 0.1 *N* acid, 20.52, 21.05. Calcd. for $C_9H_{14}O_3N_2$: N, 14.19. Found: 14.17, 14.13.

Ethyl Di-*n*-Amylmalonate.—From the higher boiling residue remaining from the preparation of ethyl n-amylmalonate described above, a small amount of a fraction boiling at 158–161° at 11 mm. was collected. This was a fairly pure di-amyl derivative as shown by analysis and by the preparation of the corresponding barbituric acid described below.

Anal. Subs., 0.2423: CO_2, 0.5948; H_2O, 0.2277. Calcd. for $C_{17}H_{32}O_4$: C, 68.00; H, 10.67. Found: C, 66.95; H, 10.51.

Di-*n*-Amylbarbituric Acid.—The usual method of condensing the ester with urea was employed. The free acid separated first as an oil which gradually solidified. After several recrystallizations from dilute alcohol it showed a constant melting point of 118".

Anal. (Dumas). Subs., 0.1529: N_2, 15.5 cc. at 27° and 740 mm. Calcd. for $C_{24}H_{24}O_3N_2$: N, 10.47. Found: 10.89.

Ethyl *n*-Amylethylmalonate.—This was prepared from ethyl ethylmalonate, n-amyl bromide and sodium ethoxide in absolute alcohol. Without attempting to work up intermediate fractions, the yield of pure product was 56%. The ester boils at 139–141° at 14 mm.

Anal. Subs., 0.2080: CO_2, 0.4922; H_2O, 0.1874. Calcd. for $C_{14}H_{26}O_4$: C, 65.12; H, 10.08. Found: C, 64.54; H, 10.08.

n-Amylethylbarbituric Acid.—This acid was obtained in 93% yield by condensation of the above ester with urea by means of sodium ethoxide in absolute alcohol under pressure. The sodium salt is soluble in alcohol, and when the solution is acidified the free acid separates first as an oil which gradually solidifies to well defined crystals. After recrystallization from dilute alcohol the melting point was 135°.

Anal. (Dumas). Subs., 0.2174: 23.6 cc. of N_2 at 24° and 751 mm. Calcd. for $C_{11}H_{18}O_3N_2$: N, 12.39. Found: 12.03.

The three disubstituted barbituric acids described above were subjected to preliminary tests for hypnotic action by administering the sodium salts intraperitoneally to white mice. The di-n-amyl derivative was found to be practically inert, the ethyltetrahydrofuranmethyl derivative showed some hypnotic action when given in sufficiently large doses, whereas the n-amylethyl derivative appeared to be a very effective hypnotic with a potency several times that of barbital. The n-amylethyl derivative now completes the series of homologous 5,5-ethyl-*n*-alkylbarbituric acids in which the n-alkyl is methyl to n-heptyl, inclusive. The physiological tests were performed by Dr. A. M. Hjort of the Dartmouth Medical School, who will report more in detail elsewhere.

Summary

New 5,5-disubstituted barbituric acids described in this paper are the ethyl-n-amyl, the di-n-amyl and the ethyltetrahydrofuranmethyl derivatives. The first of these is an effective hypnotic with several times the potency of barbital. n-Amylchloromalonamide, prepared from one of the intermediates, is remarkable for its intensely sweet taste, which is estimated to be about 400 times as powerful as that of ordinary sugar.

DETROIT, MICHIGAN

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

THE ACTION OF BROMINE ON BETA-PHENYL BENZALACETOPHENONE

BY R. BARRÉ AND E. P. KOHLER

RECEIVED MAY 31, 1928 PUBLISHED JULY 6, 1928

For reasons that need not be specially considered here, it became desirable to secure an unsaturated ketone which has bromine in the α-position and which is too highly substituted to combine readily with other substances. It was decided, therefore, to study anew the action of bromine on β-phenyl benzalacetophenone.

Dilthey and Last[1] seem to be the first to try the action of bromine on this particular ketone and surprisingly enough they stated that no addition took place. The action of chlorine gave them a substance which they thought was a condensation product between the dichloride of phenyl benzalacetophenone and the unchanged ketone. This substance was not analyzed and was not investigated further.

Vorlander, Osterburg and Meye,[2] studying the action of bromine on this same ketone (obtained by the same method employed by Dilthey and Last), observed an evolution of hydrogen bromide and after repeated crystallizations from alcohol obtained a product which when slowly heated melted at 121° and when heated rapidly melted at 165°. This product gave them a percentage of bromine corresponding to α-bromo-β-phenyl benzalacetophenone. An attempt to remove the bromine atom by potassium hydroxide solutions failed and the substance was not further investigated.

Moureau, Dufraisse and Mackall,[3] who had obtained β-phenyl benzalacetophenone by isomerization of triphenylethinyl carbinol, studied the action of bromine on that ketone in their endeavor to identify it.

They found that, upon exposure to light, the chloroform solution of the ketone gave with bromine a colorless compound which melted at 130–

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[1] Dilthey and Last, J. *prakt. Chem.*, 94, 50 (1916).

[2] Vorlander, Osterburg and Meye, Ber., 56, 1136 (1923).

[3] Moureau, Dufraisse and Mackall, Bull. *soc. chim.*, (4) 33, 937 (1923).

131° and had a bromine percentage corresponding to the mono-bromo derivative. In the dark, they obtained two products: one which melted at 90–96° and which they were unable to obtain in a state of purity sufficient for analysis, and another which melted at 183–184° and which gave a slightly lower percentage of bromine than that required for a monobromo derivative (21.2 instead of 22.0).

While they were engaged in that work they learned through a publication of another author that the ketone with which they were working was β-phenyl benzalacetophenone, and then apparently abandoned the study of its bromination.

It became desirable to investigate anew the action of bromine on this highly substituted ketone, which was prepared by the same method employed by Dilthey and Last.[4] The results published in this paper differ materially from the results obtained by the preceding chemists.

The action of bromine on β-phenyl benzalacetophenone gives chiefly two products, the respective amounts of which vary with the conditions of the bromination. If the chloroform solution of the unsaturated ketone is refluxed immediately after the addition of the bromine so that the hydrogen bromide which is formed is removed, the product is a-bromo-@-phenyl benzalacetophenone, which is obtained in a 90% yield.

$$(C_6H_5)_2C{=}CHCOC_6H_5 + Br_2 \longrightarrow (C_6H_5)_2C{=}CBrCOC_6H_5 + HBr$$

This compound is a colorless solid melting at 88–89'. Reduced by acetic acid and zinc, it gives diphenyl propiophenone—identified by mixed melting point with diphenyl propiophenone obtained by the reduction of β-phenyl benzalacetophenone itself.

$$(C_6H_5)_2C{=}CBrCOC_6H_5 + Hz \text{ --+ } (C_6H_5)_2CH{-}CH_2{-}COC_6H_5 + HBr$$

Along with the α-bromo β-benzalacetophenone, a small quantity of material of higher melting point has been obtained but not in a sufficient quantity to determine its structure. This compound gives on microanalysis percentages of carbon and hydrogen close to those required by the α-monobromo derivative. The investigation of this substance will be continued.

If the bromination is performed by adding the bromine to a solution of the ketone in chloroform or in ethyl bromide and the reagents are allowed to stand at room temperature for a period of at least fifteen hours, a new product is formed together with α-bromo-β-phenyl benzalacetophenone. This new substance separates from petroleum ether in yellow crystals which melt at 104–105°; it dissolves in hot alcohol forming a solution that on cooling deposits colorless crystals which melt at 130–131°. The compound which melts at 104–105° has the formula $C_{21}H_{14}Br_2$ and the compound which melts at 130–131° the formula $C_{23}H_{19}OBr$; it may be seen immediately by the inspection of these formulas that the compound which

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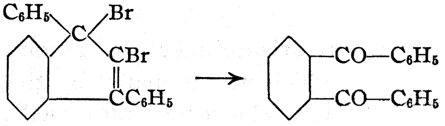
[4] Action of phenyl magnesium bromide on dibenzoyl methane and dehydration of the resulting carbinol.

melts at 130–131° is the ethoxy derivative of the compound which melts at 104–105°, and that this in turn is formed by the loss of a molecule of water from α,β-dibromo-β-diphenyl propiophenone.

$$(C_6H_5)_2C{=}CHCOC_6H_5 + Br_2 \longrightarrow (C_6H_5)_2CBrCBrHCOC_6H_5 \xrightarrow{-H_2O} C_{21}H_{14}Br_2$$

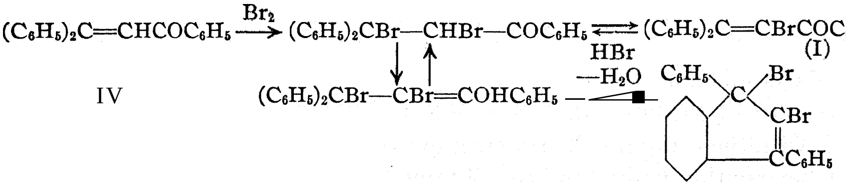
The structure of this particular dibromide was determined by ozonization; the only product obtained was o-dibenzoyl benzene, identified by mixed melting point with an authentic sample. The formation of this diketone leaves no doubt that the dibromide is 1,2-dibromo-1,3-diphenyl indene.



II III

That the substance which melts at 130–131° is the ethoxy derivative of the dibromide was confirmed by the fact that o-dibenzoyl benzene is also found during its ozonization.

It is also possible to obtain 1,2-dibromo-1,3-diphenyl indene from the α-bromo-β-phenyl benzalacetophenone by the action of hydrogen bromide in glacial acetic acid. The fact that the dibromo indene derivative is formed from both the original ketone and its mono-bromo derivative leads to the following supposition concerning the mechanism of the reaction:



VI II

First the unsaturated ketone (IV) would be expected to react with a molecule of bromine to form a dibromide (V). This dibromide (V) which contains a bromine atom linked to a carbon atom which also holds the two phenyl groups is very unstable and loses hydrogen bromide very easily. The loss of hydrogen bromide from the dibromide is reversible as is shown by the fact that the dibromo indene (II) is also obtained from a-bromo-β-phenyl benzalacetophenone by the action of hydrogen bromide. Since hydrogen bromide is also a dehydrating agent, the formation of the indene derivative (II) from the enolic form (VI) of the dibromide (V) is easily explained under the conditions of the reaction.

If hydrogen bromide is removed from the solution as soon as it is formed, the direction of the equilibrium will shift toward the exclusive formation of the a-bromo derivative (I). If hydrogen bromide remains in the solution, its dehydrating effect on the dibromide transforms it into the indene derivative and the equilibrium shifts toward the formation of the dibromide (V), which continues its transformation into the indene derivative (II).

The water formed during the reaction may be seen as a cloud when the bromination is performed in chloroform. In ethyl bromide, the water on standing becomes saturated with hydrogen bromide and collects at the bottom of the flask, then being heavier than the solvent.

The 1,2-dibromo-1,3-diphenyl indene is constituted like 1,2,3-bromo triphenyl indene, which readily forms a free radical.[5] Since it has in addition to the active bromine atom which is common to both these substances a less active bromine in place of the phenyl group on the adjoining carbon atom, its behavior toward metals is peculiarly interesting, and experiments designed to establish this behavior are under way.

Experimental Part

Action of Bromine on β-Phenyl Benzalacetophenone in Boiling Chloroform.—To a solution of 10 g. of β-phenyl benzalacetophenone in chloroform was slowly added 6 g. of bromine. The solution was immediately boiled for five hours. When no more hydrogen bromide was evolved, the chloroform solution, washed with hydrogen sodium sulfite and hydrogen sodium carbonate, was dried and the solvent removed under diminished pressure. The resulting oil was crystallized from petroleum ether after decolorizing with charcoal. The yield of α-bromo-β-phenyl benzalacetophenone was **90%.**

α-Bromo-β-Phenyl Benzalacetophenone (I).—This compound forms nearly colorless crystals which melt instantaneously by projection on a mercury bath at 88–89°. Heated before this point, it melts from 80–85°. The substance has a rather inactive bromine atom; it is not ozonized when submitted to a current of 6% ozone for two hours. It is reduced by boiling in moderately dilute acetic acid with zinc dust and forms β,β-diphenyl propiophenone, identified by mixed melting point. It is soluble in ether, chloroform, ethyl bromide, carbon bisulfide and benzene, sparingly soluble in cold alcohol and petroleum ether.

Anal. Calcd. for $C_{21}H_{15}OBr$: C, 69.4; H, 4.1. Found: C, 68.8; H, 4.1. Molecular weight, calcd.: 363. Found (in benzene): 355.

Action of Bromine on **β-Phenyl** Benzalacetophenone in Chloroform at Room **Tem**peratwe.—To a solution of 10 g. of β-phenyl benzalacetophenone in chloroform was added rapidly a solution of 6 g. of bromine in the same solvent; the solution became warm and hydrogen bromide was evolved. The reaction mixture was set aside for fifteen to twenty hours. The excess of bromine and hydrogen bromide was removed by shaking with a solution of hydrogen sodium sulfite and hydrogen sodium carbonate. The solution dried and evaporated under diminished pressure leaves a yellow oil which separates from petroleum ether (containing a little ether) in yellow and white crystals. These crystals are easily separated mechanically when the crystals are allowed to grow slowly. When a pure yellow crystal is on hand, a solution of white and yellow crystals in petroleum ether seeded by this pure crystal deposits only yellow crystals. From the white compound, α-bromo-β-phenyl benzalacetophenone, the yellow compound was obtained by dissolving the unsaturated bromo compound in a saturated solution of hydrogen bromide in glacial acetic acid. When heated a few minutes at 100°, this solution de-

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[5] Kohler, *Am.* Chem. J., **40,** 220 (1908).

posited a cloudy precipitate which was redissolved by adding a few drops of glacial acetic acid. The solution, seeded, deposited on standing the dibromo indene derivative.

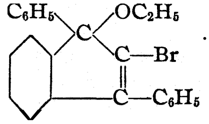
1,2-Dibromo-1,3-diphenyl Indene **(II).**—This compound separates from petroleum ether in well defined characteristic pyramids which are easily recognized. It melts at 104–105° and is stable. With cold concentrated sulfuric acid, it gives a yellow solution which turns to intense red when heated. It has an active bromine and reacts easily with boiling alcohol, forming the corresponding ethoxy derivative. It is soluble in all organic solvents, less soluble in petroleum ether.

Anal. Calcd. for $C_{21}H_{14}Br_2$: C, 59.1; H, 3.3; Br, 37.6. Found: C, 59.0; H, 3.3; Br. 37.9.

Ozonization of 1,2-Dibromo-1,3-diphenyl Indene.—A solution of 2 g. of the dibromo indene in ethyl bromide was ozonized in a current of ozone for two hours; bromine was evolved and the solution became redder and redder. At the end of this time the solution was treated with cold water and the solvent was removed. The resulting oil was boiled with water to insure the decomposition of the ozonide. The oil was taken up in ether and the ethereal solution, washed with an hydrogen sodium carbonate solution, was dried and evaporated. After decolorizing with charcoal, a colorless, crystalline substance separated from alcohol and melted at 145–146°. The substance is free from bromine.

Anal. Calcd. for $C_{20}H_{14}O_2$: C, 83.9; H, 4.9; molecular weight, 286. Found: C, 83.8; H, 5.2; molecular weight (in benzene), 290.

This compound was found to be o-dibenzoyl benzene, which melts at 146° and was identified by mixed melting point.

1-Ethoxy-2-bromo-1,3-diphenyl Indene,  .—When the dibromo indene is boiled with alcohol, the ethoxy compound separates on cooling into colorless crystals which melt at 130–131°.

Anal. Calcd. for $C_{23}H_{19}OBr$: C, 70.8; H, 4.9. Found: C, 70.4, 70.8, 70.6; H, 5.0, 5.1, 5.1.

This compound gives an intensely red coloration with cold concentrated sulfuric acid. By ozonization it gives the same results obtained by the ozonization of the dibromo indene. The insolubility of this compound in cold alcohol makes it a useful derivative for the characterization of 1,2-dibromo-1,3-diphenyl indene.

Summary

It has been shown that the action of bromine on β-phenyl benzalacetophenone gives chiefly two products: α-bromo-β-phenyl benzalacetophenone and 1,2-dibromo-1,3-diphenyl indene. The yield of the two substances depends upon the presence and the concentration of hydrogen bromide which is formed during the bromination. It has also been shown that the action of hydrogen bromide on α-bromo-β-phenyl benzalacetophenone in glacial acetic acid solution gives 1,2-dibromo-1,3-diphenyl indene. This indene derivative offers special interest because it contains two bromine atoms, one of which is very active, and thus should give free radicals. Investigations on this matter are in progress.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

DI-TERTIARY-BUTYLTETRAPHENYLETHANE

BY JAMES B. CONANT AND NEWELL M. BIGELOW

RECEIVED JUNE 1, 1928 PUBLISHED JULY 6, 1928

A study of dialkyl dixanthyls[1] has shown the effectiveness of secondary alkyl groups in promoting the dissociation into free radicals of derivatives of dixanthyl. The close relationship between dixanthyl and tetraphenylethane would lead one to expect that the substitution of secondary and tertiary groups in this hydrocarbon would give rise to compounds with a dissociable carbon to carbon linkage. Only two such compounds have been reported in the literature. One, dicyclohexyltetraphenylethane, was prepared by Ziegler[2] in an impure condition in the course of his extensive study of dialkyl-tetraphenylethanes. Its behavior toward oxygen and halogens indicated that it contained a reactive carbon to carbon linkage. The author reported these results with some reserve because of the difficulty of obtaining an analytically pure sample and because the cleavage with sodium-potassium alloy and carbon dioxide did not result in the formation of the expected diphenylcyclohexylacetic acid. The other compound, di-*tert*.-butyltetraphenylethane was mentioned in a paper by Schlenk,[3] who stated that it did not have the "Dissoziations fahigkeit" of the hexa-aryl ethanes. This statement is surprising both in view of Ziegler's results and those obtained in this Laboratory with dixanthyl derivatives.

Schlenk prepared his compound by the action of molecular silver on a chloride, $(C_6H_5)_2CC_4H_9Cl$, which melted at 103–106°; no description of the ethane was given beyond a statement of its method of preparation.

The identity of Schlenk's hydrocarbon is very questionable. Marvel[4] has shown that the chloride which Schlenk employed is $(C_6H_5)_2C(CH_3)$-$CCl(CH_3)_2$, since it can be prepared by the addition of hydrogen chloride to diphenyl-3,3-methyl-2-butene-1 $(C_6H_5)_2C(CH_3)_2C(CH_3)=CH_2$. The structure of this hydrocarbon was definitely established. Mme. Ramart-Lucas[5] had previously shown that two isomeric chlorides may be obtained from *tert*.-butyldiphenylcarbinol. The lower melting (71–72°) is obtained directly from the carbinol at room temperature by the action of thionyl chloride; the other is obtained by dehydrating the carbinol and adding hydrogen chloride to the unsaturated hydrocarbon. The higher melting chloride may also be obtained by heating the carbinol with acetyl chloride

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[1] Conant, Small and Sloan, THIS JOURNAL, 48, 1743 (1926).

[2] Ziegler and Schnell, *Ann.*, 437, 237 (1924).

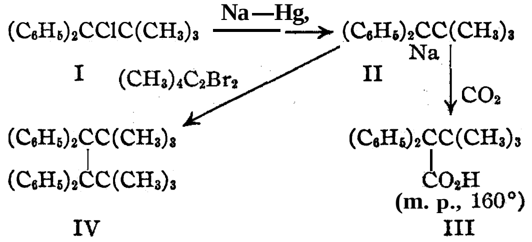
[3] Schlenk and Racky, *Ann.*, 394, 201 (1912).

[4] Bateman with Marvel, THIS JOURNAL, 49, 2914 (1927).

[5] Ramart-Lucas, *Compt. rend.*, 154, 1088 (1912); *Ann. chim. phys.*, [8] *30*, 367, 390 (1913).

(Schlenk's method); its formation in this case involves a Wagner rearrangement. Marvel attempted the preparation of di-*tert.*-butyltetraphenylethane from the low melting chloride but obtained only diphenyl-3,3-methyl-2-butene-1.

Since *tert.*-butyldiphenylchloromethane (I) (m. p. 71–72") easily undergoes rearrangement to the isomeric chloride, it is obviously necessary to use some reagent to remove the chlorine atom which will act very rapidly at low temperature. Forty per cent. sodium amalgam or a large excess of sodium-potassium alloy are both effective; the former is much more convenient. When a 20% solution of the low melting chloride is shaken in dry ether in nitrogen with either of these reagents at 0–10°, a vigorous reaction ensues and a brick red, metallic derivative (II) is soon formed. This metallic derivative may be isolated in the usual manner. On treatment with carbon dioxide it yields an acid (m. p. 160°) whose analysis and molecular weight (determined with the p-nitrobenzyl ester) correspond to *tert.*-butyldiphenylacetic acid (III). The metallic derivative may be coupled to the corresponding ethane by treating with tetramethylethylene dibromide (Ziegler's procedure). The substance obtained is very sensitive to oxygen and must be manipulated by the procedure employed in handling dissociable ethanes. It is a colorless solid (m. p. 138–141") whose analysis and molecular weight correspond to di-*tert.*-butyltetraphenylethane (IV). On shaking an ethereal solution of this hydrocarbon with 40% sodium amalgam, a brick red metallic derivative was formed which with carbon dioxide yielded *tert.*-butyldiphenylacetic acid (m. p. 160°).



$$\begin{tikzcd}
(C_6H_5)_2CClC(CH_3)_3 \arrow[r, "Na—Hg,"] & \underset{Na}{(C_6H_5)_2CC(CH_3)_3} \arrow[dl, "(CH_3)_4C_2Br_2"'] \arrow[d, "CO_2"] \\
\begin{array}{c}(C_6H_5)_2CC(CH_3)_3\\ |\\ (C_6H_5)_2CC(CH_3)_3\end{array} & \begin{array}{c}(C_6H_5)_2CC(CH_3)_3\\ |\\ CO_2H\\ (m.\ p.,\ 160°)\end{array}
\end{tikzcd}$$

I II IV III

It is important to establish that the red metallic derivative formed from the low melting chloride is really a primary product of the reaction of this chloride and is not derived from the isomeric chloride which might be the result of a rearrangement. It was found that the high melting chloride when shaken with sodium-potassium alloy in ether yields a metallic derivative which is entirely different from that produced from the low melting isomer. Both the high melting chloride and the corresponding unsaturated hydrocarbon (diphenyl-3,3-methyl-2-butene-1) form the same dark red potassium compound. On treating with carbon dioxide this yields an acid of the same composition as *tert.*-butyldiphenylacetic acid but with entirely different properties (m. p. 217° as compared with 160°). No crystalline esters could be prepared for molecular weight determinations. An amorphous p-nitrobenzyl ester showed a molecular weight double that of the corresponding ester of *tert.*-butyldiphenylacetic acid; this indicates that the acid in question has the formula $C_{36}H_{40}O_4$. On treating with Ziegler's reagent or mercuric chloride, an oil is obtained which is not sensitive to oxygen. On treatment with sodium-potassium alloy, this oil regenerates the dark red metallic derivative as shown by the action of carbon dioxide, which yields the acid melting at 217°.

Thus, in its color and all its reactions, the metallic derivative formed from the high melting chloride or unsaturated hydrocarbon differs from the substance which is formed from the low melting chloride. This fact eliminates the possibility that the product formed by the action of sodium-potassium alloy or sodium amalgam on the true *tert.*-butyldiphenylchloromethane (low melting chloride) may be derived from its rearrangement products. We have not yet completed our study of the action of sodium-potassium alloy on the high melting chloride and will reserve for another paper a further discussion of this interesting reaction.

If an insufficient amount of sodium-potassium alloy is employed in the preparation of potassium *tert.*-butyldiphenylmethyl, the yield is much lowered and about half of the chloride is converted into a hydrocarbon isomeric with di-*tert.*-butyltetraphenylethane. The substance is not sensitive to oxygen and does not react with sodium-potassium alloy in ether after twelve hours' shaking. It seems probable that this hydrocarbon is comparable to Chichibabin's hydrocarbon (*p*-benzhydryltetraphenylmethane) which is formed by the action of metallic sodium on triphenylchloromethane.[6] The use of a 40% sodium amalgam (a liquid) avoids its formation and it is for this reason that this reagent is preferable to sodium-potassium alloy.

Properties of Di-*tert.*-butyltetraphenylethane

The new hydrocarbon is very similar in its reaction to dibenzyldixanthyl and it is clear that it contains a very labile carbon to carbon linkage. Thus, at 20" in bromobenzene it absorbs the theoretical amount of oxygen in four minutes but no peroxide could be isolated. At the same temperature it reacts with 40% sodium amalgam in benzene and ether at an appreciable rate, but not with 1% amalgam in ether; this behavior classes it with the primary alkyl dixanthyls and distinguishes it from ethanes such as hexaphenylethane[7] which are considerably dissociated in solution at room temperature. Even its dilute solutions were only very faintly colored at 25°; the difference between the slight colors of a 0.0125 molar

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[6] Schlenk and Marcus, ***Ber.***, 47, 1664 (1914).

[7] Conant and Garvey, **THIS** JOURNAL, **49**,**2599** (1927).

solution at 30° and 0" however, was definite. A 0.05 molar solution on warming to 50° became lemon yellow; on cooling the color faded. This could be repeated a number of times. At 100° the color was brighter and seemed to represent the maximum, since a similar experiment at 130° gave no deeper shade. If the solutions are kept at 100° or higher for more than a few minutes they acquire an orange-yellow color which does not fade on cooling. This permanent color is apparently connected with the rapid decomposition of the ethane at elevated temperatures. This decomposition was studied by molecular weight determinations by the freezing point method in *p*-chlorotoluene (in the complete absence of oxygen). Six minutes' heating at 100° of a 5% solution was sufficient to lower the apparent molecular weight from 390 to 266 and twelve minutes at the same temperature lowered it to 227 (theoretical value for complete cleavage 223); further heating was without effect. We have not been able to isolate and identify the products of this thermal decomposition but it is presumably a disproportionation reaction; this reaction seems to be characteristic of free radicals which contain alkyl groups attached to the methyl carbon atom.

A comparison of the facts summarized above with the well-known behavior of hexaphenylethane shows that the tertiary butyl group is somewhat less effective than the phenyl group in promoting dissociation. At room temperature the dilute solutions of di-*tert.*-butyltetraphenylethane must contain less than a few per cent. of the free radical; at 50°, however, the amount of the dissociated form is certainly appreciable. As a rough basis of comparison, we estimate that in a 0.05 molar solution the following substances are just appreciably dissociated (a few per cent.) at the following temperatures: hexaphenylethane, 0"; di-*iso*propyldixanthyl, 0"; di-*tert.*-butyltetraphenylethane, 50"; dibenzyldixanthyl (and di-isobutyl dixanthyl), 75°; dibutyldixanthyl, 130°. If the temperature coefficient of the logarithm of the equilibrium constant is nearly alike for all these substances, these temperatures are a measure of the relative free energy of dissociation in solution.

It has long been known that the xanthyl group is considerably more effective than two phenyl groups in causing dissociation. The fact that di-*iso*propyldixanthyl is appreciably dissociated at 0° and di-tert.-butyltetraphenylethane only at 50° is thus consistent with the idea that secondary and tertiary alkyl groups are approximately equivalent in their dissociating influence. Unfortunately no facts are as yet available which enable us to make a direct comparison of these two classes of alkyl groups. It may be pointed out in conclusion that the somewhat greater influence of the phenyl group as compared to the tertiary butyl group may not reside in the unsaturated nature of the phenyl group. If the presence or absence of hydrogen atoms in the α- and β-positions are a determining factor, one should really compare the phenyl group with such a tertiary group as $C(CH(CH_3)_2)_3$. The accumulation of evidence in recent years certainly points to the conclusion that the lability of a carbon–carbon linkage is to a large extent a function of the branching of the carbon chain with the corresponding elimination of hydrogen atoms in critical positions.

Experimental Part

***Tert.*-butyldiphenylcarbinol** and ***Tert.*-butyldiphenylchloromethane.**—The carbinol was prepared by three different methods: by the reaction of *tert.*-butylmagnesium chloride on benzophenone, by the reaction of phenylmagnesium bromide on trimethylacetophenone and by the reaction of phenylmagnesium bromide on ethyl trimethylacetate.[3,4] The latter method proved the most satisfactory. The preparation of the chloride followed the directions of Mme. Ramart-Lucas.[5] From 10 g. of carbinol and 6.0 g. of thionyl chloride, 8.5 g. of chloride melting at 71° was obtained; at no time in the preparation was the material heated above room temperature.

Preparation of *Tert.*-butyldiphenylmethyl Sodium.—Five grams of the low melting chloride was dissolved in 25 cc. of dry ether in a side-arm test-tube and to this solution was added 10 cc. of 40% sodium amalgam. The air in the test-tube was replaced with pure nitrogen and the tube shaken by hand, with frequent cooling in an ice-bath. The reaction was very brisk, heat was given off and a gray suspension of sodium chloride was rapidly formed. In about five minutes the characteristic brick red color of the sodium derivative appeared. This grew rapidly deeper and the solution became quite thick. The tube was then shaken for about twelve hours on a machine. The sodium derivative is somewhat soluble in ether but is almost insoluble in petroleum ether; it may be partially purified by washing with this solvent.

Tert.-butyldiphenylacetic Acid.—The sodium compound formed from 5 g. of low melting chloride was decomposed with carbon dioxide and the acid isolated in the usual manner. The freshly precipitated, amorphous acid tended to sinter together into a gummy mass; hence the precipitation, washing and filtration were done in chilled solutions and as rapidly as possible. The yield of crude acid was 3 g., about 60%. The acid may be recrystallized from a mixture of methyl alcohol and water. It melts at 160°.

Anal. Calcd. for $C_{18}H_{20}O_2$: C, 80.5; H, 7.4. Found: C, 80.6, 80.3; H, 7.5, 7.4.

Combining weight with NaOH. Calcd. for $C_{28}H_{20}O_2$, 268. Found: 271. 264, 268.

***p*-Nitrobenzyl** Ester.—The *tert.*-butyldiphenylacetic acid was converted into the *p*-nitrobenzyl ester by warming for one hour on the steam-bath an alcoholic solution of the sodium salt with *p*-nitrobenzyl bromide. The ester was recrystallized from alcohol; it melted at 77°; 1.6 g. of acid yielded 1.5 g. of ester.

Anal. Calcd. for $C_{25}H_{25}O_4N$: C, 74.4; H, 6.25. Found: C, 74.2; H, 6.5.

Mol. *Wt.* (by the cryoscopic method in benzene). Benzene, 9.39 g.; calculations from the second increment. Subs., 0.1949: $At = 0.274°$, m. w. = 388; subs., 0.1595, $At = 0.222°$, m. w. = 392. Calcd. for $C_{25}H_{25}O_4N$: 403.

Di-*tert.*-butyltetraphenylethane, $C_4H_9(C_6H_5)_2CC(C_6H_5)_2C_4H_9$.—The preparation of the sodium derivative was carried out in a 500-cc. round-bottomed flask to which a side tube and stopcock were attached at right angles to the mouth. The side tube is bent below the stopcock at 45°. In this flask 5 g. of the low melting chloride was dissolved in 50 cc. of dry ether and 15 cc. of 40% sodium amalgam was added. In the mouth of the flask was placed a cloth filter backed by copper gauze, the filter being held in place by a cork ring which fitted tightly into the neck of the flask. The mouth of the tube was closed by a one-holed rubber stopper fitted with a glass stopcock.

The air in the flask was removed by evacuation and replacement with pure, dry nitrogen; the flask was shaken vigorously by hand, with cooling in ice as necessary. In about five minutes the red color of the sodium derivative appeared, the suspension in the flask becoming quite thick. At this point the shaking was carried on in a shaking machine; this was continued for about sixteen hours.

At the end of this time the reaction was considered complete; the excess amalgam was removed by suction through the side arm. Twenty-five cc. of low boiling petroleum ether was added to decrease the solubility of the sodium derivative, the mother liquors were removed by filtration with suction through the cloth filter and the filter cake was washed with petroleum ether. The flask was immersed in an ice-bath with the rubber stopper uppermost and 25 cc. of dry ether sucked in through the filter. Tetramethyl ethylene bromide (1.5–2.5 g.) dissolved in 10 cc. of dry ether was then added in small portions with constant shaking. The course of the reaction was followed by the change of color from red to colorless.

The colorless solution of the ethane was filtered from the sodium bromide in an atmosphere of nitrogen. The solution was concentrated by evaporation under diminished pressure until crystals of the ethane began to form. An equal volume of petroleum ether was added and the crystallization of the ethane made as complete as possible by cooling to $-10°$. The crystals were filtered off in an atmosphere of nitrogen, washed with small quantities of petroleum ether and dried at room temperature in a stream of nitrogen. The apparatus was then opened to the air and the solid transferred to a Fischer pistol in which it was kept in an atmosphere of nitrogen. All the manipulations except the final transfer were carried out in an atmosphere of nitrogen carefully freed from oxygen and moisture. A slight modification of the usual type of apparatus employed in such work made possible the filtration from the sodium bromide and the crystallization of the ethane.

The ethane was recrystallized from a mixture of ether and petroleum ether in an atmosphere of nitrogen. It melted at 138–141° in nitrogen to a red melt; in air it melts at 40–50°. It is stable indefinitely in the dark under pure dry nitrogen and is not affected by subdued daylight. In the air the dry crystals become slightly sticky in about a half hour, and in twelve to eighteen hours it turns into a sticky brown mass. The weight of the sample decreases during this process; in sixteen hours the sample loses about 2% of its original weight. In two instances the crystals, on being removed from the recrystallizing machine, decomposed almost instantaneously to a yellow oil; white fumes smelling something like benzophenone were given off, and the oil became too hot to touch. The whole yield did not undergo this decomposition; the unchanged powder, guarded from contact with the oil, usually, although not always, did not decompose, but if any part of a sample came in contact with the oil, it decomposed in turn. This decomposition may be due to impurities or to moisture. In one of the cases in which the formation of the oil occurred, the sample had been dried for only a half hour; however, a small sample of the pure ethane slightly moistened with petroleum ether did not decompose on short exposure to air.

Anal. Calcd. for $C_{34}H_{38}$: C, 91.4; H, 8.6. Found: C, 90.6, 91.6; H, 8.5, 9.0.

Molecular weight (cryoscopic in an atmosphere of nitrogen). (a) Benzene (8.08 g. of solvent). Subs., 0.0766 g.: $\Delta t = 0.125°$, mol. wt. = 372; subs., 0.1491, $\Delta t = 0.205°$, mol. wt. = 440.

(b) In *p*-chlorotoluene (10.7 g.) (first increment disregarded). Subs., 0.2106 g.: $\Delta t = 0.272°$, mol. wt. = 404; subs., 0.1769 g.; $\Delta t = 0.222°$, mol. wt. = 418. Calcd. for $C_{34}H_{38}$ = 446.

Oxygen Absorptions.—The method used was the same as that employed in the previous work on free radicals in this Laboratory. The bottle containing the bromobenzene solution of the ethane and oxygen was shaken vigorously. The percentage oxygenation was calculated from the weight of the sample and the volume of oxygen corresponding to the formation of a peroxide. A 0.05 molar solution in bromobenzene absorbed oxygen at 14° at the following rate: two minutes, 70%; five minutes, 106%; eight minutes,' 122%; twenty-five minutes, 126%; twenty hours, 165%. These results were reproducible within a few per cent. No peroxide could be isolated from the oxygenation in ether or other solvents.

Cleavage with Alkali Metals,—A determination of the activity of the ethane toward the alkali metals was carried out according to the method previously described." The ethane was rapidly cleaved by sodium-potassium alloy in ether and also in benzene; it was not, however, acted on by 1% amalgam in ether. It was cleaved by 40% sodium amalgam in ether and also in benzene. In all these runs, 0.10 g. (0.00025 moles) of the ethane was placed in a small test-tube with a constricted neck. After the air in the tube had been displaced by pure dry nitrogen, 5 cc. of the solvent and 1 cc. of liquid alloy or amalgam were introduced through a separatory funnel. The tube was then sealed off at the constriction and shaken vigorously by hand for five minutes. In all cases in which color was reported, it developed practically at once; the tube containing the 1% alloy was shaken on a machine for twenty-four hours without the development of color. The metal derivative formed in all these cases, when decomposed with carbon dioxide, yielded the *tert.*-butyldiphenylacetic acid (m. p. 160").

Color Changes on Heating.—A 0.05 molar solution of the ethane in ethyl benzoate in an atmosphere of nitrogen at room temperature showed a faint but definite coloration. When heated for thirty seconds in a water-bath at 50°, a light lemon-yellow color appeared. This color disappeared when the tube was plunged into an ice-bath. This could be repeated several times. A similar solution heated for thirty seconds at 100° was a bright lemon-yellow color; when the tube was immersed in ice and water the color vanished immediately. Heated again at 100" for two and one-half minutes, the color reappeared; on subsequent cooling the color faded but did not entirely disappear, indicating that the latter was due to a different cause. The color at 130° after forty-five seconds was the same shade as at 100". If these solutions are heated to 100° for three hours, the yellow color first formed passes through a brownish-yellow into a bright orange color.

Decomposition of the Ethane in Solution on Heating.—The rate of disproportionation at 100° was measured by the decrease of apparent molecular weight in *p*-chlorotoluene by the cryoscopic method. The apparatus was of special construction and was kept filled with oxygen-free nitrogen. The results are tabulated below; the somewhat low initial molecular weight was probably due to the fact that the sample employed was only crystallized once.

TABLE I

DECOMPOSITION OF THE ETHANE ON HEATING

Sample, g.	Solvent, g.	Heating period Time, min.	Temp., °C.	Freezing point depression, °C.	Apparent mol. wt.
0.4078	10.70	0	20	0.547	390
.5241	10.70	3	100	.880	312
.5241	10.70	6	100	1.032	266
.5241	10.70	9	100	1.146	139
.5241	10.70	12	100	1.208	227
.5241	10.70	17	100	1.221	224
.5241	10.70	22	100	1.212	226

A sample removed at the end of the experiment had no oxygen absorption capacity. When heated to 100" for the first time, a bright yellow color was observed; on cooling this faded slightly but a marked color remained. After the first heating, no variation in color was observed between the hot and cold solutions. No orange color developed.

Isomeric Ethane.—Four and one-half g. of low melting chloride, dissolved in 40 cc. of dry ether, was shaken with 2 g. of sodium-potassium alloy for twenty-four hours. At the end of this time the solution had acquired a light red color. Carbon dioxide was introduced and the *tert.*-butyldiphenylacetic acid obtained in the usual manner. The ethereal layer containing the non-acid material yielded crystals on evaporation. These were washed with a little ether, filtered and recrystallized from alcohol and ether; yield, 1.7 g.; m. p. 145°.

Anal. Calcd. for $C_{34}H_{38}$: C, 91.4; H, 8.6. Found: C, 91.0; H, 8.52.

Mol. wt. by the freezing point method in 9.81 g. of benzene. Subs., 0.2748 g.: $\Delta t = 0.352°$, m. w. = 411; subs., 0.4122 g.: $\Delta t = 0.517°$, m. w. = 419. Calcd. for $C_{34}H_{38}$: m. w. = 446.

The substance did not react with oxygen or with sodium-potassium alloy after twelve hours' shaking in ether.

Potassium Derivative from Isomeric Chloride and from **Diphenyl-3,3-methyl-2-butene-1.**—The unsaturated hydrocarbon (diphenyl-3,3-methyl-2-butene-1) and the corresponding chloride were prepared according to Marvel's directions.[4] When a 20% solution of either of these substances in anhydrous ether was shaken with sodium-potassium alloy (2 g. per 25 cc. of solution), a dark red potassium derivative was formed. This substance was not identical with the red metallic derivative formed from *tert.*-butyldiphenylchloromethane, as the following experiments prove.

(a) Decomposition with Carbon Dioxide.—The suspension of the metallic derivative was treated with carbon dioxide and the acid obtained in the usual manner. It was precipitated from an aqueous solution of its sodium salt by the addition of mineral acid as a white, amorphous solid. The yield was about 32%. It could be recrystallized by solution in methyl alcohol at room temperature, addition of water to incipient turbidity and setting aside; m. p. 218–224° with decomposition.

Anal. Calcd. for $C_{18}H_{20}O_2$: C, 80.5; H, 7.4. Found: C, 80.8, 80.2; H, 7.61, 7.23.

Combining weight with NaOH, calcd. for $C_{18}H_{20}O_2$: 268. Found: 267,258.

The p-nitrobenzyl ester was prepared by the action of p-nitrobenzyl bromide on an aqueous solution of the sodium salt of the acid. The ester was an amorphous yellow powder. All attempts to recrystallize it were unavailing.

Mol. wt. by the micro method in camphor. Subs., 0.0105 g.; camphor, 0.1141 g.: $\Delta t = 5.2°$, m. w. = 705; subs., 0.0273 g.; camphor, 0.1078 g.: $\Delta t = 14.6°$, m. w. = 695. Calcd. for $C_{50}H_{48}O_8N_2$: 804.

Attempts to prepare a crystalline methyl ester and an amide yielded only amorphous, gummy materials.

(b) Decomposition with Tetramethylethylene **Dibromide.**—When the metallic derivative was treated with tetramethylethylene dibromide in the manner described above, the color disappeared. The resulting ether solution on evaporation in nitrogen yielded an oil which failed to crystallize. This oil did not absorb oxygen at any measurable rate in bromobenzene solution. On shaking an ethereal solution of it with sodium-potassium alloy, the dark red metallic derivative was formed. On treating with carbon dioxide, the acid melting at 218–224° was obtained.

Summary

1. Di-*tert.*-butyltetraphenylethane has been prepared from sodium *tert.*-butyldiphenylmethyl. This was formed when the corresponding chloride was treated with a large excess of sodium-potassium alloy or 40%

sodium amalgam. No rearrangement was involved in this reaction since the isomeric chloride was shown to yield an entirely different metallic compound when treated with the alloy.

2. Di-*tert.*-butyltetraphenylethane absorbs oxygen rapidly in solution at 25°. On heating a dilute solution to 55° a reversible color change indicative of dissociation appears. On heating for a few minutes in solution at 100°, in the absence of air, it disproportionates completely. These results show that the effect of the tertiary alkyl group in promoting the dissociation of the carbon linkage is similar to the effect of the secondary groups studied in the dixanthyl series.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE POLARIMETRY SECTION, BUREAU OF STANDARDS, UNITED STATES DEPARTMENT OF COMMERCE]

RELATIONS BETWEEN ROTATORY POWER AND STRUCTURE IN THE SUGAR GROUP.

XVIII. ALPHA-METHYL d-LYXOSIDE TRIACETATE[1,2]

BY F. P. PHELPS AND C. S. HUDSON

RECEIVED JUNE 8, 1928 PUBLISHED JULY 6, 1928

In Article VII[3] it was assumed that the alpha forms of methyl d-xyloside and d-lyxoside possess the same ring structure and the rotation of the latter was calculated from that of the former by use of the known difference of rotation between the alpha forms of methyl d-glucoside and d-mannoside, which at that time were supposed to have like ring structures. Subsequent results[4] indicated, however, that the glucoside possesses a 1,4-ring and the mannoside a 1,5-ring and consequently in Article XII[5] it was suggested that a-methyl d-lyxoside does not possess the 1,5-ring of methyl d-xyloside but rather a 1,4-ring. The 1,3-ring appeared to be excluded because 1,3-ring glycosides in the mannose and rhamnose series are hydrolyzed very rapidly by dilute acids, whereas a-methyl lyxoside is hydrolyzed far more slowly even by stronger acid solutions. It has now been sought to obtain further evidence on this question of the possibility of a 1,3-ring structure in α-methyl d-lyxoside by examining the behavior of its fully acetylated derivative, a triacetate, toward alkaline saponification. It has been found that the acetates of methyl mannoside[6] and methyl rhamnoside,[7] of the 1,3-ring type, retain one acetyl group (presumably that

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[1] Publication approved by the Director of the Bureau of Standards.

[2] Article XVII was published in THIS JOURNAL, 48, 2435 (1926).

[3] Hudson, *ibid.*, 47, 272 (1925).

[4] Hudson, *ibid.*, 48, 1424, 1434 (1926).

[5] Phelps and Hudson, *ibid.*, 48, 503 (1926).

[6] Dale, *ibid.*, 46, 1046 (1924).

[7] Fischer, Bergmann and Rabe, *Ber.*, 53, 2362 (1920).

attached to carbon atom 2) under conditions of strong alkalinity and it would therefore be supposed that a triacetate of a-methyl lyxoside, of the 1,3-ring type, would behave similarly since the configurations of mannose, rhamnose and lyxose are alike with respect to carbon atoms 1, 2, 3 and 4. The experimental results now to be reported show that the three acetyl groups of a-methyl d-lyxoside triacetate are easily removed by alkali, and we therefore conclude that the ring is not in the 1,3-position. It must, therefore, be a 1,4- or a 1,5-ring if ring 1,2 is excluded as an improbable structure for stable, difficultly hydrolyzable glycosides of the true sugars.

Since the molecular rotation (+ 25,240) of a-methyl d-xyloside of the 1,5-ring type[8] differs from that of a-methyl d-lyxoside ((59.4)(164) = + 9740) by a value (15,500) that is far removed from the "epimeric difference of rotation"[9] (6700) for glycosides, it is concluded that the substances are not epimeric structures and that, therefore, α-methyl d-lyxoside possesses the 1,4-ring. The value now reported ((30.1)(290) = + 8730) for the molecular rotation of the triacetate of this substance leads to the same conclusion, since it differs from that of a-methyl d-xyloside triacetate (+ 34,700) by an amount (25,970) far removed from the epimeric difference of rotation (11,300) for acetylated glycosides.

It becomes possible from the preceding conclusions to calculate the rotations of several members of the d-xylose series of the 1,4-ring type and likewise several of those of the *d*-lyxose series of the 1,5-ring type, by the use of the epimeric difference of rotation. Thus the specific rotation of the unknown a-methyl d-xyloside (*1,4*) is calculated to be (9740 + 6700) ÷ 164 = + 100 in water, and that of its triacetate to be (8730 + 11,300) ÷ 290 = + 69 in chloroform. Likewise the specific rotation of the unknown a-methyl d-lyxoside (*1,5*) is calculated to be (25,240 − 6700) ÷ 164 = + 113 in water, and that of its triacetate to be (34,700—11,300) ÷ 290 = + 80 in chloroform. These calculations can obviously be extended to the a- and β-forms of xylose and lyxose, of both the 1,4- and 1,5-ring types, and to various derivatives of these pentoses other than those just considered. Since the rotation of a-d-lyxose (+ 5.5) differs normally from that of a-methyl *d*-lyxoside,[3,5] it is concluded that this crystalline form of the pentose possesses the 1,4-ring structure.

Experimental

Preparation of α-Methyl d-lyxoside **Triacetate.**—One *g.* of pure α-methyl d-lyxoside ($[\alpha]^{20}_{\mathrm{D}} = +59.4°$ in water) was heated with 6 cc. of acetic anhydride and 3 cc. of dry pyridine for half an hour on the steam-bath. On pouring the solution into ice water a sirup separated and quickly crystallized, yielding 0.9 g. of crystalline triacetate ($[\alpha]_{\mathrm{D}} = +29.2°$ in $CHCl_3$). Extraction of the mother liquor with $CHCl_3$ yielded 0.6

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[8] Hirst and Purves, J. *Chem. Soc.,* 123, 1352 (1923).

[9] Hudson, THIS JOURNAL, 48, 1439 (1926).

g. of crystals of nearly the same rotation. Three grams of the substance was thus prepared in two experiments. One recrystallization from hot water gave a pure product, the rotation of which was not changed by four subsequent recrystallizations; m. p. 96°. The rotation measurements on the final product are recorded in the table, the tube length being *2* dm. and the solvent being pure chloroform. The angles are in all cases dextro-rotations.

TABLE I

ROTATION OF PURE a-METHYL*d*-LYXOSIDE TRIACETATE IN CHLOROFORM SOLUTION

Concn., g./100 cc. of soln.	Sodium yellow λ = 589		Mercury yellow A = 578		Mercury green λ = 546		Mercury blue X = 436	
	α	$[\alpha]^{20}_{D}$	α	$[\alpha]^{20}_{578}$	α	$[\alpha]^{20}_{546}$	α	$[\alpha]^{20}_{436}$
0.745	+0.438	+29.4	+0.461	+31.0	+0.530	+35.6	+0.705	+61.0
1.307	+ .803	+30.7	+ .838	+32.1	+ .941	+36.0	+1.62	+62.0
1.776	+1.074	**f30.2**	+1.137	+32.0	+1.274	+35.8		
1.908			+1.208	+31.7	+1.358	+35.6	+2.40	**f62.9**
Average		**$30 1**		+31.7		**$35.8**		+62.0

A Zeisel analysis showed **10.4%** of methoxyl **(0.3222 g.** of substance yielded **0.1552** g. of AgCl) in comparison with the value **10.7** required by the formula $C_{11}H_{15}O_7OCH_3$ (m. w., **290).**

An acetyl estimation by the method of Kunz[10] agreed with this formula for a triacetate **(0.2126** g. of substance was equivalent to **21.5** cc. of **0.1** M HCl).

Summary

Pure a-methyl d-lyxoside triacetate has been prepared and it is concluded from a comparison of its rotation with that of a-methyl d-xyloside triacetate that the lyxoside derivative possesses a 1,4-ring structure, and that crystalline a-lyxose ($[\alpha]_D = +5.5$) also has this ring structure since its rotation differs normally from that of a-methyl d-lyxoside.

WASHINGTON, D. C.

NEW BOOKS

A Comprehensive Study of Starch Chemistry. Volume I. Compiled and edited by ROBERT P. WALTON in collaboration with twenty other authors. The Chemical Catalog Company, Inc., **419** Fourth Avenue, New York, **1928. 240** + iv + **360** pp. Illustrated. **18** × **26** cm. Cloth. Price, **$10.00.**

In the introductory paragraph of the Preface the compiler writes: "The most prominent aspects of the subject have been treated by authorities who have contributed significantly to the advancement of the field and who are actively engaged in further investigations or developments." This statement describes adequately the nature of the first part of the book and the material presented in it.

The nineteen papers comprising the symposium and the first *235* pages of the volume range in subject matter from various aspects of the molecular constitution and physical and chemical properties of starches and

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[10] Kunz and Hudson, THIS JOURNAL, **48,1978 (1926).**

related substances by Pictet, Irvine, Ling, Pringsheim, Samec, Taylor (T. C.), Katz and Sherman, through the role of starch in such industrial processes as bread making and fermentation by Alsberg, again Katz and Fernbach; the manufacture and use of starches, gums and adhesives by Moffett, Preuss, Bloede, Alexander, Nivling and Farrow; and starch-converting enzymes by H. C. Gore and others. The final article is a review of the early development of starch chemistry and manufacture (to 1811) by the editor of the book.

The latter half of the volume comprises an elaborate list of verified references to books and articles on starches, dextrines and amylases that appeared in the period 1811–1925. These are grouped under six general divisions and 46 classifications. Following each reference is a brief "discriminative" abstract or description of the material contained in it, often quoted from abstracts previously published in the literature.

Each of the two parts of this book—the symposium and the bibliography—covers material that is amply sufficient in itself to justify publication. Together they comprise a survey of the field of the starches and their congeners that makes the book of extraordinary value, both to the student and to those trained workers whose activities are concerned with these substances.

WILLIS A. BOUGHTON

Tables of Physical and Chemical Constants and Some Mathematical Functions. By G. W. C. KAYE, D.Sc., Superintendent of the Physics Department, the National Physical Laboratory and T. H. LABY, Sc.D., Professor of Natural Philosophy, University of Melbourne. Sixth edition. Longmans, Green and Company, 55 Fifth Avenue, New York, 1928. iii + 163 pp. 16.5 × 25 cm. Price $4.75.

Except for a table of Isotopes and one of the Thermal Conductivities of Gases, this edition appears to be a reprinting of the fourth and fifth editions (1920 and 1926). The table of atomic weights is that of 1925.

ARTHUR B. LAMB

The Journal of the American Chemical Society

VOL. 50 AUGUST, 1928 No. 8

[CONTRIBUTION NO. 9 FROM THE RESEARCH LABORATORY, NATIONAL BISCUIT COMPANY]

STUDIES OF HYDROGEN ION CONCENTRATION MEASUREMENTS. I. METHODS OF MEASUREMENTS

BY CLARKE E. DAVIS AND GLENN M. DAVIDSON

RECEIVED AUGUST 29, 1927 PUBLISHED AUGUST 4, 1928

Introduction

Beans and Oakes[1] state that their investigation undertaken for the purpose of developing a method of measuring the hydrogen ion concentration of pure water as directly as possible became a problem of developing and applying a new method of measuring potential differences in which the resistance of the circuit would not affect the accuracy of the results, and which at the same time would not require an excessive amount of current for operation. In other words, this new method was to have all the advantages of the potentiometer arrangement with the additional advantage of being independent of the internal resistance of the cell.

It is also stated that the application of such a method would not be limited to the cell mentioned above. This same method could be applied to all concentration cells, finding its greatest use, however, in connection with the measurement of the electromotive force of cells having such a high internal resistance as to render them impossible of measurement so long as the potentiometer method is the only one available. The method so developed consisted of the employment of a high grade condenser, standard cell and ballistic galvanometer. The diagram of the connections is shown in Fig. 1.

A similar method was described by Carhart;[2] Potter,[3] also, describes the condenser method of determining the conductivity of cells of high internal resistance.

Considerable data have been accumulated on acids and bases by Davis, Oakes and Salisbury,[4] where a standard procedure was employed throughout, using the apparatus described by Beans and Oakes.[1]

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[1] Beans and Oakes, THIS JOURNAL, 42, 2116 (1920).

[2] Carhart and Patterson, "Electrical Measurements," Allyn and Bacon, Boston, 1900, pp. 188–189.

[3] Potter, *Proc. Roy. Soc. London*, 84B, 260–275 (1911–1912).

[4] Davis, Oakes and Salisbury, *Ind. Eng. Chem.*, 15, 182 (1923).

In consideration of the moderate cost of the apparatus as pointed out by Beans and Oakes,[1] a standard Leeds and Northrup condenser, capacity of one microfarad, subdivided into five sections was used by Davis, Oakes and Salisbury.[4] Several anomalies in the data as obtained by Davis, Oakes and Salisbury[4] were noted and reasons suggested for such discrepancies; however, it seemed there were experimental errors in the general ballistic method outlined by Beans and Oakes[1] which have hitherto been overlooked.

The primary purpose, therefore, of this investigation was to test the effectiveness and technique required in electrometrically determining hydrogen ion concentration of a solution by means of the condenser arrangement. It was also our purpose to determine the significance of the individual data obtained by the condenser arrangement and the precision necessary to secure a given accuracy for the resultant electromotive force. In order to secure accuracy of final results, it was necessary to compare directly measurements of electromotive force by the condenser method with those obtained by the standard potentiometer method.

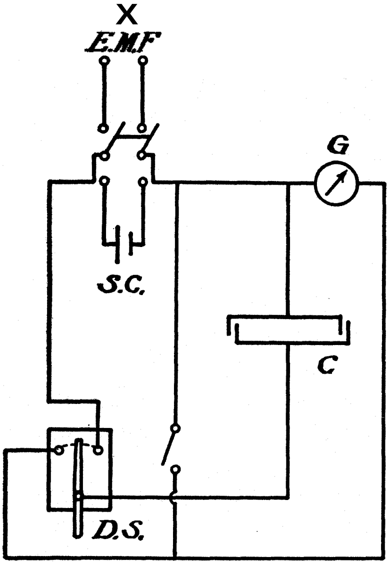

Fig. 1.

Apparatus and Method of Measurement

The investigation was divided into three major parts: (1) the measurement of the inherent errors in the ballistic galvanometer method of hydrogen-ion determinations; (2) the titration of typical acids with sodium hydroxide to point out the significance of such errors as was noted in part one; (3) a mathematical discussion of the formula used in calculating the unknown electromotive force as determined by the ballistic galvanometer method.

Part (1) of this experiment was conducted in the following manner. The condenser was charged with a definite electromotive force obtained from the potentiometer. This charge was then released through the ballistic galvanometer and the swing accurately noted to plus or minus 0.1 mm. A swing as nearly equal as possible was then made with the standard cell using the proper condenser capacity. The agreement of the swings in most cases could be obtained within 2 to 10 mm. Knowing the ratio of the plates used and the voltage of the standard cell, the electromotive force equivalent to this swing can then be calculated. The difference between the calculated electromotive force and the charging electromotive force from the potentiometer was considered an inherent error in the ballistic galvanometer method. The diagram of the connections is shown in Fig. *2*.

The apparatus used consisted of a Leeds and Northrup Type K Precision Potentiometer with Leeds and Northrup Type H highly sensitive galvanometer, Leeds and Northrup standard mica condenser of one microfarad capacity subdivided into five sections having values of 0.5, 0.2 and 0.05 microfarads' capacity, respectively, Type R highly sensitive galvanometer and two Weston Standard cells.

The standard cells used were checked against two Eppley cells, standardized by the U. S. Bureau of Standards, as well as calibrated by means of a Wolff potentiometer in the Ernest Kempton Adams Laboratory, Department of Physics, Columbia University.

Discussion of the Galvanometer and Condenser

Many precautions are to be observed and possible errors guarded against in the operation of the general ballistic galvanometer method.

The individual errors of leakage and inequality of swings have been pointed out to a certain extent while many inherent errors of the ballistic galvanometer and condenser have been omitted. These errors are many in number and may be neutralized one by the other or may be additive. In this respect, Zeleny[5] and White[6] have noted several precautions and possible errors which apply to the ballistic galvanometer method.

In ballistic work the throw that is equal at least to the maximum that is to be used is given to the coil so that a set is affected in the direction of the throw that is to follow.

The coil on returning to the null point must not be allowed to move past, as otherwise part of the set is removed. Subsequent throws in the same direction cause little or no addition to the set.

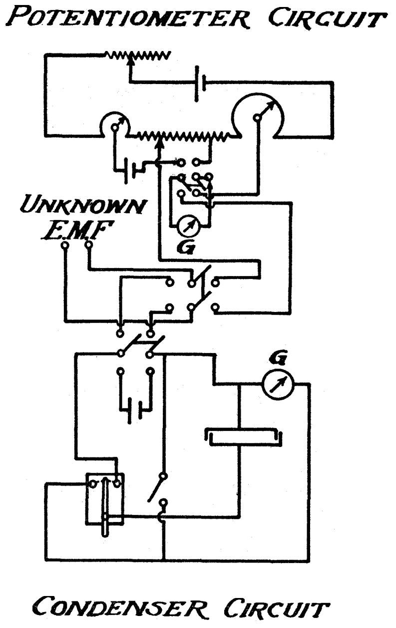

Fig. *2*.

Hysteresis Effects.—The first throw of the galvanometer is generally at least 0.3% more than the following ones and should be discarded.

When a ballistic throw is to be taken while the coil is not entirely at rest, the discharge must be made when the coil is at either turning point of its motion. The throw in either case must be computed from the natural zero point and not from the point at which the throw originated, as is sometimes stated.

In all cases the galvanometer should be used on an open circuit; it is

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[5] Zeleny, *Phys. **Rev.***, 23, 399 (1906).

[6] White, *ibid.*, 23, 382 (1906).

then more sensitive and the quantities more nearly proportional to the throws. When the circuit is closed an error may be introduced by the thermo-electric current that usually exists in a closed circuit, which itself produces an appreciable deflection.

The ballistic galvanometers for use in the condenser method have a relatively short period and the possibility of reading the throw accurately is very difficult and is generally taken as plus or minus 0.1 millimeter. Calculations show that amount of error in the resultant electromotive force due to this personal error in reading cannot be overlooked.

The zero shift of the ballistic galvanometer amounts to 3.0 to 7.0 mm. during the usual period required in titration work. This effect is due to such factors as change in temperature, lengthening and shortening of the suspensions, hysteresis in the suspensions from magnetic foreign material, possible set in the suspension fiber and other mechanical disturbances in the system.

With this knowledge of the working peculiarities of a ballistic galvanometer, it would be difficult to calibrate the galvanometer deflections and construct a graph so as to read electromotive forces directly. As will be noted, the zero point will change from time to time, and shifting the zero point on the scale to equal the original zero will now create a possible variation in the angular deflection of the galvanometer and thus change its calibration, as the relationship between the electromotive force and deflection of the galvanometer for a given capacity is not a straight line function but curvilinear. It will be seen that such a precaution is eliminated in using the galvanometer as a null instrument because in such a case the deflections when in service are small and do not disturb the zero position.

In the operation of the ballistic galvanometer method, it is necessary to select by trial a set of plates of one capacity for the standard cell and a set of plates of another capacity for the unknown electromotive force in order to secure proper equality of ballistic deflections. The arrangement of the plates in either case to secure the proper capacity may have been either in series or parallel. The guaranteed accuracy as stated by the manufacturers is plus or minus 0.1 to 0.25% for each individual set of plates. With this idea in mind, it is very probable and possible that in such an arrangement of the plates, to secure proper agreement in swings, this error is additive, for instance, positive error for the standard cell and negative error for the unknown electromotive force. Calculations will show these errors to be of primary importance in the resultant electromotive force.

It was noted in a previous paragraph that the errors due to inaccuracy in reading the galvanometer deflections plus or minus 0.1 mm. were of like magnitude, as pointed out above, thus making the total error of significant value. From this standpoint of errors originating from the use of several sets of plates, it would seem only logical to use a fixed condenser of suitable capacity, that is, 0.3 or 0.6 microfarad. This particular idea was pointed out by Beans and Oakes[1] where they suggest the use of a single unit condenser, thus eliminating the capacity factor in the equation $E_1/E_2 = d_1C_2/d_2C_1$. With such an arrangement it is obvious that the capacity value would not appear in the calculations for the unknown electromotive force and the calibrated value of such a fixed condenser need not be accurately known. This method, however, could not be used with any degree of accuracy, as the equality of the swings in such a case would never be possible and errors of such magnitude as shown in Fig. 4 would be encountered.

There is also a serious objection to the condenser method inasmuch as the condenser will maintain with uncertainty the same capacity from time to time. This would invalidate calibration data being used over various periods of time. The condenser plates are held together by the insulating materials only, usually the paraffin in which they are imbedded. If the temperature of the room varies to any great extent, or in case the condenser were placed in such a manner so as to be subjected to external heating, the plates would change their relative positions and thus raise or lower their stated capacity. It is obvious from this consideration that great care should be exercised in preventing such temperature variations and the condenser should be tested from time to time for its accuracy.

In the selection of a condenser for such electromotive force measurements as herein discussed, it is of great importance to secure an instrument which has a very small absorbed charge. The absorption charge in good mica condensers will vary from 0.1 to 1.5%; each condenser or set of plates will have its own characteristic property as to absorption.

Furthermore, and of greater importance, is the adoption of a condenser which can be properly calibrated. Condensers designed for precision measurements are of two general types, namely, fixed single-unit condensers and condensers subdivided into several sections so as to provide various parallel and series combinations.

When considering the use of a condenser subdivided into several sections so as to eliminate errors in the swing of the galvanometer, such as would be encountered when using a fixed condenser, we find there are two general classes of this type of condenser. The first class consists of those with binding posts fastened to the terminals of the condenser and the second class is those of the plug switch type.

With condensers of the latter type the leakage across the exposed metal bars for holding the plugs will be of an appreciable value. Also, it will be noted that each plug switch affords a small air condenser, which will play an important part when calibrating this type of condenser. The value of the error arising from these small air condensers will be directly proportional to the frequency used for calibration.

Experimental

In the discussion of the condenser method by Beans and Oakes,[1] practically no emphasis was placed on the importance of adjusting the swing of the galvanometer for the unknown electromotive force to an equal value as obtained with the standard cell.

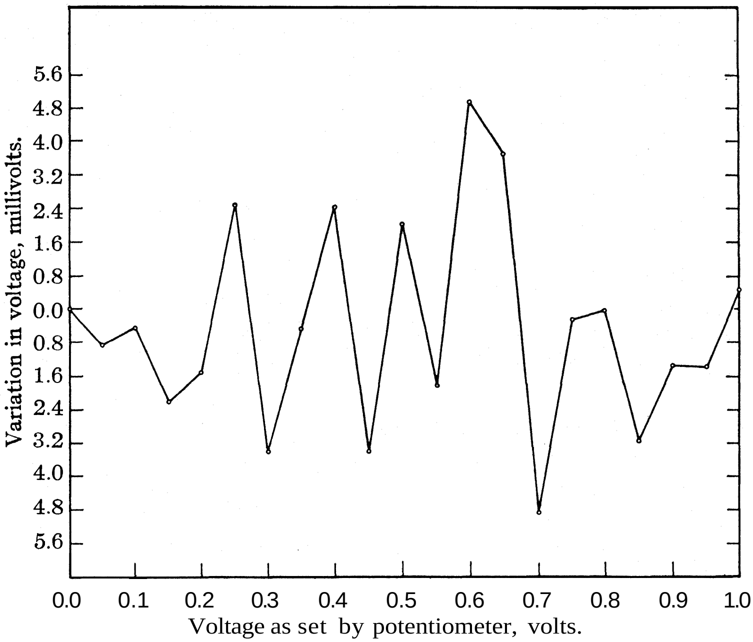

Fig. 3.

"The average deflection for this cell after reaching maximum voltage is 25.0 mm. for one microfarad capacity. Since the standard cell of 1.01823 volts gave a deflection of 50.0 mm. when used with a capacity of one microfarad, the voltage of this cell is 25/50 X 1.01823 volts or 0.5091 volt." Such a method of disregarding the equality of swings leads to extremely large errors in the final calculated electromotive force. With this precaution in mind variations in the resultant electromotive forces were determined with the swing of the galvanometer for the unknown electromotive force adjusted by trial as nearly equal as was possible to that obtained with the standard cell as a source of potential. These results are shown graphically in Fig. 3.

The average of these observations was plus or minus 2.0 millivolts, the error being plus or minus depending on whether the swing of the galvanometer for the unknown electromotive force was greater than the swing obtained with the standard cell. Actually, when the swing of the galvanometer for the unknown electromotive force was greater, the error was in all cases minus, and *vice versa.*

It will be noted from Fig. 3 that the error in 0.50000 volt was plus 2.0 millivolts. Fig. 3 was plotted from data obtained by using a Leeds and Northrup Type 1058 condenser where there are 57 possible direct series and parallel plate combinations, thus affording 57 possible variations of capacity. Actual readings of the galvanometer swings for the above point were 227.0 millimeters for the unknown electromotive force and 229.0 millimeters for the standard cell.

This is a variation of 2.0 millimeters in approximately 230.0 millimeters, the result of which is a difference of less than 0.9%. Even with this small variation in galvanometer swings, the resultant error was large, namely, 2.0 millivolts. This error might have been slightly reduced in case the use was made of a high grade precision condenser where a greater number of plate combinations is possible. It will be readily seen that such a means of decreasing this error as noted above, by a cut and try method of finding the exact combination of plates which would give *a* swing for the unknown electromotive force more nearly approximating that of the standard cell, would result in an excessive waste of time when compared with the potentiometer method for obtaining the same result.

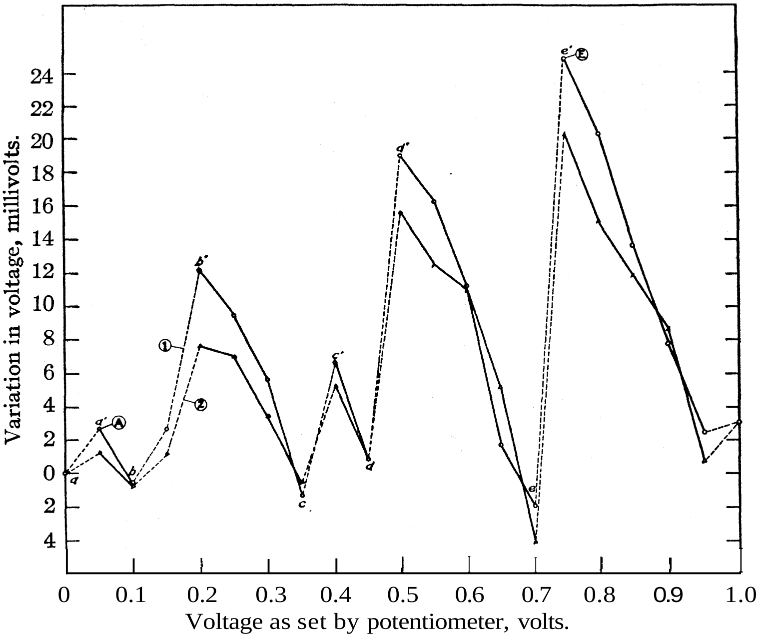

Fig. 4.

Fig. 4 shows several possible sources of error: first, the large error obtained when no account is taken of the equality of the galvanometer swings for the unknown electromotive force and the standard cell. This error is not a fixed one and depends largely on the differences between these two values of swing. This error is also a factor of the voltage, that is, point (A) was obtained with a difference in the swings of 67.0 millimeters, while with point (E) there was 25.0 millimeters' variation. This points out that large differences at low voltages will give less error than small differences at higher voltages. In other words, the best range at which to operate the swing on the galvanometer would be below 100 millimeters' rather than around 200 millimeters' deflection, as is generally assumed. In the next case, the slopes a-a', b-b' and c-c' are significant because they show a decrease in the error with the increase in voltage for each particular slope. The points on the slope a-a' were taken with one definite combination of plates; likewise for b-b' and c-c'. In each case it will be seen that as the voltage increases the deflection differences decrease and the error between the electromotive force for the potentiometer and that calculated from the standard cell with the condenser approaches a small value.

Finally, the error due to a high humidity condition surrounding the apparatus was considered. Curves 1 and 2 of Fig. 4 were plotted from data obtained with relative humidities 39.0 and 66.0%, respectively. Although these observations were made on separate days, care was exercised in order to have approximately all conditions except the humidity the same in each case. In other words, the combination of the plates of the condenser arranged for the proper capacity at each point was made identical, thus eliminating any possible error due to a change in plates or an error which might arise due to a marked difference in the deflection of the galvanometer. It will be seen from these, two graphs that with a high humidity the error is apparently decreased; this is no doubt due to a leakage of the charges from the plates and from the system comprising the condenser apparatus. Humidity will cause a difference in the insulation resistance of the condenser arrangement and consequently a variation in the leakage. This would include leakage across the terminals of the galvanometer, leakage across the terminals of the charge and discharge key and leakage between the leads to and from the various instruments. It will be noted that this is an important factor which might easily be overlooked and give conflicting results in case the atmospheric conditions were disregarded.

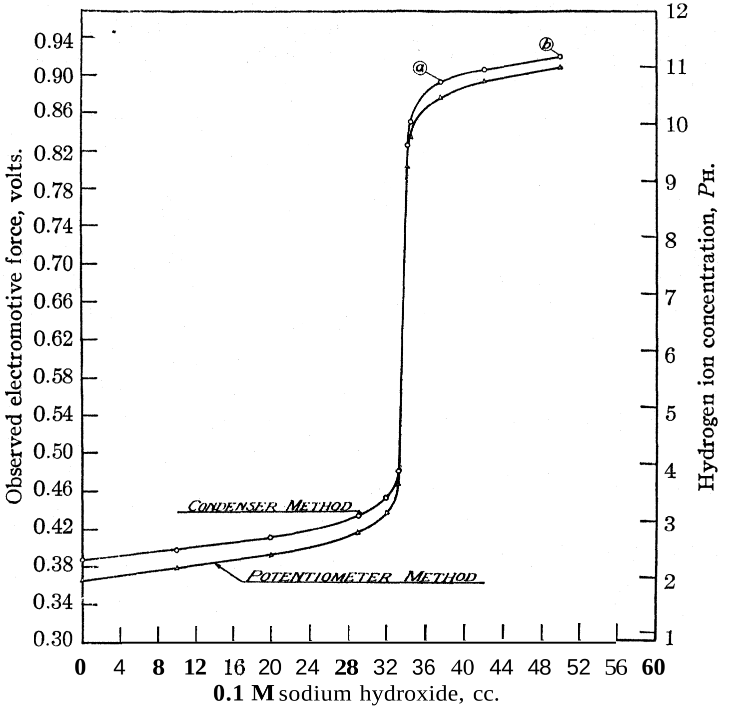

Fig. 5.—Titration of sulfuric acid with 0.1 M sodium hydroxide.

Fig. 5 represents a change in voltage when sulfuric acid was titrated with sodium hydroxide and shows typically the displacement which occurs when the condenser method is used to determine this electromotive force. Considering the irregularities of the errors obtained on different readings, one might assume that the curve obtained with the condenser would be somewhat jagged and not smooth in character. The lower section of the curve up to the beginning of the break does not agree with this view but is quite regular and is a very smooth curve. The reason for this is no doubt the fact that over this region one set of plates was used on the condenser. The accumulated errors on the plates were apparently greater than the errors set up by the inequality of the swings on the ballistic galvanometer. Therefore the displacement was practically constant throughout this region.

It will be seen that the curve obtained with the potentiometer and that with the condenser coincide at the inflection point. This must be so since the points are vertically displaced and the inflections here have assumed a perpendicular touching all the points of the two systems. Where the upper part flattens out again we have another disagreement between the two systems. The amount of this difference is slightly less than in the lower section of the curve. This again is no doubt due to the accumulated errors on the combination of the plates used on the condenser. Another consideration which seems to indicate that the plate error is considerably greater than the error of unequal swings is shown at points (a) and (b). At (a) the difference in the swing between the unknown and the standard electromotive force on the galvanometer was 7.5 mm., and at (b) this difference was practically zero. Even with this equality of swings the displacement for both points is nearly equal, which points out strongly that the error of displacement is from some other source which might well be due to the errors in the calibration of the plates of the condenser.

An important point which must be emphasized here is that the center of the break in the curve as obtained with the potentiometer is equivalent to a *P*H of 6.9, while with the condenser the center is equivalent to 7.2 in PH value. Although this difference may not have significance in a curve of one deflection, it is of vital importance when two deflections occur, such as in the titration of orthophosphoric acid.

What was said of the sulfuric acid curve regarding the displacement of the two systems as being due primarily to the summation of the plate errors, may also apply in the phosphoric acid titration curve. It can readily be appreciated that if the two breaks in the phosphoric acid curve are displaced due to the errors mentioned above, that difficulty might be encountered in showing the true relationship for the first and second end-points.

The purpose of the curve in Fig. 6 is to show the variation in the trend of the curve with a change in the combination of plates of the condenser. The section a-b was obtained by titrating orthophosphoric acid with sodium hydroxide and with the use of one combination of plates arranged for the most suitable capacity. The displacement is in accordance with that found in titrating sulfuric acid. Section b-c was obtained with a second combination of plates. It will be seen that the slope of the curve breaks very sharply at point b-b' due to the difference in the accumulated errors in the two sets of combinations. The smoothness of the curve when using the condenser method depends, therefore, upon the number of times the combinations of plates are changed. If any changes are made, a jagged curve is certain to arise. This is seen in Fig. **3,** where for each point a different set of plates was used.

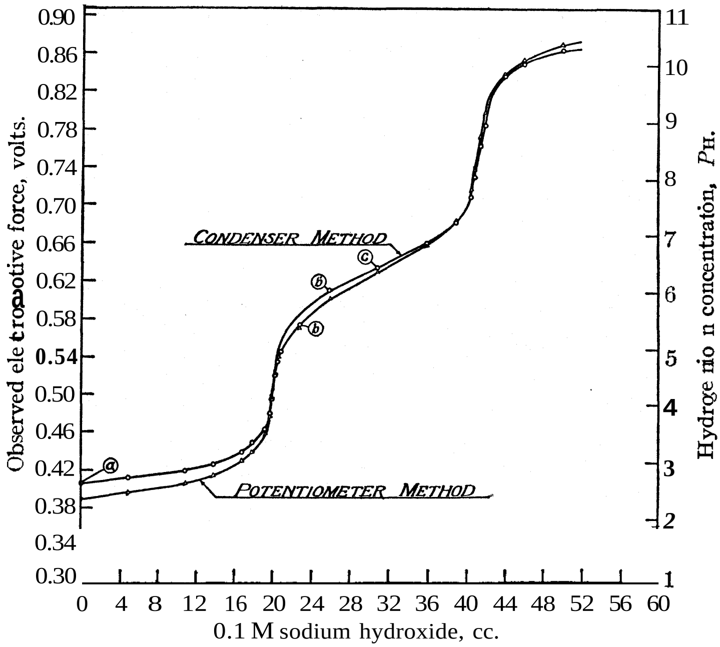

Fig. 6.—Titration of orthophosphoric acid with 0.1 M sodium hydroxide.

Mathematical Discussion of Errors

Since the galvanometer cannot be read to a value closer than plus or minus 0.1 mm., the following calculations will show the magnitude of such errors in the resultant electromotive force due to the personal error in reading the swing of the galvanometer.

$$\text{Electromotive force of the standard cell} \times \frac{\text{Gal. Swing Unknown}}{\text{Gal. Swing Known}} \times \frac{\text{Con. Cap. Known}}{\text{Con. Cap. Unknown}}$$

is equal to the Unknown Electromotive Force.

The following figures are taken from actual data as obtained during these experiments, the condenser arrangement being identical with that used by Davis, Oakes and Salisbury.[4]

$$1.01850 \times \frac{230.3}{229.0} \times \frac{0.183}{0.250} = 0.74979$$

Assuming a plus or minus 0.1 mm. difference of the two readings of the galvanometer, we have

$$1.01850 \times \frac{230.5}{228.8} \times \frac{0.183}{0.250} = 0.75106$$

This gives us an error of 0.00127 volt or 1.27 millivolts.

Since each plate of the standard mica condenser used is only accurate to plus or minus 0.25% and the manipulation to obtain equality of swing necessitates the arrangement of as many as five plates in parallel and series, one can easily see that an extremely large error may result from this cause. Calculating the resultant error due to the percentage variation on the average of three plates used for this point, we have

$$1.01850 \times \frac{230.3}{229.0} \times \frac{0.18346}{0.24937} = 0.75357$$

Here the difference between this value and the original value of 0.74979 volts gives an error of 0.00378 volt or 3.78 millivolts.

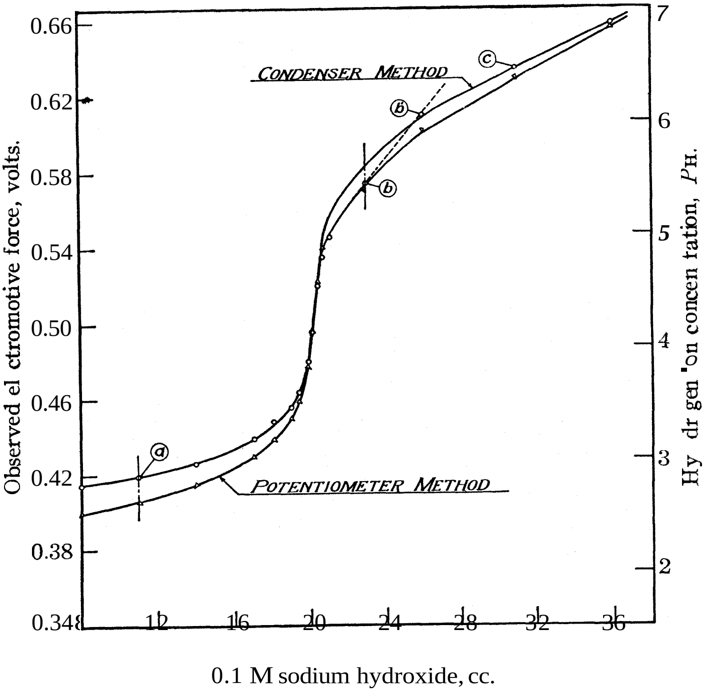

Fig. 7.—Section from Fig. 6 enlarged.

Since it is quite possible that the plate errors and errors due to the reading of the galvanometer swings might occur at the determination of the particular electromotive force stated above, we have a maximum possible error equal to the sum of these two errors, which is 5.05 millivolts.

When considering the use of a precision condenser similar to the type employed by Beans and Oakes[1] (Plug Type Precision Standard Mica Condenser, manufactured by Jas. G. Biddle), we have the values of capacitance accurate to approximately 0.1%. Calculating the resultant error due to this particular percentage variation in capacitance, for the above point in question, we have

$$1.01850 \times \frac{230.3}{229.0} \times \frac{0.18318}{0.24975} = 0.75128 \text{ volt}$$

With this added accuracy in capacitance values, we have still a noticeable error amounting to 0.00149 volt or 1.49 millivolts. Now we will have as a maximum possible error occurring at the determination of the particular electromotive force indicated above, a value equal to 0.00276 volt or 2.76 millivolts. These calculated maximum errors of 5.05 and 2.76 millivolts are equal to more than ten and five times, respectively, that quantity given by Beans and Oakes,[1] which states a precision of plus or minus 0.5 millivolt for the condenser system of measuring potentials.

It might be well to mention here that with small deflections amounting to approximately 70.0 mm., the above errors are greatly reduced because the multiplying factor is of a smaller quantity.

Although this may theoretically give a smaller error it will be apparent to those who have used a ballistic galvanometer that, for small deflections the time period is so much shorter than in higher ranges, it is doubtful whether the readings can be made to as close a value as plus or minus 0.1 mm. as assumed above. It would not be at all surprising if this error approached a value of approximately plus or minus 0.2 mm. It can be seen therefore that it is almost impossible to judge the accuracy of any electromotive force measurement as obtained by the use of the condenser system, and further it seems almost impossible to eliminate one or many of these sources of error.

The above formula as used for these calculations of the unknown electromotive force and, as recommended by Beans and Oakes,[1] requires the use of the electromotive force of the standard cell, which is assumed to be accurate to one or two in the fifth decimal place and multiplies this value by a factor, condenser capacity, which is accurate to only one in the third place.

When several independent sources of error conspire to produce a resultant error, we find that if any term in the operation is in doubt by say 1.0%, the product or quotient will be in doubt by 1.0% on account of that term alone. In other words, the product or quotient cannot therefore be more precise than the percentage precision of the least precise factor entering into the computation.[7] In the case of the example mentioned above, we can calculate the probable resultant error as follows.

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[7] F. W. Mellor, "Higher Mathematics for Students of Chemistry and Physics," Longmans, Green and Co., London, 1919.

$$Q = \frac{q^1\, q^2\, q^3}{q^4\, q^5}$$

where q^1 = electromotive force of the standard cell; q^2 = ballistic swing of the unknown electromotive force; q^3 = condenser capacity of the known electromotive force; q^4 = ballistic swing of the known electromotive force; q^5 = condenser capacity of the unknown electromotive force.

The percentage deviations are used in these calculations, for in such a function as above the percentage error in any component factor produces the same percentage error in the final quantity, that is

$$100\,\frac{\Delta q_n}{q_n} = 100\,\frac{\frac{\delta Q}{\delta q_n}\,(\Delta q_n)}{Q}$$

The value of Q was found to be equal to 0.74979 volt. Consequently, if E is the actual error in Q caused by errors e_1, e_2, e_3, e_4 and e_5, which arise from errors in the components, the percentage error in Q will be given by

$$100\,\frac{E}{Q} = \sqrt{\left(\frac{100\,\Delta q^1}{q^1}\right)^2 + \left(\frac{100\,\Delta q^2}{q^2}\right)^2 + \left(\frac{100\,\Delta q^3}{q^3}\right)^2 + \left(\frac{100\,\Delta q^4}{q^4}\right)^2 + \left(\frac{100\,\Delta q^5}{q^5}\right)^2}$$

from which the actual error E can be computed.

Using the data of the foregoing calculations, the percentage precision of Q becomes ±0.35%. The actual error E is then 0.74979 × 0.0035, which is 0.00252 volt or 2.52 millivolts.

The percentage precision of Q when using a precision condenser similar to the one employed by Beans and Oakes[1] becomes 0.15%. The actual error E would then be 0.74979 × 0.0015, which is 0.00112 volt or 1.12 millivolts. Here the value of the error is reduced somewhat as the accuracy of the condenser plates is plus or minus 0.1%.

General Summary and Conclusions

1. The use of the condenser and ballistic galvanometer in determining electromotive forces of solutions was employed by Carhart[2] and by Potter.[3]
2. The important errors in this method are due to the accumulation of errors on the plates of the condenser, the throw of the galvanometer, humidity and the formula used in the calculation of the unknown electromotive force.
3. The important errors have been calculated and graphs drawn to show the significance of such errors in the titration of sulfuric acid and orthophosphoric acid.
4. The accumulative error may sometimes reach a value approximating plus or minus 3.0 to 4.0 millivolts.
5. Results seem to indicate that the condenser system of electromotive force measurements cannot be used where precise work is required, such as in the titration of solutions or in the determination of equilibrium constants.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF HARVARD UNIVERSITY AND OF THE WEST VIRGINIA GEOLOGICAL SURVEY]

THE NORMAL POTENTIAL OF THE IODINE–IODIDE ELECTRODE

BY GRINNELL JONES AND B. B. KAPLAN

RECEIVED FEBRUARY 23, 1928 PUBLISHED AUGUST 4, 1928

Historical Introduction

There is considerable confusion in the literature because of different definitions of the normal potential of the iodine–iodide electrode by various authors. In the following discussion we shall use the term normal potential of the iodine–iodide electrode to mean the potential of the cell Pt, I_2 (solid), I^- (activity = 1.0); 1.0 *N* KCl, HgCl, Hg containing a platinum electrode immersed in a solution which is in equilibrium with solid iodine and which has the iodide ion present at such a concentration that its activity is unity, measured against a normal (1 mole of KCl per liter) calomel electrode, and with corrections applied for liquid junction potentials. In accordance with the usual convention a positive sign of the potential would mean that the mercury is the positive pole of the cell and the platinum the negative pole. As a matter of fact, in this case the platinum is positive and the mercury negative, which is indicated by using a negative sign.

The other definition used by some authors postulates instead of solid iodine a solution in which the activity or concentration of the dissolved free iodine is unity. The concentration of free iodine (I_2) in water saturated with iodine at 25° is 0.00132.[1] Since this solution is dilute and free from ions the activity of iodine may be taken as equal to its concentration, 0.00132, and this figure may be used for any aqueous solution saturated with iodine. Therefore the difference between these two definitions at 25° is $(RT/2F) \ln 1.0/0.00132 = 0.0851$ volt.

At 0° the activity[2] is 0.000635 and therefore the difference between the two definitions is $(RT/2F) \ln 1.0/0.000635 = 0.0866$ volt. These corrections will be applied if necessary in the following discussion to make the results of the various authors comparable. In case the other authors referred to have omitted liquid junction corrections or defined the normal calomel electrode differently, no correction will be applied for this variation from the definition given above.

The work of Crotogino[3] and of Sammet[4] is similar in technique and the

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[1] W. C. Bray, THIS JOURNAL, 32, 932 (1910); W. C. Bray and E. L. Connolly, *ibid.*, 33, 1485 (1911).

[2] Grinnell Jones and B. B. Kaplan, *ibid.*, 50, 1845 (1928).

[3] F. W. Küster and F. Crotogino, Z. anorg. *Chem.*, 23, 87 (1900); F. Crotogino, *ibid.*, 24, 247 (1900).

[4] V. Sammet, Z. *physik. Chem.*, 53, 674 (1905).

results agree within one millivolt. They measured the potential of a platinum electrode immersed in solutions of potassium iodide varying from about 0.001 N to 1.0 *N* saturated with solid iodine against a calomel electrode. Crotogino did not attempt to compute a normal potential from his data. Sammet computes the normal potential on the assumption that exactly one-half of the iodide is converted into tri-iodide and that the concentration can be computed from the conductivity and applies no liquid junction corrections. It is now known that both of these assumptions are only approximately true. These results show an apparent shift in the normal potential with dilution from —0.256 volt in the more concentrated solutions to —0.278 in 0.001 N KI. He regards the value obtained with the more concentrated solutions as the more reliable, which would not be the modern interpretation.

Maitland[5] was the first to use solutions of potassium iodide containing less iodine than is required to saturate the solutions (about $^1/_3$ to $^1/_{30}$ saturated). The amount of free iodine was determined by distribution experiments using carbon tetrachloride. The concentration of the potassium iodide varied from 1.0 N to 0.1 N. The degree of ionization assumed was based on conductivity data. No liquid junction correction was applied. The results show a distinct systematic variation with the degree of saturation of iodine and with the concentration of the potassium iodide but Maitland averages all of the results, obtaining —0.2569 in good agreement with Sammet's result derived from 1.0 N KI saturated with iodine. Unfortunately Maitland's measurements did not extend below 0.1 *N*. All the earlier workers either made no measurements below 0.1 N or rejected their measurements in dilute solutions as unreliable.

Jones and Schumb[6] made measurements with saturated iodine electrodes with 0.1 *N*, 0.05 N and 0.02 N KI, interpreted by the use of data by Bray and MacKay[7] on the tri-iodide formation, obtaining —0.2658, —0.2558 and —0.2549 at these concentrations. They were the first to apply the liquid junction correction. All investigators agree that the more dilute the KI solution the greater is the difficulty in obtaining definite and reproducible experimental results; but the theoretical interpretation of the data on dilute solutions is more reliable. Jones and Schumb also made measurements at 0° which when recomputed with the definition given above give —0.2536, —0.2534 and —0.2528 with 0.1 N, 0.05 N and 0.02 N KI, respectively. The systematic variation of the results with concentration made it desirable to extend the measurements to still greater dilution but Jones and Schumb were unable to obtain definite results with 0.01 N

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[5] W. Maitland, *Z. Elektrochem.*, **12,** 263 (1906).

[6] Grinnell Jones and W. C. Schumb, *Proc. Am.* Acad., 56, 226 (1921).

[7] Bray and MacKay, THIS JOURNAL, **32,** 914 (1910); Grinnell Jones and M. L. Hartmann, *ibid.*, 37, 241 (1915).

solution and therefore the results were averaged, giving —0.2555 at 25° and —0.2533 at 0°.

The measurements of Maitland have been recomputed by Lewis and Randall,[8] who were the first to reject the calculation of the concentration of the ions from the conductivity and substitute instead the activity of the iodide ion as determined from thermodynamic considerations. They also use a new conventional definition of the normal calomel electrode as the potential measured against 0.1 N KCl, 1 N KCl, HgCl, Hg, with no correction applied for the liquid junction potential between 0.1 *N* KCl and 1 N KCl. The usual formulas for the computation of liquid junction potentials give 0.0004 volt for this potential, the dilute solution being negative. Therefore to make this result comparable with results against 1 N KCl calomel electrode without the intervention of 0.1 N KCl, a correction of – 0.0004 volt should be applied. Lewis and Randall used Maitland's results with 0.1 N KI only and assumed that the activity coefficient of the iodide ion in this solution is 0.794 (instead of assuming that the degree of dissociation is 0.86 as was done by Maitland), with the following results.

TABLE I

NORMAL POTENTIAL OF IODINE–IODIDE ELECTRODE COMPUTED BY LEWIS AND RANDALL AFTER MAITLAND

KI, KI_3	Degree of saturation	*E*
0.1 *N*	0.3127	–0.2530
.1 *N*	.0881	– .2541
.1 *N*	.0686	– .2542
.1 *N*	.0338	– .2539

The change in the method of calculation thus influences the result by more than 2 millivolts.

The results of a research by Lewis and Faragher (which so far as we know has not been published in detail) are also given by Lewis and Randall. In these experiments several mixtures of potassium chloride and potassium iodide were shaken with a standard solution of iodine in carbon tetrachloride to make them 0.1411 saturated with iodine. The normal potential is computed by the use of the activities of the ions from the tables of Lewis and Randall, giving —0.2539 volt.

By combining measurements by Gerke[9] of an iodine electrode against a lead–lead iodide electrode with measurements by Lewis and Brighton[10] of this lead–lead iodide electrode against a normal calomel electrode (as defined by Lewis and Randall) the result —0.2531 has been computed.

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[8] G. N. Lewis and M. Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Company, New York, 1923, p. 428.

[9] R. H. Gerke, THIS JOURNAL, 44, 1703 (1922).

[10] G. N. Lewis and T. B. Brighton, *ibid.*, 39, 1906 (1917); G. N. Lewis and M. Randall, ref. 8, p. 430.

McKeown[11] has carried out experiments similar to those of Crotogino and of Sammet, using solutions saturated with iodine varying from 0.1 N to 0.001 N in potassium iodide. McKeown's results differ greatly from all others. He regards his data obtained with the 0.001 N solutions as the most reliable and concludes that –0.2454 is the normal potential of the iodine electrode. This value is nearly one centivolt different from the value obtained by all other investigators and since McKeown fails to point out any source of error in the earlier work this figure does not deserve serious consideration,

Murray[12] measured the potential of a cell Pt, $xI_2 + yKI$ 0.1 N KCl, HgCl, Hg in which x and y were much less than 0.1 N. The effect of triiodide formation was allowed for by computation. He determined the equilibrium constant 0.001390 by the distribution method for this purpose and uses Lewis and Randall's tables of activities. He gives 0.6204 against the hydrogen electrode for an assumed free iodine of unit activity. If this is reduced to the normal calomel electrode by applying the correction –0.2818 (see pages 2075–2076) and to saturated iodine by the correction –0.0851, it becomes –0.2535.

Experimental

The innovation of Lewis and Randall in using the activity of the iodide as determined thermodynamically is undoubtedly sound but the experimental basis for the values of the activity coefficients of the individual ions at the various concentrations[13] is yet meager and is not fully explained by them except in general terms. The values given in their table for the activity coefficient of the iodide ion at various concentrations are not supported by references to experimental data but are probably mainly based on the assumption that they are the same as the chloride ion at the corresponding concentration. They do not give references to experimental proof of this assumption but it wins some support from the measurements of Pearce and Fortsch.[14]

It therefore seemed desirable to check up the values for the activity coefficient of the iodide ion, f, as given in the table of Lewis and Randall. The change in activity coefficient of the iodide ion with dilution can be computed from measurements of the potential of concentration cells with transference, with silver–silver iodide electrodes. The relative activity coefficients at the two concentrations can then be computed by the well-known formula

$$E_2 - E_1 = -2t_K \frac{RT}{F} \ln \frac{c_2 f_2}{c_1 f_1}$$

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[11] A. McKeown, *Proc. Faraday Soc.*, **17**, 517 (1922).

[12] H. D. Murray, *J. Chem. Soc.*, *127*, 882 (1925).

[13] G. N. Lewis and M. Randall, ref. 8, p. 382.

[14] J. N. Pearce and A. R. Fortsch, THIS JOURNAL, 45, 2852 (1923).

Fortunately in this case the mobility of the potassium ion (74.8) and of the iodide ion (76.5) are so nearly alike that the liquid junction potential is small. The factor $2t_K$ (twice the transference number of the potassium ion), which gives the effect of the unequal mobilities of the ions at the liquid junction on the measured potential, is $(2 \times 74.8)/(74.8 + 76.5) = 0.989$. Therefore the liquid junction potential is only 1.1% of the measured potential. We measured the potential of a silver–silver iodide electrode in 0.1 N KI against a similar electrode in various other concentrations of KI at 25°. The ground stopper type of cell was used. An electrostatic condenser was used to increase the sensitiveness as described by us in an earlier paper.[15] Constant and reproducible results were obtained using 0.05 N and 0.02 N KI measured against 0.1 N KI, but variable, non-reproducible, mostly abnormally high values were obtained with the more dilute solutions tried. Unfortunately the work had to be interrupted before the proper technique was developed to overcome this difficulty with the dilute solutions. Only the results which we believe to be reliable are published. The duplicate results given were obtained with

TABLE II

POTENTIALS OF CELLS OF THE TYPE Ag, AgI, 0.1 *N* KI; c_x*N* KI, AgI, Ag

c_x	Volts	$\text{Log}\,\frac{f_1}{f_x}$
c_1 0.1 N	0.0000	
c_2 .05 N	.0160	
	.0159	
Mean	.01595	−0.0283
c_3 .02 *N*	.0376	
	.0377	
Mean	.03765	− .0552

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[15] Jones and Kaplan, THIS JOURNAL, 50, 1853 (1928). After the publication of our earlier paper and while this paper was in proof the article by Beans and Oakes, THIS JOURNAL, 42, 2116 (1920), first came to our attention. Beans and Oakes describe the use of a condenser and ballistic galvanometer to measure the voltage of a cell with high internal resistance. In their arrangement the total voltage of the cell is impressed on the condenser, then discharged through the galvanometer and the total voltage inferred from the scale reading of the calibrated galvanometer. An accuracy of 0.5 millivolt was obtained. In our arrangement the condenser and galvanometer are used as null instruments. Only the difference between the setting of potentiometer and the potential of the cell is impressed on the condenser and the potentiometer is adjusted until this difference becomes zero, so that the voltage of the cell is obtained from the setting of the potentiometer, which is an advantage. No calibration of the galvanometer is necessary. With our arrangement a senitiveness of 0.02 millivolt was obtained in measuring a cell having 1,600,000 ohms internal resistance. Moreover, our arrangement is superior to that of Beans and Oakes in avoiding errors due to leakage and dielectric absorption, since the potential impressed on the condenser need never exceed one millivolt.

new electrodes and solutions. The values given remained constant for many hours.

Brönsted[16] found empirically that the activity coefficient, f, varies with the concentration in accordance with the equation

$$\log f = -3\alpha\sqrt{c} + 2\beta c$$

where a and β are constants. This relationship has since been deduced from the Debye-Hückel theory.[17] We may therefore write

$$\log \frac{f_1}{f_2} = -3\alpha(\sqrt{c_1} - \sqrt{c_2}) + 2\beta(c_1 - c_2)$$

or

$$-0.0283 = -3\alpha(\sqrt{0.1} - \sqrt{0.05}) + 2\beta(0.1 - 0.05)$$

and similarly

$$-0.0552 = -3\alpha(\sqrt{0.1} - \sqrt{0.02}) + 2\beta(0.1 - 0.02)$$

From these equations the values of -3α and 2β have been computed and substituted in the general equations, giving

$$\log f = -0.373\sqrt{c} + 0.125\,c$$

From this equation the values of the activity coefficient, f, have been computed at various concentrations and the results are compared in Table III with the values given in the tables of Lewis and Randall and with the degree of dissociation as computed from the conductivity.

TABLE: III

ACTIVITY COEFFICIENTS OF THE IODIDE ION AT VARIOUS CONCENTRATIONS AT 25°

c	f, calcd. from our equation	f, from Lewis and Randall	Dissoc. from conductivity
0.1	0.784	0.79	0.859
.05	.837	.84	.888
.02	.891	.89	.9205
.01	.920	.92	.940
.005	.943	.95	.955
.002	.963	.97	.970
.001	.973	.98	.978
.000	1.000	1.00	1.000

The agreement between our new results and the table of Lewis and Randall is good. The values of the degree of ionization computed in the conventional manner from the conductivity are unmistakably different.

The new equilibrator which we invented for this purpose and have described in a separate article[18] gives a means of avoiding the dilemma which has introduced some uncertainty in the earlier work on the iodine electrode. Some experimenters (Crotogino, Sammet, Jones and Schumb, McKeown) have used solutions saturated with iodine, thereby making

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[16] J. N. Bronsted, THIS JOURNAL, 44, 938 (1922).

[17] E. Hückel, *Ergebnisse der exakten Wissenschaften*, 3, 249 (1924); G. Scatchard, THIS JOURNAL, 47, 648 (1925).

[18] Grinnell Jones and B. B. Kaplan, *ibid.*, 50, 1600 (1928).

liquid junctions and osmotic corrections large and risking errors due to higher polyiodides. Others (Maitland, Lewis and Randall, Lewis and Faragher) have decreased these difficulties by using solutions unsaturated with iodine but have been obliged to fix the iodine concentration by shaking with carbon tetrachloride, thereby risking analytical errors due to emulsified carbon tetrachloride, or a change in the nature of the solvents due to solution of carbon tetrachloride in the water. With the new equilibrator we can use solutions containing only a little iodine and fix this concentration accurately without the use of any other medium. Furthermore, the improvement in potentiometer which we have described[19] has made it possible to work with 0.01 *N* solutions successfully.

In Table IV below, E_s is the measured potential of the cell Pt, I_2 (solid) xN KI; 0.1 *N* KCl, HgCl, Hg, taken from the measurements of Jones and Schumb for the 0.1 N, 0.05 N, and 0.02 N solutions. We made new measurements using 0.01 N KI against 0.1 *N* calomel electrodes, using the cell with liquid junction in a ground stopper. The measured difference between the decinormal and normal calomel electrode is —0.0529 according to Lewis, Brighton and Sebastian[20] and this figure has been exactly confirmed by Jones and Schumb. For the reason explained above the liquid junction of -0.0004 should be added giving -0.0533 as the value to be added to change from decinormal to normal calomel electrode. E_2 is the measured potential of the cell Pt, I_2 (unsat.) xN KI; xN KI, I_2 (solid), Pt, in which the composition of the unsaturated solution was determined by the equilibrator and is shown at the top of the column.[21] E_j is the liquid junction correction, which is the potential between 0.1 *N* KCl and the KI solution unsaturated with iodine shown at the top of the column. It should be noted that by the use of the equilibrator this correction is reduced to a small value. This reduction in magnitude is important because the calculation is relatively uncertain. $E_c = (RT/2F) \ln I_2 \text{ (unsat.)}/0.00132$ makes proper allowance for the unsaturation of the iodine. In order to obtain the potential in a solution of unit activity in iodide ion the quantity $-(RT/F) \ln fI$ must be added. For convenience in computation and analysis, this is split up into two terms $E_0 + E_f = -(RT/F) \ln I - (RT/F) \ln f$. The values of the activity coefficient used are taken from Col. 2 of Table III.

These results show a gratifying concordance with no evidence of systematic variation with the concentration of either potassium iodide or of iodine. If the activity coefficients from the tables of Lewis and Randall are used, the following results will be obtained: 0.1 N KI, —0.25458; 0.05 N KI, —0.25447; 0.02 *N* KI, —0.25447; 0.01 *N* KI, —0.25434.

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[19] Jones and Kaplan, THIS JOURNAL, 50, 1853 (1928).

[20] G. N. Lewis, T. B. Brighton and R. L. Sebastian, *ibid.*, 39, 2245 (1917).

[21] The method of using the equilibrator with these solutions is explained in more detail in our recent paper, *ibid.*, 50, 1845 (1928).

These results show a slight systematic variation with concentration which disappears when our values for the activity coefficient are used. The difference between our value of the normal potential and the value of Lewis appears to be due chiefly to the fact that Lewis used the measured difference for the potential between decinormal and normal calomel electrode, −0.0529, ignoring the liquid junction potential between decinormal and normal potassium chloride. This potential, like all liquid junction potentials, is somewhat uncertain but it may be computed to be −0.0004 volt. If our data are computed with the Lewis convention, the result would be −0.2540 (compared with his result, −0.2539).

TABLE IVA

NORMAL POTENTIAL OF IODINE–IODIDE ELECTRODE AT 25°

	0.1 N KI		0.05 N KI			
ΣK, g. mol /l	0.10000	0 10000	0 04994	0 04977	0 04998	0 05000
% sat with I_2	9.4%	5.37%	33.4%	5.8%	2.4%	2.35%
I_2, g. mol./l.	.00012413	.000070864	,0004413	.00007647	.000031518	.00003111
ΣI_3, g. mol./l.	.0081219	.0047946	.012055	.0025935	.0011219	.0011053
ΣI, g. mol./l.	.091878	.095205	,037885	.047176	.048858	.048895
E_s: Pt, I_2 sat., D. E.	− .28040	− .28040	− .29760	− .29760	− .29760	− .29760
D.E:N.E.	− .05330	− .05330	− .05330	− .05330	− .05330	− .05330
E_2: Pt, I_2 unsat., I_2 sat, Pt	+ ,04240	+ .05030	+ .02250	+ .04950	+ .06160	+ .06180
E_j, volts	− ,00030	− .00009	− .00054	+ .00062	+ .00079	+ .00078
E_c, volts	− ,03037	− .03757	− .01407	− .03659	− .04798	− .04814
E_o, volts	+ ,06133	+ .06042	+ 08409	+ .07834	+ .07756	+ ,07754
E_f, volts	+ ,00625	+ .00625	+ 00457	+ 00457	+ .00457	+ .00457
E	− .25439	− .25439	− .25435	− .25446	− .25436	− 254356
Averages	−0.25439		−0.25438			

TABLE IVB

NORMAL POTENTIAL OF IODINE–IODIDE ELECTRODE AT 25°

	0.02 N KI		0 01 N KI
ZK, g. mol./l.	0.02000	0.02000	0.01000
% sat. with I_2	13 2%	6 3%	100%
I_2, g. mol./l.	.0001745	.00008353	.00132
ΣI_3, g. mol./l.	,0021923	.0011105	.004865
ΣI, g. mol./l.	,017808	.0188895	.005135
E_s: Pt, I_2 sat., D. E.	− .32000	− ,32000	− .33740
D.E.: N.E.	− .05330	− ,05330	− .05330
E_2: Pt, I_2 unsat., I_2 sat. Pt	+ ,03710	+ .04830	0
E,, volts	+ .00097	+ .00130	− .00121
E_c, volts	− .02599	− ,03546	0
E_o, volts	+ .10349	+ ,10197	+ .13543
E_f, volts	+ .00296	+ 00296	+ .00214
E	− .25477	− .25423	− .25434
Averages	−0.2545		− ,25434

In similar fashion measurements are carried out at 0° and reported in Table V.

TABLE V

NORMAL POTENTIAL OF THE IODINE–IODIDE ELECTRODE AT 0°

ZK, g. mol./l.	0.10017	0.10017	0.10017	0.10017
% sat. with I_2	14.7%	8.3%	4.2%	4.1%
I_2, g. mol./l.	0.00009328	0.00005241	0.000027008	0.00002624
ΣI_3, g. mol./l.	.011297	.0069116	.0036460	.0035358
ΣI, g. mol./l.	.088873	.093258	.096524	.096634
E_s: Pt, I_2 sat., D. E.	− .2753	− .2753	− .2753	− .2753
D. E.. N. E.	− .0489	− .0489	− .0489	− .0489
E_2: Pt, I_2 unsat., I_2 sat., Pt	+ .0317	+ .0391	+ .0478	+ .0483
E_j, volts	.0000	+ .0002	+ .0004	+ .0004
E_c, volts	− .0226	− .0294	− .0372	− .0375
E_o, volts	+ .0570	+ .0559	+ .0551	+ .0550
E_f, volts	+ .0057	+ .0057	+ .0057	+ .0057
E: Pt, I_2 sat., I = 1.0, N. E.	− .2524	− .2527	− .2524	− .2523
Average			− .2524	

	0 05 *N* KI			0 02 *N* KI		0 01 *N* KI
ΣK, g. mol./l.	0.05000	0 05000	0 05000	0.02000	0.02000	0.01000
% sat.	4.8%	4 6%	4.3%	9.8%	2.8%	100%
I_2, g. mol./l.	.000030255	.00002935	.00002712	.000062015	.00001758	.000635 .
ΣI_3, g. mol./l.	.0019537	.0019746	,0017969	.0015885	.00048242	.004719
XI, g. mol./l.	.048046	.048025	,048203	.018412	.019518	.005277
E_s	− .2909	− .2909	− ,2909	− .3114	− ,3114	− .3275
D. E., N. E.	− .0489	− .0489	− .0489	− .0489	− .0489	− .0489
E_a	+ .0474	+ .0475	+ .0489	+ 0380	+ .0539	0
E_j	+ .0008	+ .0008	+ .0008	+ .0010	+ .0013	− .0015
E_c	− .0358	− .0362	− .0371	− .0274	− .0422	0
E_o	+ .0715	+ .0715	+ .0714	+ .0940	+ .0926	+ .1234
E_f	+ .0042	+ .0042	+ .0042	+ .0027	+ .0027	+ .0020
E	− .2517	− .2520	− .2516	− .2520	− .2520	− .2525
Averages		−0.2518		− .2520		− .2525

These results are not so concordant or reliable as the results for 25° for two reasons. (1) It is more troublesome to maintain a constant temperature at 0° in the equilibrator for the longer time necesssary to obtain equilibrium with iodine (unfortunately this work had to be done in June and July and there were several very hot nights so that the ice in the tub was nearly gone by morning). (2) Owing to unavoidable interruptions of the work, we have no direct measurements of the activity coefficient of the iodide ion at 0° but are compelled to assume provisionally that the activity coefficients are the same at 0° as at 25°.

The results on the normal potential of the iodine–iodide electrode are summarized in the following table. In this table the figures given by the authors have been changed if necessary to make them applicable to a saturated iodine electrode; but no corrections to the authors figures have been applied on account of liquid junction potential, variations in definition of normal calomel electrode, or to the use of activity instead of concentration.

TABLE VI

THE NORMAL POTENTIAL OF THE SATURATED IODINE–IODIDE ELECTRODE WITH IODIDE ION AT UNIT ACTIVITY AGAINST THE NORMAL CALOMEL ELECTRODE

Observer	Date	At 25°, volts	At 0°, volts
Crotogino	1900	−0.266	......
Sammet	1905	− .256	......
Maitland	1906	− .2569	......
Jones and Schumb	1921	− 2555	−0 2525
McKeown	1922	− 2454	......
Gerke	1922	− 2531	......
Lewis and Randall	1923	− .2539	......
Lewis and Faragher	1923	− .2539	......
Murray	1925	− 2535	......
Jones and Kaplan	1928	......	......
From 0.1 N KI		− ,25439	− .2524
From 0.05 N KI		− .25438	− .2518
From 0.02 N KI		− .2545	− .2520
From 0 01 *N* KI		− ,25434	− .2525
Averages		− .2544	− .2522

It is of some interest to express the normal potential of the iodine–iodide electrode against the hydrogen electrode instead of against the calomel electrode. Unfortunately, there seems to be more uncertainty as to the difference between the hydrogen and calomel electrodes than between the iodine and calomel electrodes. In 1917 Lewis, Brighton and Sebastian found for Hg, HgCl, KCl (1 mole per liter), 0.1 N KCl, H^+ (activity 1.0), H_2, (g); E = −0.2828. In 1923 Lewis and Randall in their book on Thermodynamics, p. 407, changed this figure to −0.2822. The change is caused by revision of the activity coefficients used in the calculations. This value has come into common use. Very recently Randall and Young[22] have cast serious doubt on the reliability of this figure. They find that the presence of air influences the potential of the hydrochloric acid calomel electrodes but not the potassium chloride calomel electrode. They also redetermine the activity coefficients of hydrochloric acid solutions. From these experiments they conclude that the difference between the calomel and hydrogen standards is −0.2812, a value differing by 1 millivolt from the figure of Lewis and Randall. In a matter of this importance independent confirmation is desirable. Pending such confirmation and systematic recomputation on the hydrogen basis of all normal potentials determined by the aid of the calomel electrode, we shall provisionally use the older value of Lewis and Randall, −0.2822. This must be changed by 0.0004 volt on account of the different definitions of the calomel electrode used by Lewis and Randall and the definition adopted in this paper (see page 2066). The result will thus be on the same basis as most other recent values for normal potentials. We may therefore write

[22] M. Randall and L. E. Young, THIS JOURNAL, 50,989 (1928).

Pt, I_2 sat., I^- ($a = 1.0$), 1 *N* KCl, HgCl, Hg	$E = -0.2544$
Hg, HgCl, 1 *N* KCl, 0.1 *N* KCl, H^+ ($\alpha = 1.0$) H_2 (g), Pt	$E = -0.2822$
Liquid junction correction 1 N KCl, 0.1 N KCl	$E = +0.0004$
Pt, I_2 sat., I^- ($a = 1.0$), H ($\alpha = 1.0$) H_2 (g)	$E = -0.5362$

No attempt will be made at this time to compute the normal potential of the iodine–iodide electrode referred to the hydrogen electrode at 0°, owing to inadequate data on the difference between hydrogen and calomel electrodes at this temperature.

Summary

The normal potential of the iodine–iodide electrode has been redetermined, using solutions containing so little free iodine that the effect of formation of tri-iodide is minimized and can be accurately allowed for. The activity of the iodine has been determined by a new device. The activity coefficient of the iodide ion in solutions of potassium iodide has been determined by measurements of the potential of iodide concentration cells with transference containing silver–silver iodide electrodes. The results can be expressed by the formula of the form suggested by Bronsted: $\log f = -373\sqrt{c} + 0.125\,c$. The normal potential of the iodine–iodide electrode against the normal calomel electrode at 25° is found to be —0.2544 volt; and at 0° is found to be —0.2522 volt.

CAMBRIDGE, MASSACHUSETTS
MORGANTOWN, WEST VIRGINIA

[CONTRIBUTION FROM THE DEPARTMENT OF PHYSIOLOGY, YALE UNIVERSITY]

THE EXTRAPOLATION OF ELECTROMOTIVE FORCE MEASUREMENTS TO UNIT IONIC ACTIVITY

BY DAVID I. HITCHCOCK

RECEIVED APRIL 7, 1928 PUBLISHED AUGUST 4, 1928

The relation between the electromotive force, E, of a cell such as Ag, AgCl, HCl, H_2 and the mean activity coefficient, γ, of the ions of the electrolyte is given by the equation

$$E = E_0 - 2k \log m - 2k \log \gamma \qquad (1)$$

Here m is the molality of the acid, k is 2.3026 RT/NF, and E_0 is the electromotive force which the cell would have if the mean activity of the ions, or the product $m\gamma$, were equal to unity. In order to calculate activity coefficients from electromotive force data alone, it is necessary to determine the value of E_0 by extrapolation. This has usually been done, following Lewis and Randall,[1] by plotting the quantity E_0', which is defined as E + 2k log m, against $\sqrt{m}$. Since $\gamma = 1$ when m = 0, it follows from equation (1) that $E_0' = E_0$ when m = 0. Curves which have

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[1] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, 1923, p. 335.

been obtained in this way for aqueous hydrochloric acid[1,2] are straight lines only for the region of extreme dilution (well below 0.01 M), where the scattering of the points makes the position of the line, and hence the extrapolated value, somewhat uncertain.

If the Debye-Huckel equation, in its simplest approximate form

$$-\log \gamma = 0.5\sqrt{m} \tag{2}$$

applies to the data, it follows from Equations (1) and (2) that a plot of E_0' against $\sqrt{m}$ should be a straight line of slope equal to k over the range where the approximate equation holds. Scatchard[2a] found it possible to draw a curve whose slope approached this value asymptotically at $m = 0$, using data obtained by himself, by Linhart,[3] and by Noyes and Ellis.[4] Nonhebel[2b] found that his data when plotted in this way gave points falling around a line having a slope equal to $0.78k$. He concluded, therefore, that his data were not in agreement with the Debye theory.

The method of extrapolation just described lays great weight on the determinations in very dilute solutions, where the measurements are reproducible only with difficulty and where, as Randall and Young[5] have pointed out, all existing data are probably erroneous on account of the solubility of glass. It would therefore be desirable to find a method of extrapolation from the more reliable determinations at somewhat higher concentrations.

If the Debye-Huckel theory holds, any experimental data should agree with the second approximate equation over a wider range than with the first. For the case in question this equation is

$$-\log \gamma = 0.5\sqrt{m} - Bm \tag{3}$$

where B is an additional constant whose value is not known independently. This form of equation has been shown by Brönsted,[6] Scatchard,[7] and others to apply to a number of electrolytes, in some cases up to 0.1 M. The combination of Equations (1) and (3) gives

$$E + 2k\log m - k\sqrt{m} = E_0 - 2kBm \tag{4}$$

or

$$E_0' - k\sqrt{m} = E_0 - 2kBm. \tag{4a}$$

Over the range where Equation (3) holds, it follows that the left member of Equation (4) or (4a), which may be called E_0'', should be a linear function of m.[8] Moreover, if Equation (4) holds, it follows that $E_0'' = E_0$ when $m = 0$.

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[2] (a) Scatchard, THIS JOURNAL, *47, 641 (1925);* (b) Nonhebel, *Phil. Mag.,* [7] *2,* 1085 *(1926).*

[3] Linhart, THIS JOURNAL, 41, *1175 (1919).*

[4] Noyes and Ellis, *ibid.,* **39,** *2532 (1917).*

[5] Randall and Young, *ibid., 50,989 (1928).*

[6] Bronsted, *ibid., 45,2898 (1923).*

[7] Scatchard, *ibid.,* 47, *648 (1925).*

[8] The quantity E_0'' was used by Nonhebel and Hartley, *Phil. Mag. [6]50,* **729** (1925), who called it E_0 Debye, and found, in the case of hydrogen chloride in methyl alcohol, that it was a linear function not of m but of $\sqrt{m}$.

Hence this furnishes a method of extrapolation for the determination of E_0. If the experimental points fall on a straight line over a range of concentration where the data are reliable, a linear extrapolation to $m = 0$ may be made with considerable confidence.

If the complete equation of Huckel[9] applies to the data, this method of plotting cannot give a truly straight line for more than a limited range. Scatchard[10] has calculated values of γ from this equation for aqueous hydrochloric acid at 25°, using electromotive force data only for the empirical determination of two constants in the equation. By substituting these values of γ in Equation (1), it is possible to calculate values for $E - E_0$ and hence, using the definition of E_0'', values of $E_0 - E_0''$. These calculated values, when plotted against m, appear to deviate slightly from a straight line above 0.02 M. A straight line through the points at 0.02 and 0.05 M makes the extrapolated value 0.2 millivolt too low. Hence the complete theory is not in agreement with an exactly linear plot. The theoretical points, however, deviate so little from a straight line, even up to 0.1 M, that it is possible to make an exact extrapolation from them by the use of a flexible spline which is held on the points at 0.01, 0.02, 0.05 and 0.1 M. Below 0.02 M the curvature is inappreciable. Hence this method of extrapolation, if a spline is used instead of a straight rule, gives a result in full agreement with the complete equation of Hiickel.

The application of this method to the available experimental data[2a,b,3,4,5,11] for aqueous hydrochloric acid up to 0.1 M, at the temperatures 20, 25 and 30° is shown in Fig. 1. The curves were drawn with a spline from the points at 0.01 M and above, before the points for lower concentrations were plotted. The deviation of these curves from straight lines is so slight below 0.05 M that its effect on the extrapolated value is less than 0.1 millivolt. The position of the line for 25° is rather arbitrary on account of the multiplicity of discordant determinations. The values extrapolated from these curves are: for 20°, $E_0 = 0.2253$ volt; for 25°, 0.2223; and for 30°, 0.2193. Previous values are. for 20°, 0.2255 (Güntelberg), 0.2253 (Randall and Young, from Giintelberg's data); for 25°, 0.2234 (Linhart, Lewis and Randall), 0.2226, 0.2224, or 0.2223 (Scatchard, from compiled data), 0.2228 (Nonhebel), 0.2221 (Randall and Young, from compiled data adjusted to agree with freezing point determinations); at 30°, 0.2187 (Randall and Young, from two points of Harned and Brumbaugh, adjusted as above).

The ultimate test of such a method of extrapolation must lie in its application to points at low concentrations. Such determinations should

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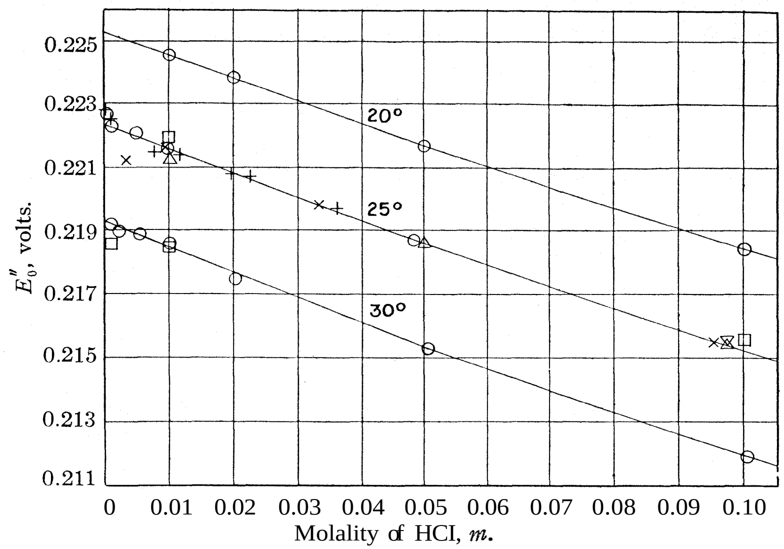
[9] Huckel, *Physik. Z.*, 26, 93 (1925).

[10] Scatchard, THIS JOURNAL, 47, 2098 (1925).

[11] (a) Harned and Brumbaugh, ibid., 44, 2729 (1922); (b) Harned and Swindells, *ibid.*, 48, 126 (1926); (c) Giintelberg, *Z. physik. Chem.*, 123, 199 (1926); (d) Hitchcock, *J. Gen. Physiol.*, not yet published.

be made, as suggested by Randall and Young, in quartz vessels. At present the new method seems to apply reasonably well to all the data except those for 25° below 0.003 *M*. The large number of points obtained by Nonhebel in this range made it impossible to show them all in Fig. 1, but their trend is clearly toward a higher value of E_0. This agrees with the smaller slope found by him in using the older method of plotting. If this slope is correct, then neither the new method of extrapolation nor the Debye theory is applicable. The extrapolation as given here, then, must stand or fall with the constant 0.5 of the Debye equation.



○ Giintelberg at 20°; Linhart at 25°, Hitchcock at 30°; + Nonhebel;
X Noyes and Ellis; △ Scatchard; ▽ Randall and Young; ☐ Harned.

Fig. 1.—Extrapolation of e.m.f. data for Ag, AgCl, HCl(aq), H_2.

This method should be of use in the treatment of electrolytes of other valence types. In such cases Equations (1) to (4) will be of correspondingly different form.

Summary

A method is given, based on a partially expanded form of the Debye and Hiickel equation, for an almost linear extrapolation of electromotive force data to unit ionic activity. The method is applied to compiled data for aqueous hydrochloric acid at 20, 25 and 30°. It is pointed out that the method is in agreement with the complete theoretical equation of Hiickel, as well as with experimental data, up to 0.1 M.

New Haven, Connecticut

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY, No. 576]

SILVER ION CATALYSIS OF PERSULFATE OXIDATIONS. III. THE OXIDATION OF AMMONIUM ION[1]

BY CECIL V. KING

RECEIVED APRIL 20, 1928 PUBLISHED AUGUST 4, 1928

Introduction

It was found by Marshall[2] that ammonium persulfate in solution, in the presence of silver salts, decomposes at a measurable velocity, according to the following equation

$$NH_4^+ + 4S_2O_8^{--} + 3H_2O \xrightarrow{Ag^+} 10H^+ + 8SO_4^{--} + NO_3^- \qquad (1)$$

Presumably, according to the recent work of Yost, the first step in this oxidation will be[3]

$$S_2O_8^{--} + Ag^+ \longrightarrow 2SO_4^{--} + Ag^{+++} \qquad (2)$$

It is difficult to postulate a mechanism for the succeeding reaction; the following occurs, but whether in one step or more, one cannot say

$$4Ag^{+++} + NH_4^+ + 3H_2O \longrightarrow 4Ag^+ + NO_3^- + 10H^+ \qquad (3)$$

In any case, from the preceding work on persulfate oxidations catalyzed by silver ion, it was expected that reaction (2) would be the velocity determining reaction; that is, (3) or its equivalent would be comparatively immeasurably rapid. Then, since the Ag^+ ion is regenerated and its concentration would remain constant, one should obtain a "pseudo-unimolecular" reaction with the velocity independent of the concentration of ammonium ion, *provided the salt concentration is held constant throughout the course of the reaction.* The above two conditions were practically fulfilled in the experiments of Marshall and Inglis, with 0.5 *N* and 1.0 N salt solutions.

These investigators found that with 0.25 molar ammonium persulfate and 0.0005 molar silver nitrate the reaction proceeded practically according to a unimolecular curve; that the acid formed did not interfere much with the reaction—though it appears that there was a little oxidation of water and that this was greater if the solution contained 0.25 molar nitric or sulfuric acid at the start; and that the salt effect was negative. All of this agrees with the above postulated mechanism. However, if one starts with quite dilute solutions, the change in salt concentration during the reaction is comparatively enormous—for instance, if one starts with 0.0005 molar ammonium persulfate and 0.0005 molar silver nitrate, the total equivalent concentration at the beginning will be 0.0015, and at the

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[1] Sections I and II of this series will be found in THIS JOURNAL, **49,** 2689 (1927).

[2] (a) Marshall, *Proc. Roy. Soc. Edinburgh,* 23, 163 (1900); (b) Marshall and Inglis, *ibid.,* **24,** 88 (1902).

[3] (a) Yost, THIS JOURNAL, 48, 152 (1926); (b) *ibid.,* 48, 374 (1926).

end 0.0026. With such concentrations, the salt effect will be quite pronounced, and in this case we should not expect the velocity to follow the unimolecular scheme, but to fall off from this considerably as the reaction progresses. Then we should expect the velocity to follow the Brönsted scheme

$$\frac{\mathrm{d}C_{S_2O_8^{--}}}{\mathrm{d}t} = kC_{S_2O_8^{--}}C_{Ag^+}f_2^2 \qquad (4)$$

where f_2 is the activity coefficient of the $S_2O_8^{--}$ and is continually decreasing as the reaction proceeds; and C_{Ag^+} is a constant. Now in sufficiently dilute solutions f_2 can be expressed as a function of the concentration, according to the formula

$$-\log f_2 = 0.5 \times 2^2 \sqrt{\mu} \text{ at } 25° \qquad (5)$$

where μ is the ionic strength; whence

$$f_2 = 10^{-2\sqrt{\mu}} \qquad (6)$$

and (4) becomes

$$\frac{\mathrm{d}C_{S_2O_8^{--}}}{\mathrm{d}t} = kC_{S_2O_8^{--}}C_{Ag^+}10^{-2\sqrt{\mu}} \qquad (7)$$

μ can be expressed as a function of $C_{S_2O_8^{--}}$; if we let the initial $C_{S_2O_8^{--}} = a$, at time t, $C_{S_2O_8^{--}} = (a - x) F$ and $C_{Ag^+} = b$, then $\mu = 3a + 3.25x + b$, and (7) becomes

$$\frac{\mathrm{d}x}{\mathrm{d}t} = kb(a - x)\, 10^{-\sqrt{3a \times 3.25x + b}} \qquad (8)$$

It was hoped that this equation might be applied but as will be shown later the correct expression for the velocity of this reaction is probably much more complicated than (8); in fact, (8) could scarcely be used even as a first approximation.

The fact that the ion concentration changes by such a large amount during the reaction makes it possible to find the rate of reaction by following the conductivity of the solution, provided the mechanism above is correct. The conductivity does change enormously, especially since hydrogen ion is formed. The conductivity of a solution containing 0.0005 M ammonium persulfate and 0.0005 *M* silver nitrate was 2.2 X 10^{-4} reciprocal ohms at the start and 6.2 × 10^{-4} reciprocal ohms at the end of the reaction. In other solutions the change was smaller or greater according to the concentrations.

Materials and Measurements

Ammonium persulfate and silver nitrate were prepared by recrystallizing from distilled water. No measurements were made on solutions having a conductivity less than 100 times that of the water and consequently ordinary distilled water was used.

Conductances were measured in cells with constants ranging from 0.3455 to 0.3819, as measured with 0.005 *N* KCl. The electrodes were unplatinized. The source of current for the measurements was a radio tube oscillator adjusted to near 1000 cycles per second.[4] The bridge was a Leeds and Northrup ratio coil bridge and resistance box which had been checked with 1000 cycle current against a standard A. C. bridge. A two-stage radio amplifier was used to make the reading of the null point easy. Air and mica condensers were used across the resistance arm of the bridge to balance capacity effects of the cells. The cells were immersed in a small thermostat electrically controlled to ±0.02°. All errors due to temperature and to conductance measurements were undoubtedly well within the other errors of reaction velocity measurements.

Solutions of ammonium persulfate and silver nitrate were made up of twice the concentration desired for the experiments; 10 cc. of one was placed in the conductivity cell in the thermostat and 10 cc. of the other withdrawn from a bottle standing in the thermostat and allowed to run into the cell, which was then shaken to mix the solutions thoroughly. The first conductivity reading could be taken one minute, or two minutes at the most, after the solutions were mixed. This turned out to be quite important, as it gave valuable information about the first stages of the reaction, showing that it has an autocatalytic character, a fact which is not evident if one discards the measurements of the first hour. This factor is not apparent in the before-mentioned measurements of Marshall and Inglis, since measurements were not made during the first few minutes of the reaction; however, perhaps an effect of it is seen in the fact that their "unimolecular" constants seem to increase steadily by 3–6% throughout the course of the reaction.

TABLE I

THE CONDUCTIVITY CHANGE IN AMMONIUM PERSULFATE–SILVER NITRATE SOLUTIONS AT 25°

Experiment 3				Experiment 6			
0.0005 M $(NH_4)_2S_2O_8$; 0.0005 M $AgNO_3$				0.001 M $(NH_4)_2S_2O_8$; 0.0005 M $AgNO_3$			
Time, min.	$\kappa \times 10^4$	Time, min.	κ X 104	Time, min.	$\kappa \times 10^4$	Time, min.	κ X 104
0	2.203	87	2.442	0	3.620 (extrap.)	165	4.407
1	2.203	248	2.859	1	3.633	253	4.788
2	2.203	452	3.314	2	3.647	389	5.336
6	2.206	626	3.655	3	3.656	486	5.700
8	2.209	721	3.824	4	3.663	746	6.586
10	2.213	1199	4.521	6	3.670	1282	7.938
14	2.222	1559	4.910	10	3.681	1512	8.388
18	2.231	1974	5.250	15	3.702	1861	8.950
22	2.243	3151	5.792	20	3.728	2185	9.369
32	2.274	∞	6.181	25	3.754	2980	10.10
42	2.305			58	3.954	3545	10.44
						∞	11.24

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[4] The author wishes to thank Mr. W. W. Macalpine of the Columbia University Department of Physics for assistance in building and adjusting this oscillator.

Results of the Measurements

Table I gives the details of two typical experiments, and several experiments are shown graphically in Figs. 1 and **3.** Figs. 2 and 4 show the first stages of these same experiments on a much enlarged scale. These figures show that experiments could not be duplicated with certainty. In general, the reaction seemed to be autocatalytic, as shown in Experiments 2, 3, 4, 7 and others not recorded here, but sometimes such effects as shown in Experiments 5 and 6 were present. At any rate, the divergence of the results for duplicate experiments seemed to be due to divergence at the start: this was probably dependent on the exact manner of mixing the solutions, though several experiments failed to show this conclusively. Catalytic effects by the walls of the cell, by the platinum electrodes or by "dust" particles are not ruled out, though rather unlikely.

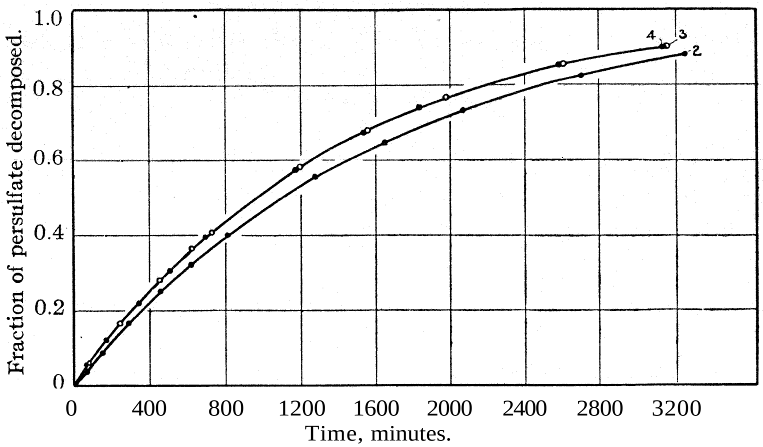

Fig. 1.—Rate of decomposition of 0.0005 M ammonium persulfate with 0.0005 M silver nitrate as catalyst.

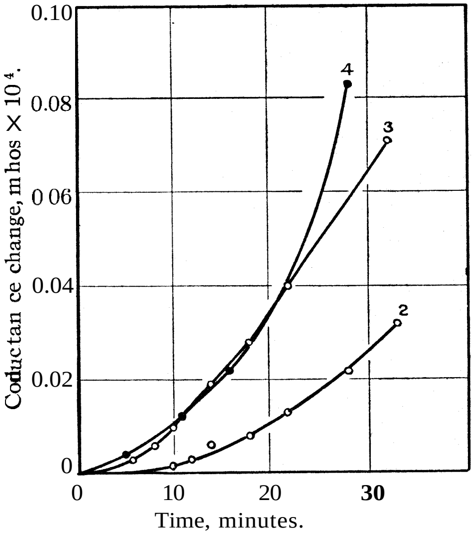

Fig 2.—The initial part of the curves of Fig. **1.**

It has been assumed above that the measured conductivity change is proportional to the amount of persulfate decomposed, an assumption which must be proved. The autocatalytic character of the curves indicates that reaction **(3)** is not immeasurably rapid, and this means that some small concentration of Ag^{+++} ion is built up in the solution.

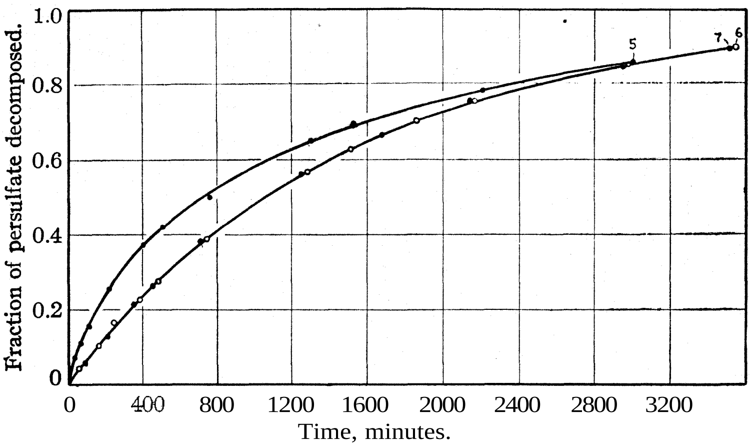

Fig. 3.—The rate of decomposition of 0.001 M ammonium persulfate with 0.0005 M silver nitrate as catalyst.

The conductance of 0.001 M $AgNO_3$ at 25° was 1.360 X 10^{-4} mhos; that of 0.001 *M* $(NH_4)_2S_2O_8$ was 3.042 X 10^{-4} mhos. The mean of these is 2.201 X 10^{-4} mhos. When 10 cc. of each of these solutions were mixed, the conductance was 2.203 X 10^{-4} mhos. This indicates that in this dilute solution the conductances were additive and there was little, if any, immediate compound formation or reaction of any kind. In the experiments recorded in Table II, various proportions of the freshly mixed solution and the same solution after complete decomposition were mixed and the conductance of these mixtures was compared with the points on the conductance curve to which they would be expected to correspond. To make this clear: in Experiment 3, the freshly made solution had the conductance 2.203 × 10^{-4} mhos. The conductivity after the persulfate was

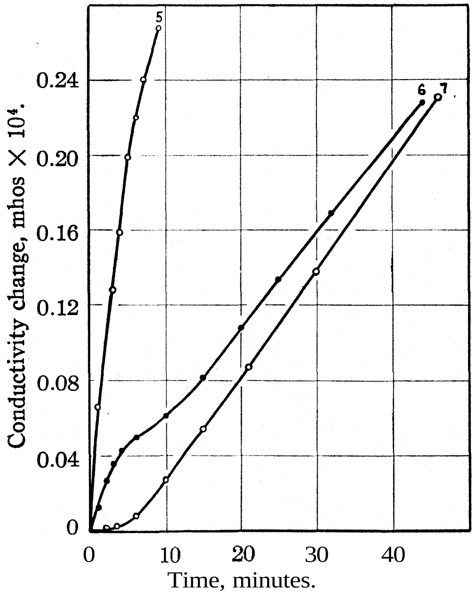

Fig. 4.—The initial **part** of the curves of Fig. **3.**

entirely decomposed was 6.181×10^{-4} mhos. The mean of these is 4.192×10^{-4} mhos. A mixture of 10 cc. each of the fresh solution and the decomposed solution gave 4.108×10^{-4} mhos. Further values are given in Table II.

TABLE II

COMPARISON OF CONDUCTIVITIES OF MIXTURES OF INITIAL AND FINAL SOLUTIONS WITH CORRESPONDING POINTS ON THE VELOCITY CURVE

Solutions of Experiment 3	$\kappa \times 10^4$	Corresponding κ from curve	Solutions of Experiment 6	$\kappa \times 10^4$	Corresponding κ from curve
40 cc. init., 10 cc. final	3.05	3.00	40 cc. init., 10 cc. final	5.20	5.14
20 cc. init., 10 cc. final	3.59	3.53	20 cc. init., 10 cc. final	6.25	6.16
10 cc. init., 10 cc. final	4.20	4.19	10 cc. init., 10 cc. final	7.55	7.43
20 cc. init., 30 cc. final	4.57	4.59	10 cc. init., 20 cc. final	8.88	8.70
10 cc. init., 20 cc. final	4.86	4.85			
10 cc. init., 30 cc. final	5.23	5.19			

This shows that there are no intermediate compounds formed in the solution in concentration high enough to affect the conductance by more than, say, 1% and that the conductance change really corresponds closely to the persulfate changes.

Discussion of Results

The autocatalytic character of the curves indicates that both reaction (2) and reaction (3) are comparatively slow. As (1) proceeds, a higher and higher concentration of the intermediate compound is built up and reaction (3), being dependent on the concentration of this, proceeds faster and faster, though there is never enough of the intermediate to greatly affect the conductance. There must soon be reached an equilibrium concentration of this intermediate compound; otherwise the "induction" period would be longer; or if persulfate were present in excess of the amount required for all the ammonium ion, the velocity would perhaps keep on increasing indefinitely, until all the ammonium ion was used up. Also, if any appreciable concentration of the intermediate compound were built up in the solution, we should expect it to precipitate. No such precipitation occurred in any of the solutions recorded, but if more concentrated solutions are used, this does occur. If equal volumes of 0.05 M solutions of ammonium persulfate and silver nitrate are mixed, the solution becomes discolored at once and there is a slow precipitation of the black compound of trivalent silver. This reaches a maximum amount and if the solution is shaken, all disappears in the course of two hours. This also indicates that the oxidation of the ammonium ion by the trivalent silver is not "instantaneous."

If we were sure that Equation (3) is correct, we could set up an equation for the resultant velocity of the two reactions, However, there are several reasons why this is impracticable. First, we do not know that (3) is the correct expression of the second slow reaction. Second, the equation would be too complicated to test experimentally. Third, the non-reproducibility of the experiments shows the presence of some factor that is as yet unknown. It seems probable that the velocity of the second reaction is of the following form

$$\frac{dC_{NH_4^+}}{dt} = k_2 C^n_{Ag^{+++}} C_{NH_4^+} F \qquad (9)$$

where F is the kinetic activity factor and depends on the value of n, the number of Ag^{+++} ions taking part in the velocity determining reaction. A combination of (4) and (9) would then give the velocity of oxidation of the ammonium ion in terms that could be tested experimentally, were the expression not so complicated. The mathematics of some types of consecutive reactions has been thoroughly worked out and tested by Wegscheider, Skrabal and others,[5] but no case similar to this, where there is both a continually regenerated catalyst and an activity factor in one or both velocity expressions, has been worked out.

If one neglects the short induction period, and calculates "k" in equation (4), considering $f_2 = 1$, it might be expected that "k" will be much higher than the unimolecular constants obtained by Marshall and Inglis for 1 N and 0.5 N solutions; and that "k" will decrease throughout the reaction as the salt concentration increases. That this is true is shown in Table III. The corresponding k for the 1 N solution is 0.218. In these solutions of equivalent salt concentration 0.0015 to 0.0025, the velocity is, at the start of the reaction (after the induction period), about eight times as rapid.

TABLE III

"k" FROM THE UNIMOLECULAR EQUATION FOR EXPERIMENT 3

Time, min.	67	135	228	432	606	1179	1539	1954
"k"	1.86	1.70	1.59	1.51	1.50	1.48	1.49	1.49

It is seen too, in Table III, that the value of "k" does not decrease as much during the course of the reaction as would be expected from the salt concentration change. This is, no doubt, due to the effect of the second reaction.

Discussion of Other Reactions

In the oxidation of ammonia by persulfate, in alkaline solution, catalyzed by silver ion, studied by Yost and by the present author, there was no noticeable autocatalytic effect. The reaction is much faster, however, in the same salt concentration than the present reaction; and the facts

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[5] Wegscheider and others, *Monatsh.*, 36, 471 (1915); *ibid*, 37, 137 (1916); *ibid*, **39,** 741 (1918), and other papers.

that none of the black compound of trivalent silver is precipitated even from comparatively concentrated solutions, and that this black compound, prepared by mixing potassium persulfate and silver nitrate, dissolves very rapidly in ammonia, with evolution of nitrogen, indicate that in this case the second reaction is very much faster. This undoubtedly makes the autocatalytic character of the curve disappear.

Equation (9) makes the velocity dependent on the concentration of reducing agent. The effect of ammonium ion concentration was not thoroughly studied in this investigation; but while experiments **3** and 4 should be faster than 6 and 7, due to the lower salt concentration, they show about the same velocity. This is probably due to the fact that the ammonium ion concentration was lower in experiments *3* and 4. Some experiments with 0.0001 M ammonium persulfate and 0.0005 M silver nitrate showed a somewhat higher velocity, though again not as much higher as would be expected with the lower salt concentration. This was probably also due to the fact that the ammonium ion concentration was lower, as well as the total salt concentration. Yost[3] found a linear relation between ammonia concentration and reaction velocity; this he explained by assuming that in more concentrated ammonia solutions more of a higher complex with Ag^+ ion than $Ag(NH_3)^+_2$ is formed. The present work makes it seem quite possible that even though the second step of the oxidation is fast compared to the first, it is not so fast that the concentration of the reducing agent does not have some influence on the resultant velocity.[6]

One might suspect that other "catalytic" reactions would show this autocatalytic type of velocity curve. The unimolecularity of the inversion of sugar, catalyzed by acid, has been questioned; it seems that the first part of the curve may be irregular.[7] The measured velocity constants increase as the reaction proceeds, even if correction is made for the "mutarotation lag" of the inversion products. This would be in accord with a slight autocatalytic effect, in a reaction where there is no salt effect due to change in ion concentration during the course of the reaction. It is probable that a hydrated sugar molecule is inverted by hydrogen ion in

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[6] It should be noted that the oxidation of ammonia and ammonium ion has not been investigated in solutions containing both these ions over a wide range of relative concentrations. Marshall's work indicated that the oxidation to nitrate is quantitative in solutions originally containing only neutral ammonium persulfate and silver salt. An experiment by the present writer showed that no appreciable amount of nitrogen was evolved during twenty-four hours from such a solution. Some of the solutions recorded in section I of this series contained ammonium ion, increasing in concentration as the reaction progressed, but also an excess of free ammonia, and no diminution in the amount of nitrogen evolved was observed. It would be valuable to investigate the nature of the reaction in solutions of intermediate PH.

[7] Fales and Morrell, THIS JOURNAL, 44, 2071 (1922); Pennycuick, *ibid.*, 48, 6 (1926); see, however, Scatchard, *ibid.*, 48, 2259 (1926).

two steps, which we may represent as follows, neglecting hydration of the hydrogen ion and the corresponding complications

$$C_{12}H_{22}O_{11}\cdot nH_2O + H^+ \longrightarrow C_{12}H_{22}O_{11}\cdot nH_2O\cdot H^+ \qquad (10)$$

$$C_{12}H_{22}O_{11}\cdot nH_2O\cdot H^+ \longrightarrow \text{invert sugar} + H^+ \qquad (11)$$

Only if reaction (11) is "instantaneous" would we expect a unimolecular sugar inversion; if (11) is slow enough that the intermediate compound increases in concentration for a time, the curve will have at least some indication of an autocatalytic character.

The hydrogen ion catalysis of ester hydrolysis does not present the irregularities that the sugar inversion does. If the mechanism is similar to that of the sugar inversion, this would mean that the reaction corresponding to (11) is very rapid compared to that corresponding to (10).

The esteracid–water system has been investigated to find if there are any ternary compounds formed immediately on mixing the solution and no conclusive evidence of any appreciable concentration of such compounds was found,[8] although previous work made it seem quite certain that the hydrolysis proceeds through the formation of intermediate compounds.[9] However, the investigation mentioned was not extended to looking for a slow accumulation of such ternary compounds as the reaction proceeds; but as mentioned before, the unimolecularity, or rather "pseudo-unimolecularity" of the hydrolysis makes it unlikely that there is any such accumulation. On the other hand, in the case of the sugar inversion, it is possible that there is a slight accumulation of such an intermediate, and this might be detected experimentally.

Summary

The velocity of oxidation of ammonium ion by persulfate ion, catalyzed by silver ion, has been measured in much more dilute solutions than before.

It is shown that the conductance method used gives a nearly correct measure of the velocity.

The velocity curves are mostly autocatalytic, though not strictly reproducible, showing that the reaction proceeds through at least two steps of comparable velocity. In previous work on persulfate oxidations catalyzed by silver ions it has been assumed that the second step is immeasurably fast.

It is suggested that the irregularities in sugar inversion catalyzed by hydrogen ion may be due to a slight autocatalytic effect similar to the one measured here.

NEW YORK, N. Y.

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[8] Kendall and King, J. Chem. *Soc.*, 127, 1778 (1925).

[9] Kendall and Booge, THIS JOURNAL, 38, 1712 (1916); J. Chem. *Soc.*, 127, 1768 (1925).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY, No. 5771

SILVER ION CATALYSIS OF PERSULFATE OXIDATIONS. IV. OXIDATION OF OXALATE ION[1]

BY CECIL V. KING

RECEIVED APRIL 20, 1928 PUBLISHED AUGUST 4, 1928

Introduction

It was found by R. Kempf[2] that oxalic acid is only slowly, if at all, oxidized by persulfates, at room temperature, in the absence of any catalyst, while in the presence of a small amount of a silver salt the oxidation proceeds quite rapidly, and presumably quantitatively, according to the following reaction

$$H_2C_2O_4 + K_2S_2O_8 \longrightarrow 2KHSO_4 + 2CO_2 \qquad (1)$$

This oxidation is given as a quantitative method for estimating persulfates by Treadwell and Hall.[3] A neutral oxalate seems to be oxidized just as completely and rapidly as an acid solution (perhaps more rapidly); silver salts have a much greater catalytic effect than in some of the other persulfate oxidations.[4] The purpose of this investigation was to study the velocity of the reaction quantitatively with a view to the elucidation of its mechanism and its differences from the other reactions mentioned.

Theoretical

This reaction was expected, in accordance with the others, to proceed in two steps, as follows

$$S_2O_8^{--} + Ag^+ \longrightarrow 2SO_4^{--} + Ag^{+++} \text{ (slow)} \qquad (2)$$
$$C_2O_4^{--} + Ag^{+++} \longrightarrow 2CO_2 + Ag^+ \text{ (faster)} \qquad \text{i3)}$$

If reaction (3) were extremely fast, then the net rate should be "pseudo-unimolecular," and independent of the oxalate ion concentration, so long as the oxalate, and not the persulfate, is in excess in the solution; if the persulfate is in excess a modified unimolecular curve will result. On the other hand, if reaction (3) is comparatively slow, trivalent silver ion will increase in concentration as the reaction proceeds and autocatalytic curves may be obtained as in the case of the ammonium ion oxidation.[5] From the complete ionic equation

$$S_2O_8^{--} + \text{GO}\sim - \xrightarrow{Ag} 2SO_4^{--} + 2CO_2 \qquad (4)$$

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[1] Sections I, II and III of this series will be found in THIS JOURNAL, 49, 2689 (1927) and 50,2080 (1928).

[2] Kempf, *Ber.*, 38, 3965 (1905).

[3] Treadwell-Hall, "Analytical Chemistry," Vol. II, 6th ed., John Wiley and Sons, Inc., New York, 1924, p. *535*.

[4] See Section II of this series.

[5] Section III of this series.

it is seen that there is no change in ionic strength in the solution during the course of the reaction (or very little; a small amount of ionized carbonic acid will be formed) and consequently there will be little salt effect during the course of the reaction. Of course, with different initial concentrations or in the presence of a foreign salt the velocity will be changed.

However, the oxidation proceeds, it will be seen, much faster than does reaction (2)—judging from the velocity of the reactions studied before. Consequently, the preceding mechanism is perhaps entirely ruled out as an explanation for this reaction. No complete explanation for the results obtained in this investigation can be offered, but some of the factors involved will be discussed and tentative explanations proposed.

Experimental

Potassium persulfate, sodium oxalate, silver sulfate and nitrate were all prepared by recrystallization and thorough drying of the crystals; the salts were either weighed directly for each experiment or to make standard solutions.

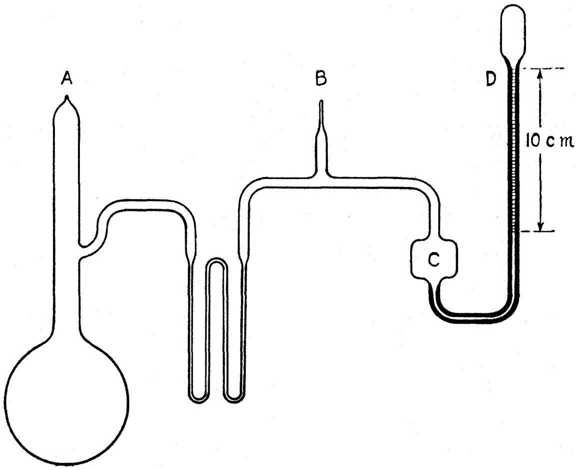

Fig. 1.—The modified apparatus for measuring the rate of gas evolution.

Since carbon dioxide is evolved, the easiest way to follow the reaction is to follow the evolution of this gas. This was done in a modification of the apparatus designed by Brönsted.[6] The modified apparatus is shown in Fig. 1. All stopcocks and ground stoppers were eliminated. The solution, containing (usually) the oxalate and the silver salt, was introduced into the flask and the solid persulfate was suspended in a small glass capsule, from a platinum loop sealed in the side of the neck of the flask. D was a closed manometer, well evacuated and "boiled out," with a 5cc. bulb at the top, to prevent error from any traces of gases remaining above the mercury. The bulb C was made large enough to accommodate this extra mercury. When all was ready for an experiment, A was sealed off, the system evacuated through a capillary at B and this

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[6] (a) Brönsted and Duus, Z. *physik. Chem.*, **117, 299 (1926)**; (b) Bronsted and King, THIS JOURNAL, **47, 2523** (1925).

then sealed off. At the close of an experiment only the tip of B was broken off at first, so that the air entered the apparatus slowly, otherwise the mercury, rising rapidly in the manometer, might break the bulb D.

This form of the apparatus is somewhat more difficult to manipulate than the older style but if it is made of Pyrex glass the seals are not difficult and it has the advantages that accidental leaks are almost completely eliminated and, besides, it can be used for reactions in which gases are evolved that attack the usual vacuum-tight stopcock lubricants.

Some of the experiments were carried out at 20 ± 0.02°, others at 25 ± 0.02°, as indicated in the tables. During each experiment the room temperature was kept slightly higher than that of the bath to prevent distillation of water from the reaction flask to other parts of the apparatus.

The Measurements

Some preliminary Experiments and Experiments 44, 45, 46 and 47 were made to find whether the reaction between $S_2O_8^{--}$ and $C_2O_4^{--}$ had an appreciable velocity with no silver ion present as catalyst. The velocity is small; the results are not in very good quantitative agreement and it is possible that the reaction is due to traces of "accidental" catalysts. The velocity is negligible compared to that in most of the experiments with silver ion as the catalyst. The results are given in Table I.

TABLE I

THE REACTION BETWEEN $S_2O_8^{--}$ AND $C_2O_4^{--}$ WITH NO CATALYST AT 25°

Concentrations: 0.01 *M* $Na_2C_2O_4$, 0.005 *M* $K_2S_2O_8$

Time. min.	Frac. persulfate decomposed Expt. 44	Expt. 45	Time min.	Frac. persulfate decomposed Expt. 46	Expt. 47
120	0.001	0.000	120	0.007	0.007
240	.007	.007	210	.010	.015
440	.015	.010	360	.019	.030
620	.025	.018	420	.025	.034
1380	.104	.061	1110	.142	.136

In Experiments 34 and 35, which have the same concentrations as the above, with the addition of 0.00002 M silver nitrate, the velocity was nearly unimolecular. Table II gives a part of the experimental figures to illustrate this, and the entire curves are shown graphically in Fig. 2.

TABLE II

VELOCITY "CONSTANTS" WITH A SILVER SALT PRESENT AT 25°

Concentrations: 0.01 M $Na_2C_2O_4$, 0.005 M $K_2S_2O_8$, 0.00002 M $AgNO_3$

$$``k" = \frac{2.3}{t \times C_{Ag^+}} \ln \frac{a}{a - x}$$

Expt. 34	Time, min.	50	70	120	240
	"*k*"	213.2	217.9	208.4	190.7
Expt. 35	Time, min.	50	70	120	240
	"*k*"	263.6	260.5	251.5	237.5

However, the experiments recorded in Table II, although carefully made up duplicates in concentration, do not agree with each other within reasonable experimental error, and this is by no means the worst case of disagreement in the velocity in solutions that duplicated each other in concentration. Further, the velocity was not always as nearly unimolecular as in the above cases. In several instances typical autocatalytic curves were obtained, while in others there was a very short autocatalytic period at the beginning of the reaction, as in the ammonium ion oxidation; sometimes this autocatalytic period was not evident but the velocity curve was flattened at the beginning, no doubt due to the same cause. Table III gives the details of concentration and temperature, and Figs. 3–5 show the data graphically for several experiments carried out with an excess of oxalate present.

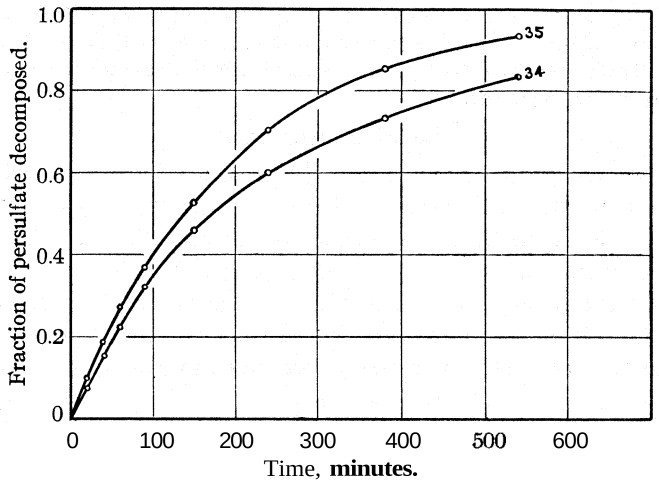

Fig. 2.

TABLE III

CONCENTRATION AND TEMPERATURE FOR EXPERIMENTS PLOTTED IN FIGS. 3–5

Expt. no.	$Na_2C_2O_4$, *M*	$K_2S_2O_8$	$AgNO_3$	Ag_2SO_4, *N*	Temp., °C.
4, 6, 7, 8, 9, 17	0.01	0.005	....	0.00002	20
36, 37	.005	.0025	0.00003	....	25
38, 39	.005	,0025	.00004	....	25
40, 41, 54, 55	.005	.0025	.00002	....	25
42, 43	.005	.0025	.00001	....	25

All of the experiments in Fig. 3 were duplicates and should agree; but their velocity is far different. As a rule, when experiments were run with different concentrations, the velocity was changed in the direction expected, but there was no quantitative agreement. For instance, 43, with 10^{-5} M Ag+ is slower than 38, with 4 X 10^{-5} M Ag^+, but much more than one-fourth as fast. Many other similar discrepancies can be noted. Nevertheless, the order of magnitude of the velocity was always the same. The experiments at 25°, for instance, were run about a year later than those at 20°, with entirely new salts and new reaction flasks, and still are of the same order of magnitude.

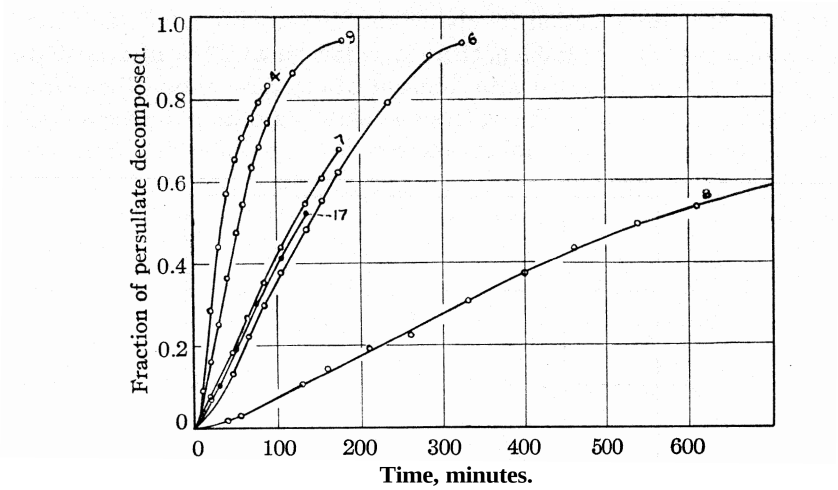

Fig. 3.

When persulfate is present in excess instead of oxalate, conditions are somewhat different. While the velocity may be somewhat dependent on the concentration of oxalate, it is more dependent on the persulfate

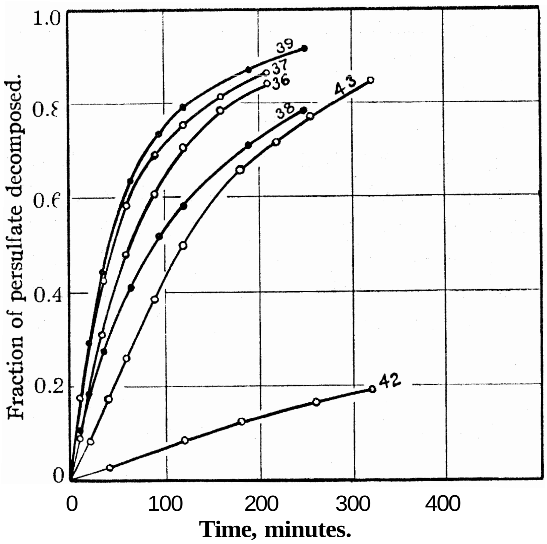

Fig. 4.

concentration, as is shown by the nearly unimolecular nature of some of the above curves. The autocatalytic character of some of these curves indicates, however, that an intermediate, unstable compound is formed, presumably by the interaction of the persulfate and silver ions, and if persulfate is present in sufficient excess, the silver ion concentration is high enough and the reaction involving the decomposition of the intermediate compound is slow enough, there is no reason why this intermediate should not keep on increasing in concentration throughout the entire reaction and consequently the rate of oxalate oxidation increase continuously. Several experimental curves were found to have this character; in Table IV are given the details of concentration and temperature and in Figs. 6–8 are shown graphically several examples, some with twice as much persulfate as oxalate, some with a larger excess. Again, however, it must be noted that experiments could not at all be duplicated, in spite of care in making up the solutions and in cleaning the vessels used, and attempts to trace the cause of these discrepancies were not very successful.

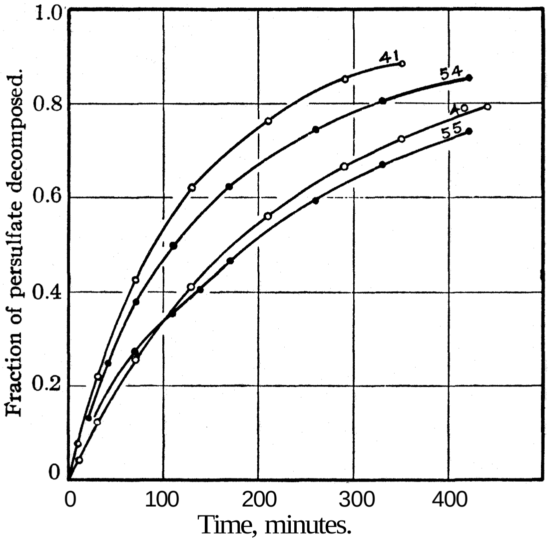

Fig. 5.

TABLE IV

CONCENTRATIONS AND TEMPERATURE FOR EXPERIMENTS PLOTTED IN FIGS. 6–8

Expt. no.	$Na_2C_2O_4$, *M*	$H_2C_2O_4$, M	$K_2S_2O_8$, *M*	$AgNO_3$	Ag_2SO_4, *N*	Temp., °C.
3, 14, 15, 19	0.005	..	0.01	....	0.00002	20
11, 13, 21, 22	...	0.005	.01	....	.00002	20
23, 24	.005	..	.05	0.00001	....	25
25, 26	.005	..	.05	.00002	....	25
27, 28	.0025	..	.05	.00002	...	25
29	.0025	..	.05	.00001	....	25
48, 49, 50	.0025	..	.01	.00003	....	25
51, 52, 53	.0025	..	.01	.00002	....	25

It was suspected that the reaction might be catalyzed by the diffuse daylight or electric light that reached the flasks, but a 200-watt tungsten lamp placed just outside the thermostat quite near one of the reaction flasks had no appreciable effect on one rather slow experiment. Also, the divergences could scarcely be ascribed to a difference in illumination of the two flasks used, or of one flask at different times. It was suspected that the exact manner of mixing the last reagent in the solution caused the velocity to vary. Usually the persulfate was dropped in last, and sometimes it dissolved rapidly (30–40 sec.), sometimes more slowly (2-4 min.)

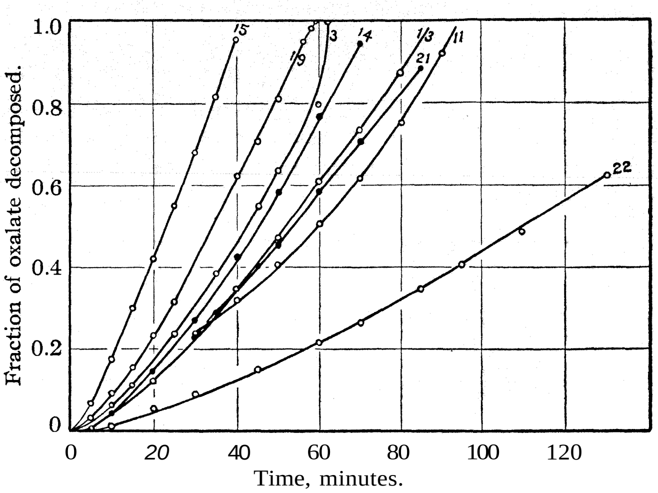

Fig. 6.

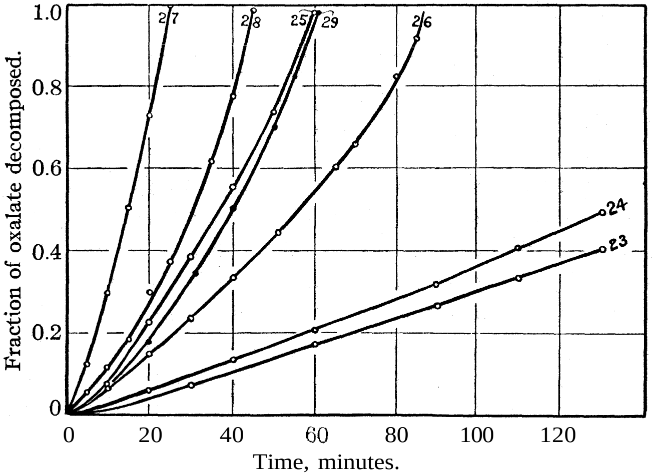

Fig. 7.

depending on the exact manner in which the glass capsule fell into the solution. So in Experiments 38 and 40 the solid persulfate was allowed to dissolve slowly (6 min.) with very little shaking of the flask, while in **39** and 41, run side by side with 38 and 40, the persulfate was dropped in and dissolved in a few seconds. The difference is no greater than in many other experiments in which the rate of solution of the persulfate was approximately the same. In other experiments the silver nitrate was dropped in last, and in general these experiments seemed to have a slightly higher velocity than the others with the same concentrations, but the effect was not pronounced.

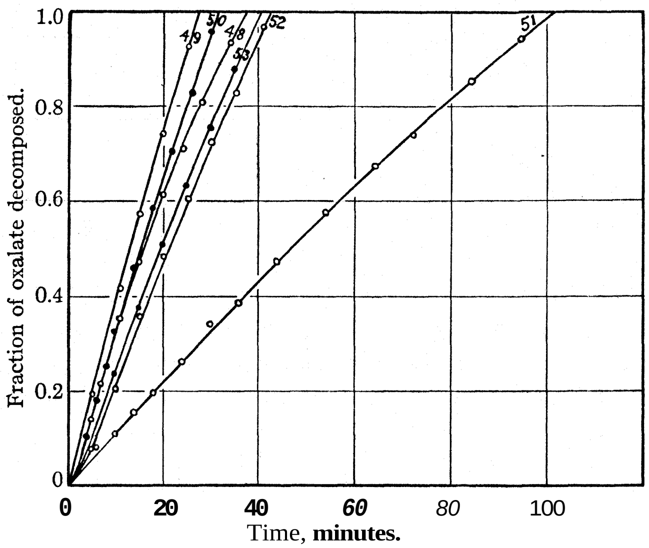

Fig. 8.

If the autocatalytic effect is due to an accumulation of intermediate compound formed by reaction of the persulfate and silver ions, then if these two are mixed and allowed to react until the maximum amount of the intermediate is present, the autocatalytic character should disappear and the curve be either a "zero order" curve—if this maximum concentration of the intermediate is maintained--or a concave curve, if the concentration of the intermediate diminishes after the oxalate is added. For Experiment 15, the persulfate and silver sulfate were mixed, and one hour later the oxalate was added and the experiment started. The autocatalytic character almost disappeared, and the reaction was somewhat faster than the others of the same concentrations. Possibly the reaction between the persulfate and silver ions was not complete in one hour.

Only one consistent discrepancy was noticed in any series of experiments;

for a time, when duplicates were run side by side in the two pieces of apparatus, those in apparatus No. 1 were consistently slower than those in apparatus No. 2. This is shown by Experiments 34, 36, 38, 40, 42 and 48, which were run in apparatus No. 1, and were, respectively, duplicates of and were run beside Experiments 35, 37, 39, 41, 43 and 49 in apparatus No. 2. This suggested catalysis by the flask walls and to see if an increase in the glass surface would change the velocity considerable broken glass was introduced into flask No. 1 while Experiments 42 and 43 were run. If there was any catalytic effect it was negative. Next the wall of flask No. 1 was thoroughly etched with hydrofluoric acid, and Experiments 52 and 54 were run side by side with 53 and 55. Fifty-three in No. 2, was slightly faster than 52, in No. 1; while 54, in No. 1, was faster than 55 in No. 2. Any effect was slight, however, compared to the differences between duplicate solutions run in the same apparatus on different days.

It is possible that there was some catalysis by "dust" in the solutions,[7] though there was probably no large effect from this source. Small amounts of precipitated silver oxalate could scarcely he responsible; in all the solutions reported here, care was taken that the concentrations should be below those at which silver oxalate would precipitate and no precipitation was discernible. Several experiments were run with concentrations high enough to cause a slight visible precipitation, without any pronounced effect that would indicate such a catalysis.

Discussion

The experiments mentioned before make it seem quite likely that there is some wall catalysis. No simple procedure is sufficient to prevent this or make it possible to duplicate its effects except accidentally. The fact that broken glass in the flask, or etching the flask, had no pronounced effect, makes it seem impossible that this wall catalysis could be responsible for the enormous difference in velocity between these experiments and the oxidation of other reducing agents. It is just possible that "dust" or some unknown impurities could be responsible, for many reactions are extremely sensitive to traces of catalysts. For example, the effect of Cu^{++} and Fe^{++} and mixtures of these two on the persulfate oxidation of iodide ion may be cited,[8] also the effect of traces of impurities on some isomeric changes.[9]

If most of the catalysis were heterogeneous, one would expect a zero order or a unimolecular reaction in all cases. This is nearly true in some of the solutions. Expts. 48, 49, 50, 51, 52 and 53 are almost of zero order, and further showed irregularities that might very well attend wall catalysis when the shaking of the flask is not quite uniform, but the auto-

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[7] See F. O. Rice, This Journal, **48**, 2099 (1926).

[8] Price, *Z. physik. Chem.*, **27**, 474 (1898).

[9] Rice, "Homogeneous Organic Reactions," The Chemical Catalog Co., New York, 1928, Chapter V.

catalytic effect, especially in solutions containing excess persulfate, indicates rather that the phenomenon is at least largely some peculiarity of the reactions between the various ions and intermediate products, and that this makes the reaction *so* much faster than the others, while the wall catalysis probably accounts for the comparatively small differences between the individual experiments.

It should be noted that the irregularities cannot be accounted for by supersaturation of the solution with carbon dioxide and consequent failure of the manometer readings to represent the rate of reaction. This may cause small errors in such velocity measurements (say 1–3%) but not the wide variations found here, especially since precautions were taken to shake the reaction flasks in approximately the best manner.[10]

Various explanations can be advanced for the high velocity of this reaction. As was mentioned before, the oxalate is, apparently, oxidized faster than trivalent silver ion is formed. Dr. R. Livingston[11] has suggested one explanation for this. Assume that the persulfate and silver ions form first a complex ion that is relatively inactive, that is, can oxidize only good reducing agents, as the oxalate ion, but not ammonium or chromic ion. From this is formed a more active silver ion, AgO^+ or Ag^{+++}, which can oxidize the poorer as well as the better reducing agents. To fit all the existing data a series of simultaneous and consecutive reactions can be formulated which will account for the various rates, for the autocatalytic character of some of the curves and for any dependency on the concentration of the reducing agent.

We can scarcely expect the initial reaction to be represented merely by Equation (2)

$$Ag^+ + S_2O_8^{--} \longrightarrow Ag^{+++} + 2SO_4^{--}$$

except perhaps as an approximation under certain conditions. In the thermal decomposition of persulfates in water solution there are at least three reversible steps, before the final product of SO_4^{--} ion is formed from the $S_2O_8^{--}$ ion.[12] In the photochemical decomposition in water solution, sulfate ion is the only detectable product obtained,[13] but it is nevertheless quite likely that there are undetectable intermediate stages. The constitution of the persulfates is not well understood but it is unlikely that sulfate ion can be formed directly by splitting of persulfate ion, that is,

$$S_2O_8^{--} + 2\ominus \longrightarrow 2SO_4^{--}$$

(the silver ion supplying the electrons). So some mechanism similar to that of Livingston's is quite probable.

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[10] See Pedersen, THIS JOURNAL, 49, 2681 (1927).

[11] Private communication.

[12] See Price, "Per-acids and their Salts," Longmans, Green and Company, 1912, p. 31; Palme, *Z. anorg. chem.*, 112, 97 (1920).

[13] Morgan and Crist, THIS JOURNAL, 49, 16 (1927).

One might also formulate a mechanism in which the silver ion is oxidized in two steps, first to bivalent and then to trivalent silver. The slower oxidations would be sensitive only to the trivalent silver while the oxalate ion would be oxidized by the bivalent silver. Intermediate reducing agents could be oxidized rapidly by the trivalent, slowly by the bivalent form.

It is unfortunate that the irreproducibility of these experiments makes it quite impossible to tell whether the velocity is proportional to the first or the second power of the silver-ion concentration or to test properly any suggested mechanism for the reaction. Consequently, the chemistry of the persulfate oxidations cannot be much further elucidated.

Summary

The rate of oxidation of oxalate ion by persulfate ion in dilute water solution has been measured, using silver salts as the catalyst, and the following conclusions have been reached.

With no added catalyst the reaction proceeds very slowly, and it is not known whether or not this slow action is due to "accidental" catalysts or the vessel walls.

With silver salts added as a catalyst, the reaction is very much faster than the similar oxidation of ammonia, ammonium ion and chromic ion.

There is undoubtedly some catalytic effect, either positive or negative, by the glass reaction vessel walls and possibly some catalysis by accidental impurities.

However, the major portion of the difference between the velocity in this and the other oxidations is most likely due to some peculiarity in the reaction itself.

The autocatalytic character of some of the curves indicates that some intermediate compound decomposes at a speed comparable with that of its formation and that in certain cases it accumulates in the solution. This cannot be the trivalent silver ion that was postulated as the intermediate substance in the other oxidations.

Possible mechanisms for the main part of the reaction (not the wall catalysis) are discussed.

The extreme irregularity of the velocity even in carefully prepared duplicate solutions makes it impossible to elucidate the mechanism further or to study other aspects of the problem such as "salt effect" on the velocity.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE FERTILIZER AND FIXED NITROGEN INVESTIGATIONS, BUREAU OF CHEMISTRY AND SOILS, U. S. DEPARTMENT OF AGRICULTURE]

THE THERMAL DECOMPOSITION OF AMMONIA ON TUNGSTEN, MOLYBDENUM AND NICKEL. I

BY C. H. KUNSMAN

RECEIVED APRIL 21, 1928 PUBLISHED AUGUST 4, 1928

The decomposition of ammonia on the surface of hot iron catalysts has been used in experiments to give further information regarding the role played by the catalysts in the ammonia reaction.[1] In order to compare the results of these experiments with the published results of similar tests on tungsten[2] and molybdenum,[3] it was necessary to make tests on drawn tungsten and molybdenum filaments, under the same conditions as for the catalysts. As these tests were made through a wider range in temperature and give results somewhat different from those previously reported, a detailed account of these tests will be given.

The impetus toward this method of studying a heterogeneous or surface reaction and the method of interpreting the experimental result are due primarily to Hinshelwood and his collaborators.[4] They studied the decomposition of ammonia on silica, platinum, tungsten and molybdenum with the view of interpreting the temperature coefficient of the surface reaction as a measure of the heat of activation somewhat as the analogous idea is applied to a homogeneous reaction. They were also interested in the magnitude of this apparent heat of activation in relation to the catalytic activity of the surface.

In some earlier work the homogeneous decomposition of ammonia was sought by Perman and Atkinson[5] and by Bodenstein and Kranendieck[6] in porcelain and quartz vessels, respectively, at temperatures from 677 to 1111°, with the result that all decomposition could be accounted for by a wall, or surface, reaction.

Very recently Schwab[7] has studied the decomposition of ammonia on platinum and tungsten at low pressures with the view to determining the order of the reaction and the effects of the products of the reaction.

The ammonia reaction is a surface reaction of the simpler form where

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[1] Jubilee Meeting, American Chemical Society, Philadelphia, September, 1926, Science, 65, 527 (1927); Institute of Chemistry, Pennsylvania State College, July, 1927; Chemical Section, American Association for the Advancement of Science, Nashville, December, 1927.

[2] Hinshelwood and Burke, *J. Chem. Soc.*, 127, 1105 (1925).

[3] Burke, *Proc. Nat. Acad. Sci.*, 13, 67 (1927).

[4] Hinshelwood, "Kinetics of Chemical Changes in Gaseous Systems," Oxford Press, London, 1926.

[5] Perman and Atkinson, *Proc. Roy. Soc. London*, **74**, 110 (1904).

[6] Bodenstein and Kranendieck, *Nernst-Festschr.*, 1912, p. 99.

[7] Schwab, *Z. physik. Chem.*, 128, 161 (1927).

both the reacting substance, ammonia, and the products, nitrogen and hydrogen, are gases and it lends itself to kinetic treatment.

Apparatus

The apparatus consisted of a decomposition chamber of 1 or 2 liters' capacity made of Pyrex glass with heavy tungsten leads. Fig. 1 shows a late type of the chamber in which the filaments were mounted horizontally. In an earlier design the filaments were mounted vertically. The tungsten, molybdenum and nickel filaments were attached directly at one end to heavy tungsten leads and at the other to a fourth common lead through molybdenum springs and platinum strips The function of the springs was to keep the filaments taut, and of the platinum strips, which shunted the springs, to carry most of the current so that no part of the leads or filament connections became hot when current from the storage battery was used to heat the filaments. The chamber was attached to a high vacuum system and mounted so that it could be surrounded by an electric oven and baked to 500° and thoroughly evacuated to a pressure of 1×10^{-6} mm. of mercury. Ammonia gas from a liquid ammonia reservoir, previously dried in contact with sodium, was admitted into the system shown. The ammonia pressure, about one-third of an atmosphere, was read on a McLeod gage. Tank nitrogen and hydrogen were admitted to the system as desired after having been very thoroughly treated and dried by passing each gas over hot copper filings, calcium chloride, fused potassium hydroxide, a very hot tungsten spiral filament and through a liquid-air trap. A mercury trap, not shown in the figure, separated the decomposition chamber and McLeod gage from the rest of the system when the proper pressure of ammonia or gas mixture was obtained before current was applied to the filament. As the pressure in the chamber doubles when the ammonia is decomposed into N_2 and $3H_2$, the data sought were obtained by observing the rate of increase of pressure on the gage as a function of the temperature of the hot filament.

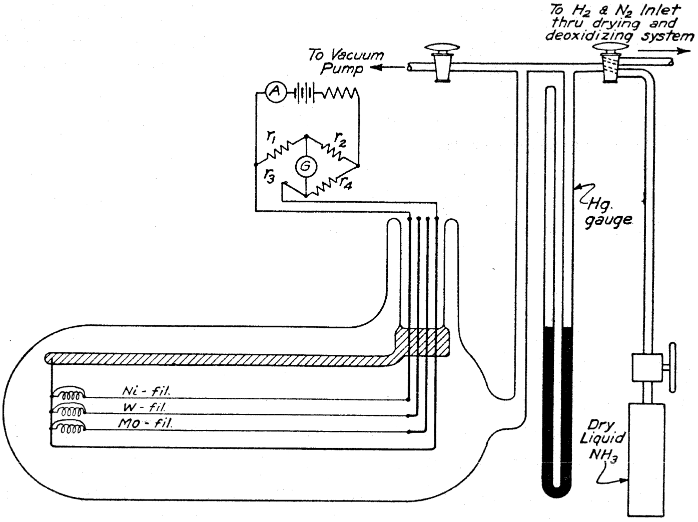

Fig. 1.—Apparatus for the study of the decomposition of ammonia on drawn filaments.

The temperature of the filament was determined by two methods: first, by direct observation with a Leeds and Northrup optical pyrometer, calibrated by the Bureau of Standards, and correcting for the emissivity of the surface and absorption of the glass;[8] second, by employing the temperature coefficient of the resistance of tungsten and molybdenum as determined by Jones[9] and Worthing.[10] These two methods were found to check within about 25° through the range of temperatures employed.

Any discrepancy in temperature was practically constant over the entire range of temperature used, and was therefore not a function of the individual observations or any part of the range.

The fact that the hydrogen formed as a decomposition product is a better conductor of heat than ammonia or nitrogen makes it necessary to increase the current through the filament in order to keep its temperature constant throughout the test or until the greater part of the ammonia is decomposed. The Wheatstone Bridge arrangement shown in Fig. 1 enables this to be done very easily and effectively. The filament is made one arm, r_3 of the bridge, which is comparable to r_4 and quite small in comparison to r_1 and r_2. As the decomposition takes place on the hot filament, the current (A) is increased, keeping r_3 constant. A sensitive galvanometer indicates when this balance is obtained.

The decomposition chamber was cooled by being immersed in a bath of continuously flowing tap water throughout all tests.

As the equilibrium concentration of ammonia with nitrogen and hydrogen at one atmosphere and at this temperature range is less than 1%, all tests were made far from equilibrium and the reaction velocities measured are, therefore, free from the effect of counter reaction.

Experimental Results

The decomposition of ammonia on hot surfaces is a chemical reaction no different from most surface reactions in that it can be expressed by Arrhenius' equation through a limited temperature range at least. Arrhenius stated that the rate of a chemical change = A $e^{-E/RT}$ holds equally well for a homogeneous gas phase, or a heterogeneous surface reaction, where R is the gas constant, 1.987 cal./deg.; T, the absolute temperature; e, the base of the Napieran logarithm, and A and E are constants.[11] In general A has to do with the number of reacting molecules at a given temperature T; E has the form of energy and is expressed in calories per gram molecule and can be obtained from the temperature coefficient of the reaction.

Arrhenius' equation may now be used to study the experimental results in order to see to what extent deductions can be made in regard to the relative significance of the A and E constants for a given reaction for various surfaces under identical experimental conditions; or to see to what extent A and E can be used to study catalysts in a heterogeneous system, rather than entering into a theoretical discussion of these constants.

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[8] Poote, Pairchild and Harrison, Bureau of Standards Technical Paper No. 170, "Pyrornetric Practice," **1921.**

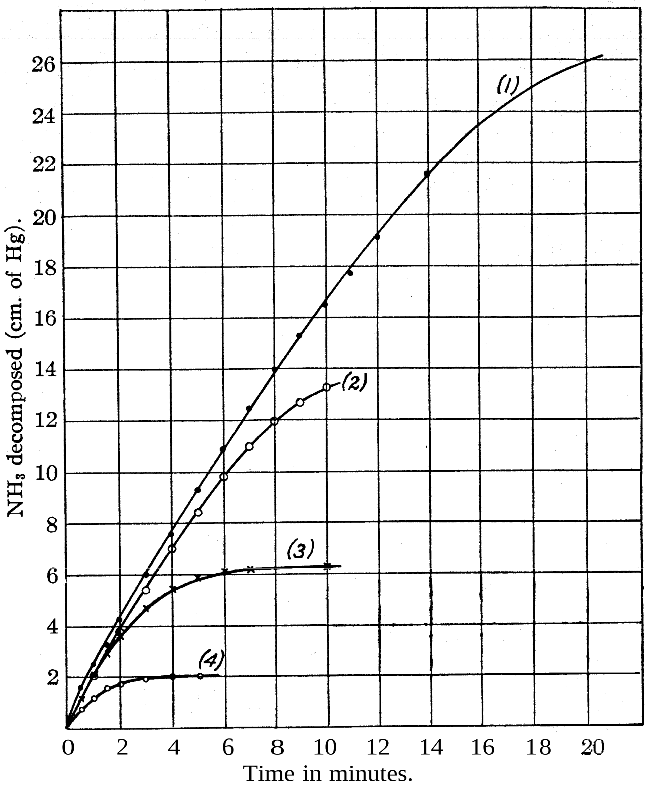
[9] Jones, Phys. *Rev.*, **28,** 202 (1926).

[10] Worthing, *Phys. Rev.*, **28,** 190 (1926).

[11] See Hinshelwood, "Kinetics of Chemical Changes in Gaseous Systems," for the meaning of these constants for the various types of reactions.

The Decomposition of Ammonia on Tungsten

The order of the reaction was determined by the usual method and found to be in general as reported by Hinshelwood and Burke, an apparent zero order. The zero order reaction is given by $dx/dt = k$, where x is the number of moles of ammonia per liter which have been changed to the resultants N_2 and $3H_2$ in time t, and k is the velocity constant which is independent of the concentration of the reactants at any time. Hinshelwood pictures the surface in the zero order as being nearly saturated with reacting gas and as molecules react and leave the surface others at once are adsorbed, so that the rate of reaction is constant regardless of the diminishing concentration in the gas phase. However, at sufficiently reduced pressure a point is reached where the surface is no longer saturated and the reaction becomes unimolecular.



Initial pressure: (1) 26.5 cm.; (2) 13 cm.; (3) 5.8 cm.; (4) 1.6 cm.
Fig. 2.—The decomposition of ammonia on a short tungsten filament at 1100°.

Typical examples of the results for tungsten are given in Fig. **2,** where the ammonia decomposed as measured by the increase in total pressure in cm. of mercury is plotted against the time, for initial pressures of ammonia of 26.5, 13.0, 5.8 and 1.6 cm. Each experiment was started with pure ammonia, that is, free from excess of either H_2 or N_2. The time for one-half of the ammonia to decompose, which is a convenient measure of the rate, is 7.6, 3.7, 1.7 and 1.0 minutes for the respective pressures, instead of 7.6, 3.73, 1.66 and 0.46 minutes, which are calculated from the ratio of the initial ammonia pressures. In a unimolecular change all "half times" would be equal. There is a tendency in these data and all tests for the "half time" to become less dependent on pressure at the lower pressures, which may mean that at the lower pressures the reaction is tending toward a unimolecular form.

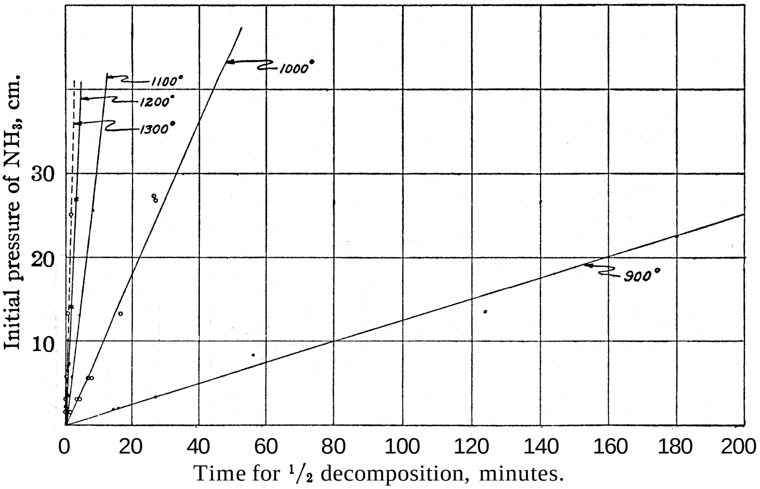
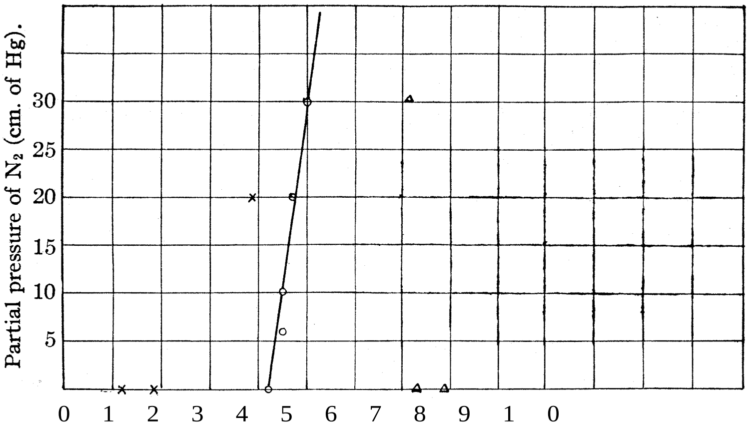


Fig. 3.—The decomposition of ammonia on a short tungsten filament from 900 to 1300°.

In Fig. 3 we have the results of tests at 900, 1000, 1200 and 1300". The "half time" is here plotted against the initial ammonia pressure. This again shows that the zero order test holds throughout the entire temperature range.

Figs. 2 and 3 are from early data on short filaments and under conditions where the exact temperature was not well enough known to give dependable values of the temperature coefficient, although the temperature was kept constant in the test for the order of the reaction as the gas pressure was varied. The "half time" or relative activity from Figs. 2 and 3 cannot therefore be directly compared with the values obtained later under improved experimental conditions.

The next important point in regard to the reaction system is the extent to which the reaction rate is influenced by the products of the reaction, N_2 and H_2. Fig. 4 gives the times required for the decomposition of one-half of the ammonia where 10 cm. was the initial ammonia pressure. To this initial ammonia pressure of 10 cm. were added, in a series of experiments, varying quantities of very carefully deoxidized and dried nitrogen, representing, respectively, 5, 10, 20 and 30 cm., and the rate of decomposition of ammonia was noted for a given temperature, 950". The pure tungsten filament was 0.18 mm. in diameter and 18 cm. long. We note that the large dilution with nitrogen has relatively little effect on the rate for a given state of activation of the surface. The slope of the curve drawn through the points is a measure of this effect. However, a far greater effect is caused by subjecting the surface to heat treatments. For example, the effect of glowing the tungsten filament in a vacuum at 1600° is to decrease the activity of the surface. This is shown by a doubling of the time for one-half decomposition, while an appreciable activation can be produced by glowing the tungsten filament in nitrogen at 1000°. This variation can best be compared by noting the points on the x-axis corresponding to the decomposition of one-half the ammonia where no nitrogen was present. The average time for the most active surface is 1.5 minutes. A value of 7.6 minutes after heat treatments in a vacuum may have been caused by a removal or modification of the active surface.



Time (min.) required for $^1/_2$ decomposition of NH_3 (initial pressure 10 cm.). OO A constant state of activity. XX Effect of glowing filament in N_2 at 1000". AA Effect of glowing filament in vacuum at 1600°.

Fig. 4.—The effect of heat treatment and nitrogen on the rate of decomposition of ammonia on pure tungsten at 950°.

Fig. 5 shows a similar test on the same filament where the decomposition of ammonia was studied in the presence of hydrogen. In this case, for the given temperature 950°, hydrogen had a larger retarding effect than nitrogen, but the actual retarding effect was small at this temperature, 950°. Preliminary tests on the activation of the tungsten filament in hydrogen gave no change in activation comparable to those observed in nitrogen.

In general, the small retarding effect due to nitrogen or hydrogen decreased and disappeared at higher temperatures and increased at lower temperatures. The observation of a definite retarding effect of hydrogen and nitrogen is qualitatively in agreement with the results of Schwab.

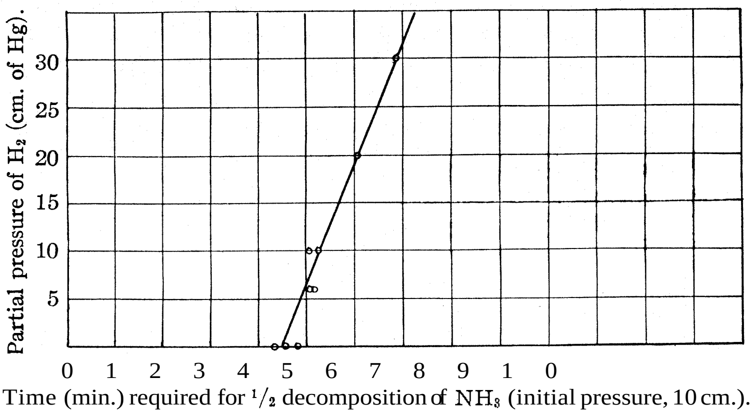


Fig. 5.—The effect of hydrogen on the rate of decomposition of ammonia on pure tungsten at 950°.

Determination of E for Tungsten

A very convenient way of representing the decomposition data is to plot the logarithm of the time for one-half decomposition against the reciprocal of the absolute temperature. Ordinarily in applying Arrhenius' equation, the velocity constant, which is the reciprocal of the time for one-half decomposition, is plotted against the reciprocal of the absolute temperature. Since the data for the entire temperature range can in no case be represented by a single straight line, we will adopt the method of resolving the data for a given filament surface into two straight lines, representing the two extremes of the temperature coefficient of the reaction. A smooth, unbroken curve can be drawn through all the points of a series of tests and is the best representation of the data. In this case E could be expressed as a function of T; then E would show a continuous decrease with increase in temperature. In this way a more accurate comparison of the values of E for the various surfaces could be made. Further studies will no doubt justify this form of presentation.

Fig. 6(a) gives the results from a very pure 7 mil (diam. 0.018, length 18 cm.) tungsten filament furnished by I. Langmuir of the General Electric Company. The total surface is 1.006 sq. cm., calculated from micrometer measurements of the filament. The value of E, which is proportional to the slope of the curve, Fig. 6, is obtained in the following way.

Arrhenius' equation states: rate = $A\, e^{-E/RT}$. Suppose the times for one-half decomposition for temperatures T_1 and T_2 are t_1 and t_2, respectively. Then $1/t_1 = A\, e^{-E/RT_1}$, and $1/t_2 = A\, e^{-E/RT_2}$. Taking logarithms, $\ln t_1 = -\ln A + E/RT_1$, and $\ln t_2 = -\ln A + E/RT_2$; by subtraction

$$\ln t_2 - \ln t_1 = E/R\,(1/T_2 - 1/T_1)$$

whence

$$E = \frac{R(\ln t_2 - \ln t_1)}{1/T_2 - 1/T_1}$$

or

$$E = \frac{2.3026\, R(\log t_2 - \log t_1)}{1/T_2 - 1/T_1}$$

E from the steeper straight line is 45,300, while E_2 from the other line is 36,470 calories.

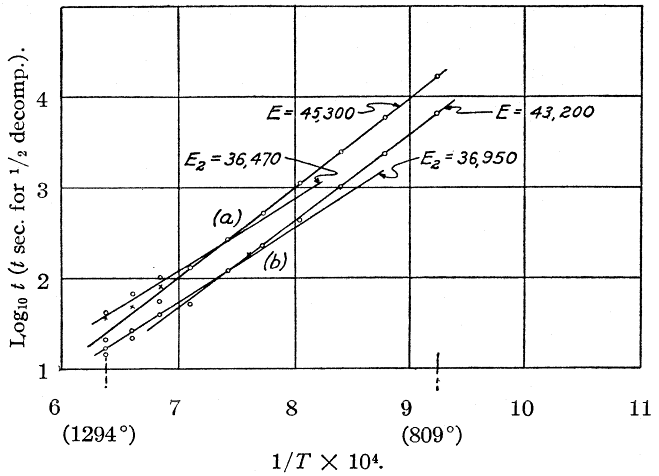


Fig. 6.—The temperature coefficient of the decomposition of ammonia on pure tungsten, for (a) "¹/₂ time" and (b) "¹/₄ time."

In Fig. 6(b) the time for one-fourth decomposition is taken from the original decomposition runs. The variation of E from that for one-half decomposition is comparable to the experimental error. This gives an added check on the method of determining E as to temperature control and effect of the products of the reaction as the reaction progresses. The temperature of the surface was obtained from a pyrometer calibration curve which was found to be 25° higher than, but parallel to, the calibration curve obtained from the temperature coefficient of tungsten by Jones. Since these two methods check so well, we are reasonably sure that although the exact temperature for a given point may not be known to within 25°, this error has no appreciable effect on the slope of the E curves.

The results for a 10 mil (diam. 0.025 cm., length 16.7 cm.) commercial tungsten filament are shown in Fig. 7, E_1 being 47,220 and E_2 34,800 calories. Similar tests were conducted on other grades of commercial tungsten and on a thoriated tungsten filament. Early tests made on the thoriated tungsten furnished by the General Electric Company and activated in a vacuum according to direction[12] showed no appreciable increase in activity over that of commercial tungsten, as was expected. However, no test, as the increase in electron emission of thoriated tungsten over tungsten, was made on the activity of the thoriated tungsten filament. Then again, as the thorium layer is very sensitive to gases, the ammonia

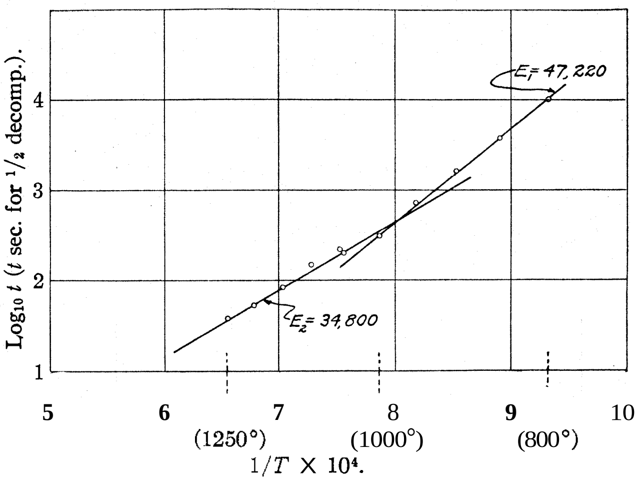


Fig. 7.—The temperature coefficient of the decomposition of ammonia on commercial tungsten.

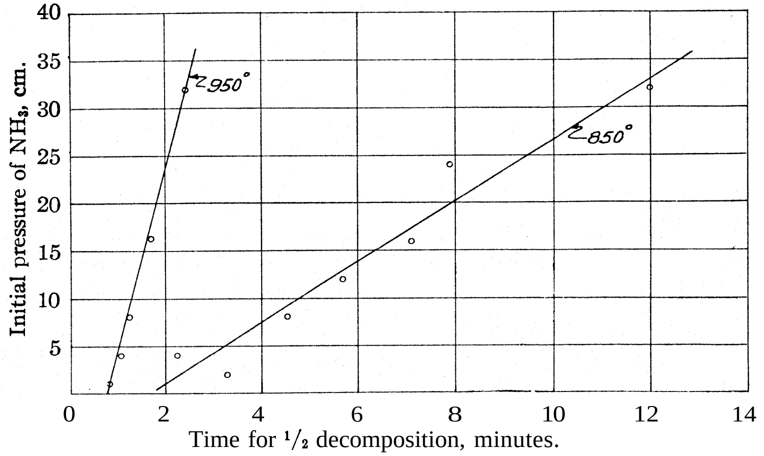


Fig. 8.—The decomposition of ammonia on molybdenum.

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[12] I. Langmuir, *Phys. Rev.*, 22, 357 (1920).

may have destroyed the added increase in activity expected from the thoriated tungsten. Sufficient tests were not made under the best experimental conditions to say that a properly activated thoriated tungsten surface is not more active than a tungsten surface.

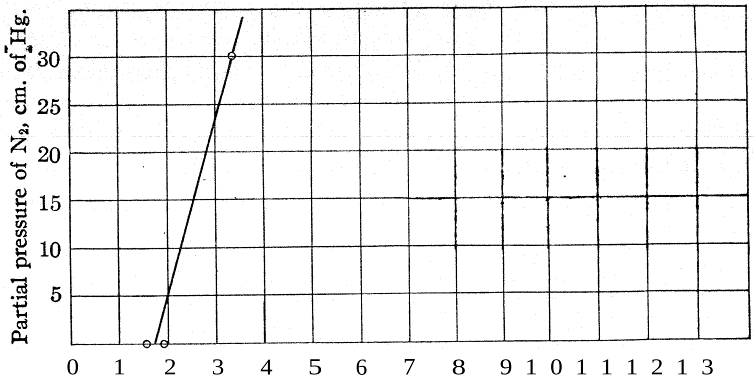

Fig. 9.—The effect of nitrogen on the rate of decomposition of ammonia on molybdenum at 850°.

Decomposition of Ammonia on Molybdenum

A 12 mil (diam. 0.030 cm., length 18 cm.) molybdenum filament from wire furnished by the Fansteel Products Company was used in these tests. Tests on the order of the reaction gave results very similar to those on tungsten, and an apparent zero reaction, Fig. 8. The effect of an initial concentration of nitrogen or hydrogen on the decomposition at 850° is shown in Figs. 9 and 10, respectively. Nitrogen has a much smaller effect than hydrogen. These results do not agree with those recently

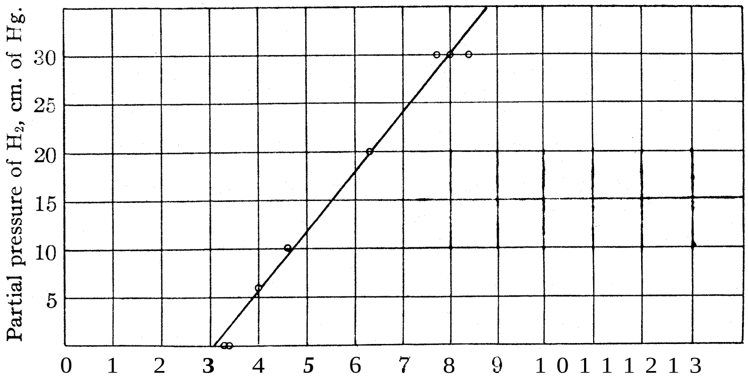

Fig. 10.—The effect of hydrogen on the rate of decomposition of ammonia on molybdenum at 850°.

published by Burke,[3] who finds no retarding effect for hydrogen and a very marked retarding effect for nitrogen. We do not know how to reconcile these two results. Water vapor or oxygen contaminations in the nitrogen used by Burke may have produced the progressive poisoning or retarding effect. Every effort was made to locate the discrepancy, but without success. Another difference has been noted in the value of E, Fig. 11. E_1 for the lower temperatures is 42,700 and at the higher temperature is 31,820 calories, while Burke's value is 53,200 between the temperatures of 824 and 955°. The experimental error is much less than 10,000 calories, the difference between these results and those of Burke.

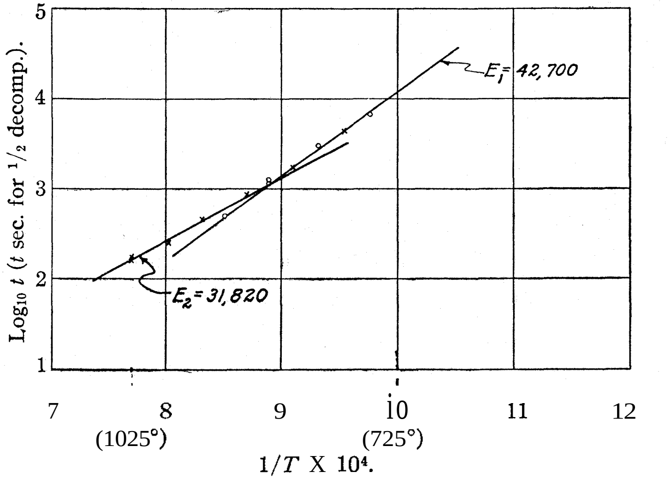

Fig. 11.—The temperature coefficient of the decomposition of ammonia on commercial molybdenum.

The Decomposition of Ammonia on Nickel

Only sufficient tests were made on a good grade of 12 mil commercial nickel wire (diam. 0.030 cm., length 16.5 cm.) to determine the relative position of nickel on a chart, Fig. 12, in respect to tungsten and molybdenum. Again we note a variation of E with temperature, starting at the low rates with values similar to tungsten and molybdenum and falling off with increase in temperature. In Fig. 12 the ordinates are based on one square centimeter of catalyst surface. Attention should be called to the general similarity of all curves and the relative activity of the respective metals for the ammonia reaction.

Discussion of Results

The experimental determinations of E for tungsten and molybdenum are not considered sufficiently reproducible for the lower temperatures to warrant deductions as to the relative values of E/T observed for a given rate of decomposition per square centimeter surface for the two materials. The observed values of E for the tests on tungsten were 45,300, 49,000, 45,250 and 49,750, with an average of 47,320; and for molybdenum, 44,200, 45,750, 44,600, 48,750 and 42,530, with an average of 45,170. Then again, at the lower temperatures, the retarding effects of the products are quite pronounced, so that although the reaction is of apparent zero order, the "true heat of activation" as expressed by Hinshelwood and Burke is not known. Tests are in progress toward a determination of more accurate values of E and a definite evaluation of the effects of the products of the reaction at the lower temperatures. There is no apparent relation between the catalytic activity of tungsten, molybdenum and nickel, and the observed temperature coefficients.

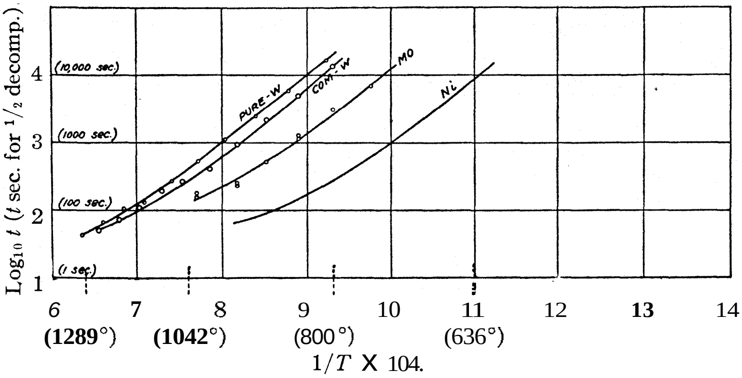

Fig. 12.—The relative activity of metal catalysts per square centimeter of surface for the decomposition of ammonia.

The catalyst surfaces were determined from careful measurements of the diameter and length of the drawn wire filaments in the absence of a better method of obtaining these surfaces. In so far as deductions can be made from the observed temperature coefficient and the measured surfaces, it would seem that the relative catalytic activity depended primarily on the catalyst surface and therefore on A, which is proportional to the number of molecules of ammonia decomposing per unit time per square centimeter surface. All curves, Fig. 12, are of the same general form and can be thought of as a shift to a higher or lower temperature, respectively.

In view of the fact that in general the log t against $1/T$ relation is curved rather than linear, and that the meaning of the heat of activation as applied to surface reactions is not too well understood, we prefer to speak of the results in terms of the temperature coefficient of the surface reaction expressed in terms of E, rather than a heat of activation. The answer to the question as to what extent the catalytic activity of a surface can be expressed in terms of the A or E constants of Arrhenius' equation is also not conclusive. At the lower reaction rates E has the value of about 45,000 calories, independent of the metal surface upon which decomposition takes place. The change of E with increase in temperature is no doubt due to a change of the surface upon which decomposition takes place. This may be due to (1) some change in the metal atoms of the surface with temperature; (2) a change in the amount or nature of the gas adsorbed on the surface with temperature; (3) not to be underestimated, a change of the physical and chemical properties of the composite surface with temperature, where the composite surface is the metal surface atoms in equilibrium with adsorbed gas molecules or atoms at any temperature; (4) a combination of (1), (2) and (3).

In dealing with surface catalysis, where the reactants need to be adsorbed before activation and reaction, the adsorbed gas no doubt has far different properties than in the gas phase. Likewise, the surface metal atoms in contact with gas would be expected to be different from atoms within the solid, so that the combination of the gas or gases on the metal surface presents a problem of the chemistry and physics of a fourth state, as considered by William B. Hardy, where the four states are: gases, liquids, solids and surfaces.

The results in Fig. 4, showing the activation of tungsten and similarly of molybdenum by glowing in an atmosphere of nitrogen, indicate the importance of the activation of a surface.

It seems of prime importance to know more of the physical and chemical properties of the catalyst surface at the temperature and conditions at which the catalyst is operating before much can be said as to the nature of the surface, mechanism of the reaction on the surface and the corresponding meaning of E. Experiments with the view of obtaining this information are now in progress at the Laboratory.

The recently reported work by Davisson and Germer[13] gives us a tool whereby surface phenomena can be investigated, namely, the analysis of diffraction patterns from slow speed electrons produced by potentials of 10 to 400 volts. These results have already shown that a thin film of adsorbed gas at room temperature has a definite solid lattice structure similar to the atoms in a nickel crystal, which lattice completely disappears at about 200° without a removal of the gas from the surface; that is, a solid or frozen lattice structure of adsorbed gas is changed into a 2-dimensional liquid structure by increasing the temperature of the surface from room temperature to 200 degrees or more.

The author wishes to express his appreciation for the interest shown and suggestions received in this work from the Laboratory staff, and especially to Mr. R. A. Nelson for constructing the apparatus and assisting through

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[13] Davisson and Germer, *Phys. Rev.*, 30,705 (1927); 31,307 (1928).

these studies; also to Messrs. E. S. Lamar and J. W. Westhaver, for assistance in the experimental work.

Summary

The decomposition of ammonia on tungsten, molybdenum and nickel has been investigated as a part of a program designed to give further information in regard to the ammonia reaction and the role played by the catalyst in this reaction. The results are expressed in terms of the A and E constants of Arrhenius' equation.

The decomposition of ammonia on tungsten and molybdenum was apparently of zero order. The reaction rate was decreased at the lower temperatures by both hydrogen and nitrogen.

The value of E as determined from the temperature coefficient was approximately constant for all surfaces at the lower reaction rates, about 45,000, decreasing for the higher temperatures to 35,000 for tungsten, 32,000 for molybdenum and 26,000 for nickel.

The relative catalytic activity of the surface investigated was not given by the observed temperature coefficient of the reaction expressed in terms of E but was given rather in terms of the surface, that is, in terms of A, in so far as comparisons can be made from the measured dimensions of the hot catalyst surfaces.

In general, the conclusions herein reached agree with the results obtained on promoted iron catalysts, which are to be published soon.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICS OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES. ORGANO-MOLECULAR INVESTIGATIONS]

INFRA-RED ABSORPTION BY THE S-H BOND

BY JOSEPH W. ELLIS

RECEIVED APRIL 26, 1928 PUBLISHED AUGUST 4, 1928

The apparent possibility of identifying the carbon–hydrogen[1] and the nitrogen–hydrogen[2] atom pairs as the probable origins of certain series of absorption frequencies in the near infra-red spectra of organic molecules has suggested a search for corresponding frequencies characteristic of the sulfur–hydrogen linkage. The spectra of the mercaptans suggest possible sources in which to look for such absorption bands. Bell[3] has obtained the spectra of several alkyl and aryl mercaptans and sulfides in the spectral region from 1–12μ. The general appearance of these spectra is strikingly similar to that of the corresponding alkyl or aryl amines recorded by Bell.[4]

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[1] (a) Ellis, *Phys. Rev.*, 23, 48 (1924); (b) 27, 298 (1926).

[2] (a) Ellis, THIS JOURNAL, 49, 347 (1927); (b) 50, 685 (1928).

[3] (a) Bell, *Ber.*, 60, 1749 (1927); (b) private communication.

[4] (a) Bell, THIS JOURNAL, 47, 2192 (1925); (b) 47, 3009 (1925); (c) 48, 813 (1926); (d) 48, 818 (1926); (e) 49, 1837 (1927).

This suggests that the main features of the spectra are assignable to origins within the substituted organic radical, some of them doubtless to the C–H linkages.

In the spectrum of a mercaptan, however, there is one band at 3.8–3.9μ which disappears, or practically disappears, in the spectrum of the corresponding sulfide. It was the opinion of the present author that this band might represent a fundamental frequency characteristic of the S–H atom pair, corresponding to the 3.4μ, **3.2–3.3μ** and 2.8–3.0μ band ascribed by him and others to alkyl C–H, aryl C–H and N–H linkages, respectively.

The present investigation was undertaken to search for possible harmonics of this 3.8–3.9μ band. The recording quartz spectrograph used in previous studies was employed here. The compounds studied were ethyl, n-propyl, n-butyl, *iso*-amyl, phenyl (thiophenol) and benzyl mercaptans and the corresponding sulfides. These were supplied by the Eastman Kodak Company.

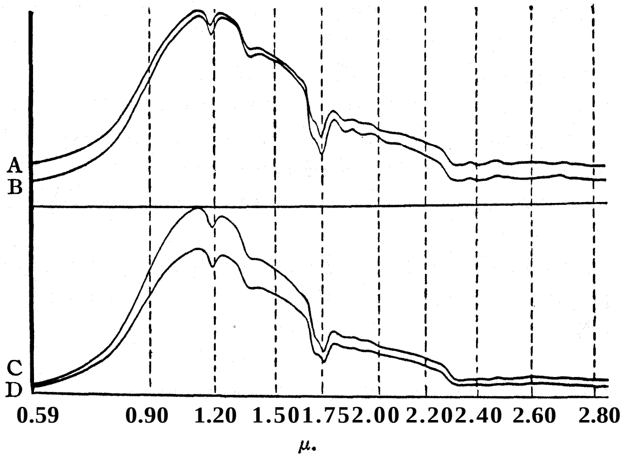

Fig. 1.—A. Ethyl mercaptan, *T* = 1 mm. B. Ethyl sulfide, T = 1 mm. C. n-Propyl mercaptan, T = 1 mm. **D.** n-Propyl sulfide, T = 1 mm.

The records of these spectra are shown in Figs. 1–4. In reproducing these records the plate containing the photographic tracing of the mercaptan was placed over that of the sulfide and these were photographed together by transmitted light. There seems to be but one distinguishing feature in the spectra of the mercaptans, namely, a band at 1.99–2.00μ. This is regarded as the first harmonic of the 3.8–3.9μ band. Both of these bands are strongest in the spectra of thiophenol and benzyl mercaptan. The presence of the overtone band may be considered uncertain in the records of 1-mm. cells of ethyl and n-propyl mercaptans, Fig. 1. However, it appears quite strongly when a 1-cm. cell of the latter substance is used, Fig. 2. An inspection of the original record of n-butyl mercaptan removes any doubt of its presence in that substance, and it is very noticeably present in the record of *iso*-amyl mercaptan in Fig. 3.

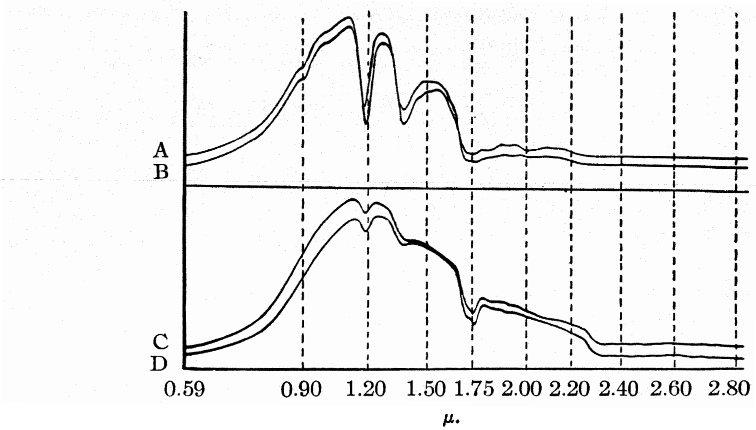

Fig. 2.—A. n-Propyl mercaptan, T = 10 mm. B. *n*-Propyl sulfide, T = 10 mm. C. *n*-Butyl mercaptan, *T* = 1 mm. D. n-Butyl sulfide, T = 1 mm.

A possible second harmonic would be superimposed upon the 1.4μ absorption region characteristic of both the mercaptan and the sulfide and hence could not be expected to be capable of detection.

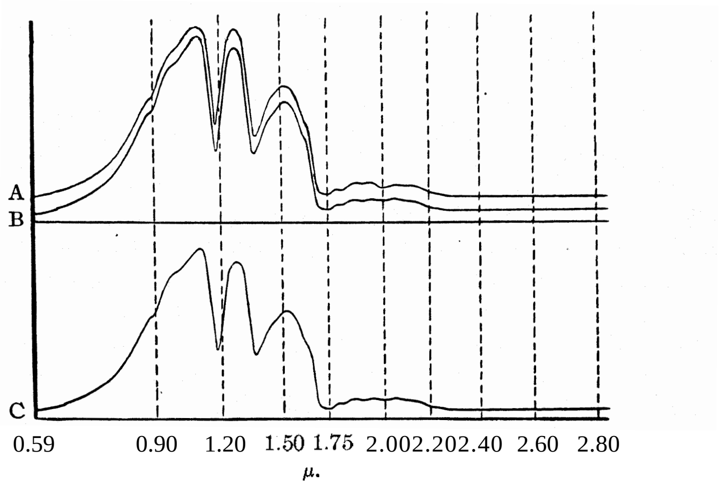

Fig. 3.—A. Iso-amyl mercaptan, T = 10 mm. B. *Iso*-amyl sulfide, T = 10 mm. C. Iso-amyl disulfide, T = 10 mm.

The deviation from true multiple relationship between the 3.8μ and the 1.99μ wave lengths for the alkyl mercaptans seems slightly greater than would be expected from comparisons with the fundamental and first overtone bands assigned to C–H and N–H atom pairs. However, the deviation is quite comparable with these latter cases in the case of the two aryl mercaptans; in these instances Bell's value (unpublished) varies from 3.85μ to 3.90μ and the overtone value from the present investigation is 2.00μ.

The main features of the spectra of the mercaptan and of the corresponding sulfide are quite similar over the whole region in which they have been studied. The main bands which occur are also found in the spectra of the corresponding primary, secondary and tertiary amines.[2,4] Certain of these, which have already been assigned to the C–H linkages, are tabulated, together with the bands assignable to S–H pairs, for the mercaptans and sulfides in Table I. Inspection of the table reveals the fact that the 3.30–3.35μ alkyl C–H value seems to be a trifle low as compared with the integral multiples of the corresponding overtone wave lengths. This fact, taken with the slight discrepancies in the S–H values discussed above, suggests a possible small systematic error in Bell's investigation of the alkyl mercaptans and sulfides.

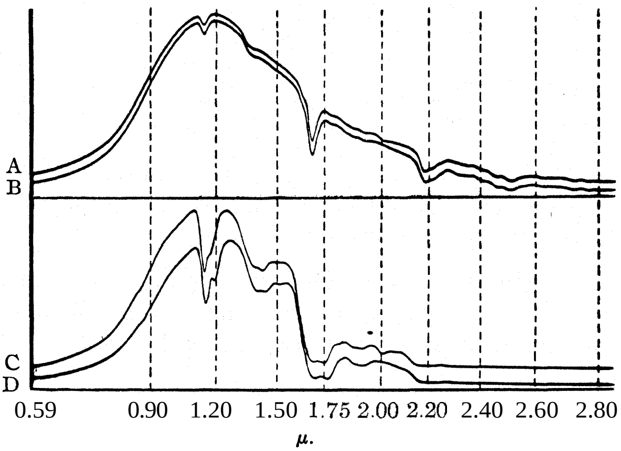

Fig. 4.—A. Thiophenol, T = 1 mm. B. Phenyl sulfide, T = 1 mm. C. Benzyl mercaptan, T = 10 mm. D. Benzyl sulfide, T = 10 mm.

The record of di-iso-amyl sulfide, Fig. 3, reveals nothing not shown by iso-amyl sulfide. Consequently, a study of the disulfides was pursued no further.

The doubling of the 1.145–1.19μ and 1.69–1.76~bands in benzyl mercaptan and benzyl sulfide is probably due, as in the corresponding amines, to the presence of both phenyl and alkyl types of C–H bonds. The doubling of the 1.7μ alkyl band, more noticeable here than in the corresponding records heretofore published by the author, has been brought about by an increase in the resolving power of the spectrograph. This increased resolution has been produced largely by focusing the spectrum upon the slit in front of the thermopile rather than upon the thermo-elements themselves. The possible significance of this revealed doubling here and in other instances will be discussed elsewhere.

All of the compounds examined are liquids at room temperature with the exception of benzyl sulfide. The record shown for this compound in Fig. 4 was taken through a 1-cm. cell of the molten substance maintained at a temperature just above the melting point. Upon cooling in an open dish, benzyl sulfide crystallizes in rhombohedral plates. A record was taken through such a specimen about 2 mm. in thickness. It was found necessary to open the slits considerably to get sufficient intensity, but the positions of the bands were found to be unchanged. This would seem to indicate that the force constants and the energy associated with the C–H bond, at least in this instance, remain unchanged during crystallization.

TABLE I

BANDS CHARACTERISTIC OF MERCAPTANS AND SULFIDES

	Bands assignable to C–H, μ							to S–H, μ	
Ethyl mercaptan			1.18	1.38	1.70, 1.74			2.00	
Ethyl sulfide			1.185	1.38	1.70, 1.74				
n-Propyl mercaptan	0.91	1.01	1.19	1.385	1.71, 1.75	3.3	6.8	1.99	3.80
n-Propyl sulfide	.91	1.01	1.19	1.385	1.71, 1.75	3.35	6.85		
n-Butyl mercaptan			1.19	1.395	1.71, 1.75	3.3	6.8	1.99	3.80
n-Butyl sulfide			1.19	1.385	1.71, 1.75	3.35	6.85		
Iso-amyl mercaptan	.90	1.00	1.18	1.38	1.73	3.3	6.8	1.99	3.80
Iso-amyl sulfide	.90	1.00	1.18	1.37	1.73	3.4	6.85		
Iso-amyl disulfide	.90	1.00	1.18	1.37	1.73				
Thiophenol			1.145	1.39	1.685	3.25	6.8	2.00	3.90
Phenyl sulfide			1.145	1.39	1.685	3.25	6.8		
Benzyl mercaptan			1.145	1.39	1.69, 1.75	3.25	6.6, 6.9	2.00	3.85
Benzyl sulfide			1.145	1.39	1.69, 1.76	3.25	6.7, 6.9		

The spectrum of hydrogen sulfide has been recorded beyond 3μ by Coblentz.[5] Inasmuch as the mercaptans are mono derivatives of hydrogen sulfide, it might be expected that the spectrum of this latter substance would show a band analogous to that at $3.8–3.9\mu$. A band at 4.2μ might

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[5] Coblentz, *Carnegie Inst. Pub.*, 1905, 35.

be interpreted as such. However, the complexity of the hydrogen sulfide spectrum beyond 4μ tends to make this comparison uncertain.

Summary

1. The infra-red absorption spectra of several alkyl and aryl mercaptans and sulfides have been examined with a recording quartz spectrograph.

2. **A** single band at 1.99–2.00μ differentiates the spectrum of a mercaptan from the corresponding sulfide. This band is regarded as the first harmonic of one found by Bell at 3.8–3.9μ, and both are interpreted as originating in the S–H bond.

LOS ANGELES, CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

GALLIUM. III. QUANTITATIVE SEPARATION OF IRON FROM GALLIUM BY MEANS OF ALPHA-NITROSO-BETA-NAPHTHOL[1]

BY JACOB PAPISH AND L. E. HOAG

RECEIVED APRIL 30, 1928 PUBLISHED AUGUST 4, 1928

The method frequently employed for separating iron from gallium is based on the property of trivalent iron to form a precipitate on the addition of an excess of fixed alkali hydroxide while gallium, being amphoteric, passes into solution as alkali gallate. This method was first used by de Boisbaudran,[2] the discoverer of gallium, and in so far as the preparation of iron-free gallium is concerned it will be found satisfactory; the resulting alkali gallate and the gallium hydroxide and oxide ultimately obtained from it will be found on spectroscopic examination to contain negligible traces of iron, provided care is taken to prevent contamination through reagents and containers. A similar examination of the residual ferric hydroxide will reveal that even after thorough washing, small quantities of gallium are retained. This can be undoubtedly ascribed to the strong adsorptive power of ferric hydroxide, a phenomenon frequently observed in similar cases.

In extracting gallium from a natural mineral or in recovering it from commercial products, iron which is always present will accompany the

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[1] This article is a corollary of experiments supported by a grant from the Heckscher Foundation for the Advancement of Research, established by August Heckscher at Cornell University. It is respectfully dedicated by the authors to Professor L. M. Dennis, and will be reprinted as article No. 9 in the Louis Munroe Dennis Quarter Century Volume to be published in 1928 in commemoration of the completion by Professor Dennis of twenty-five years of service as Head of the Department of Chemistry at Cornell University.

[2] De Boisbaudran, Compt. *rend.*, 94, **1439,** 1625 (1882).

gallium through the various stages of concentration. Furthermore, in the separation of gallium from aluminum by converting the former to the ferrocyanide, large quantities of iron are unavoidably introduced in the form of the precipitating agent. It may be worth while to remark in passing that the ferrocyanide method is among the best for separating gallium from aluminum.[3] In either case the chemist is confronted with the necessity of separating iron from the gallium. Papish and Holt[4] employed a-nitroso-@-naphtholfor this purpose. An examination of the residual iron salt obtained by this method proved that it was free, even in a spectroscopic sense, from gallium. This at once suggested itself as a suitable method for quantitative analytical work and the following experiments were undertaken to determine its applicability.

A solution of α-nitroso-β-naphthol was prepared by dissolving 1 g. of the reagent in 50 cc. of a 50% solution of acetic acid. It was made up fresh and filtered each time before using.

A solution of ferric chloride of known concentration was prepared by dissolving the salt in a definite volume of water and determining the iron content as ferric oxide by adding ammonium hydroxide to a small portion of the solution and washing, igniting and weighing the precipitate. The ferric chloride, before being dissolved, was examined spectroscopically for gallium and aluminum and was found to be free from both these elements.

Ignited gallium oxide, which on spectroscopic examination was proved to be free from iron,[5] was dissolved in hot aqua regia, boiled with separate portions of hydrochloric acid and the resulting solution of gallium trichloride, freed from the oxides of nitrogen, was diluted with water to a definite volume. The gallium content of this solution was determined in duplicate samples as follows. Two 20cc. portions were transferred to beakers and an excess of ammonium hydroxide was added to each. The solutions were boiled until a moistened piece of red litmus paper did not turn blue on exposure to the vapors evolved from them. On cooling, the precipitates of gallium hydroxide were collected on ashless filter papers and washed with a dilute solution (about 1%) of ammonium nitrate until washings gave no test for chlorides.

If it was noticed or even suspected that some gallium hydroxide adhered to the walls of the beaker, a small amount of hydrochloric acid was added and the gallium was reprecipitated with ammonium hydroxide in the manner just described. While this additional precipitate could have been added to the bulk of gallium hydroxide on the filter, it was found more expedient to collect and wash it on a separate filter paper. The tendency of precipitated gallium hydroxide to adhere to the walls of the container is to be taken into consideration while working with this substance.[6] This tendency is pronounced when the concentration of gallium

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[3] For details of this method see Crookes' "Select Methods in Chemical Analysis," 3d ed., Longmans, Green and Co., London, 1894, p. 159.

[4] Papish and Holt, *J. Phys. Chem.*, **32,** 142 (1928).

[5] As a matter of fact the small amount of iron was removed from this sample of gallium oxide by a previous treatment with α-nitroso-β-naphthol.

[6] See Dennis and Bridgman, THIS JOURNAL, 40, 1545 (1918).

is high and when the boiling is prolonged, and it becomes negligible in the case of small quantities boiled for a short time.

The filter papers and contents were transferred to previously weighed porcelain crucibles and ignited to constant weight. Freshly ignited gallium oxide is quite hygroscopic and in order to prevent errors from this source the crucible containing the oxide was placed in a stoppered weighing bottle after ignition, allowed to cool in a desiccator and weighed with the bottle.

Measured volumes of solutions of iron chloride and of gallium chloride, each of known concentration, were mixed, and to the mixture ammonium hydroxide was added carefully until a slight, permanent precipitate resulted which dissolved on the addition of a drop of hydrochloric acid. One or two additional drops of hydrochloric acid were added to insure acid reaction and an excess of a 50% solution of acetic acid was added. A very good alternate method consists in using ammonium acetate in place of acetic acid. This will insure the absence of hydrochloric acid as such, though a very small amount of this acid works no hardship with the procedure. The reagent α-nitroso-β-naphthol in acetic acid was next added to insure excess and the whole was allowed to stand for several hours. The precipitated ferric α-nitroso-β-naphtholate was removed by filtration, washed, first with a 50% solution of cold acetic acid and then with water. After drying, the filter paper and contents were transferred to a porcelain crucible and ignited to constant weight over a Méker flame. This ignition must be carried out very carefully so as to prevent mechanical loss which will be caused by too rapid decomposition of the organic compound.[7] The iron was weighed as ferric oxide.

The galliferous filtrate from the ferric α-nitroso-β-naphtholate was evaporated to dryness to expel the acetic acid and ammonium hydroxide was

TABLE I

SEPARATION OR IRON FROM GALLIUM

Sample no.	Wt. of Fe_2O_3 taken, g.	Wt. of Ga_2O_3 taken, g.	Wt. of Fe_2O_3 found, g.
1	0.0044	0.0515	0.0044
2	.0222	.0257	.0221
3	.0443	.0515	.0443

TABLE II

DETERMINATION OR IRON AND GALLIUM

Sample, no.	Wt. of Fe_2O_3 taken, g.	Wt. of Ga_2O_3 taken, g.	Wt. of Fe_2O_3 found, g.	Wt. of Ga_2O_3 found, g.
1	0.0425	0.0394	0.0420	0.0394
2	.0425	.0394	.0421	.0399
3	.0425	.0394	.0428	.0391
4	.0222	.0515	.0223	.0515

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[7] It was not found necessary to add oxalic acid to the ferric α-nitroso-β-naphthalate before ignition as suggested by Illinski and Knorre in connection with the separation of iron from aluminum, see *Ber.*, 18, 2728 (1885).

added to distinct alkalinity. From this point on the procedure was identical with the one already described in connection with the determination of gallium in the original solution of gallium chloride. The results are recorded in Tables I and II.

At the completion of the determinations the oxides of iron and gallium were examined spectroscopically[8] with the following results. The oxides of iron, as already mentioned, were invariably found to be free from gallium. The oxides of gallium contained negligible quantities of iron, a fact established by the presence only of the more persistent spectral lines of this element, λλ 2382.0, 2395.6, 2596.4 and 2599.4 Å.

Summary

A quantitative method is described for the separation of iron from gallium by means of α-nitroso-β-naphthol.

It is proved spectroscopically that the iron separated by this method is free from gallium.

It is proved spectroscopically that the gallium obtained from such a separation contains negligible traces of iron.

ITHACA, N. Y.

[CONTRIBUTION FROM THE RESEARCH DEPARTMENT OF THE MOORMAN MFG. CO.]

AN ACCURATE METHOD FOR THE DETERMINATION OF IODINE IN MINERAL MIXTURES[1]

BY M. D. KNAPHEIDE AND ALVIN R. LAMB

RECEIVED APRIL 30. 1928 PUBLISHED AUGUST 4, 1928

The addition of potassium or calcium iodide to mineral mixtures to be fed to farm animals has made necessary the accurate estimation of iodine in such mixtures, both by the manufacturer and by the feed control chemist. The volatility of iodine under certain conditions, its probable adsorption upon the charcoal which is commonly found in such mixtures and the very small amounts which are permissible, tend to complicate the situation.

Simple extraction methods, using water, alcohol or alkali, were tried by the authors and found to be entirely inadequate. Except in freshly prepared mixtures, less than half of the iodine was recovered by extraction. Using samples of mixtures containing charcoal, it was found that the sum of the iodine in the alcoholic extract and in the residue approximated the total amount present, 40 to 50% of this amount being found in the extract.

Combustion of the sample in a silica tube and determination of the iodine by the method of McClendon[2] or by a combination of this method with

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[8] See Papish and Holt, ref. 4, for the arc spectrographic method employed.

[1] Presented at the St. Louis meeting of the American Chemical Society, April 18, 1928.

[2] McClendon, J. *Biol.* Chem., 60, 289–299 (1924).

that of Kendall[3] was laborious and produced rather low results. Fusion of the sample in a special Parr sulfur bomb with sodium peroxide and potassium chlorate, followed by determination of the iodine according to Kendall, gave very low results. Fusion with a mixture of sodium carbonate, potassium carbonate and potassium nitrate in molecular proportions was not satisfactory on account of the high temperature necessary and the short life of the nickel crucible.

Extraction of the sample with sodium hydroxide in aqueous solution, followed by fusion of the evaporated extract with sodium hydroxide in a nickel crucible according to Kendall gave concordant and fairly good but still low results.

Finally the fusion of the original sample with sodium hydroxide and potassium nitrate, followed by a modification of Kendall's procedure was found to yield the most nearly quantitative results. The working out of the proper conditions and the testing of various modifications have involved running several hundred determinations. The method is still rather laborious, but six or eight determinations can easily be completed each day, the entire procedure extending most conveniently over three days. The details of the method and typical results follow.

Twenty grams of sodium hydroxide and 10 g. of potassium nitrate are fused together in a 100cc. nickel crucible. After cooling, a 10g. sample of the mineral mixture is placed evenly on top of the fused alkali and completely moistened with 5 cc. of saturated sodium hydroxide solution and 10 cc. of 80% alcohol. The crucible is then placed on a cold three-heat hot plate and the alcohol evaporated by the low heat. After half an hour the heat is cautiously increased until the crucible has been subjected to the highest temperature of the hot plate for about one and one-half to two hours. Thorough heating at this time prevents most of the trouble from effervescence of the material during the fusion. The crucible is then placed in a crucible furnace or one similar to that used by Kendall and Richardson,[4] which heats evenly both the sides and the bottom of the crucible. An ordinary electric furnace might be used, if it were not necessary to watch and sometimes cool the crucible to avoid bubbling over.

Mineral mixtures containing charcoal will require more attention during the fusion, on account of the violent reaction between the charcoal and the potassium nitrate. There is, however, no loss if the crucible is carefully watched. If the reaction becomes too violent the crucible is lifted from the furnace for a moment, and if necessary the bottom of the crucible is cooled in a beaker of water.

After the mixture is in a quiet state of fusion the crucible is tipped on all

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[3] *Kendall, J. Biol. Chem.,* **43, 149–159 (1920).**

[4] *Kendall and Richardson, ibid.,* **43, 164 (1920).**

sides in an open flame to wash down the sides of the crucible with the fusion mixture. Next a few small crystals of potassium nitrate are added until no more gas is liberated by further additions and the sides of the crucible are again washed down in the flame.

The melt is then poured out into the clean crucible cover to cool or the crucible is turned while cooling so that the material solidifies on the sides of the crucible. The cooled melt and the crucible are placed in a 600cc. beaker, covered with water and heated below the boiling point for a short time. After standing overnight at room temperature, the crucible and cover are rinsed off and removed. In order to neutralize part of the alkali and facilitate filtering, 10 cc. of sirupy phosphoric acid is added and the beaker placed on a steam-bath for about three or four hours with occasional stirring to break up the mass and insure complete solution of the iodine.

The beaker is cooled[5] and the insoluble residue filtered off in a 10cm. funnel and washed with cold water into an 800cc. beaker, adjusting the volume to about 550 to 600 cc. At this time the solution should be clear and colorless.

In order to destroy nitrites, which interfere with the titration with methyl orange, 10 cc. of 20% sodium bisulfite solution is now added, the solution brought just to the boiling point and then cooled. About 30 cc. of 85% phosphoric acid is run in from a buret, a few drops of methyl orange solution added and the addition of phosphoric acid continued to the neutral color of the methyl orange, after which 1.5 cc. of the phosphoric acid is added in excess. The total amount of phosphoric acid required is generally not over 35 cc., except when the presence of considerable charcoal in the sample has necessitated the use of more potassium nitrate, which is thus mainly reduced to carbonate. Care must be taken not to run appreciably over the end-point, since excess acid gives low results. However, the addition of the acid must be fairly rapid, as the color of the methyl orange has a tendency to fade, due to incomplete destruction of the nitrites.

After neutralization, a small lump of anthracite coal[6] (0.5 cm. in diameter) is put in and the solution is boiled for at least twenty minutes, the volume being reduced to about 400 to 500 cc. This length of time is essential in order to remove all traces of sulfurous acid. The solution is cooled again and bromine water added until a distinct and permanent yellow color is produced. The solution is then boiled until colorless by reflected light and then for exactly five minutes longer. A few crystals of salicylic acid are added to assure the removal of the last traces of brom-

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[5] A galvanized iron pan with sides about 10 to 12 cm. high and outlets at different levels is a very convenient means of cooling beakers of solution, which is necessary several times during this determination.

[6] Kendall, *J. Biol. Chem.*, **43**, 151 (1920).

ine, and the solution is cooled, after which 5 cc. of 20% reduced phosphoric acid[7] and 0.5–1.0 gram of chemically pure potassium iodide are added. The solution is then titrated in the usual manner with 0.005 N sodium thiosulfate solution, adding starch solution when the brown color of the liberated iodine is nearly gone. The volume of the solution at the final titration should be 400 to 500 cc.

The thiosulfate solution is standardized according to Kendall, by dissolving approximately 1 g. of pure iodine in a liter of 0.5% sodium hydroxide solution. This solution is then diluted ten times, 25 cc. is pipetted into a flask, diluted to 200 cc. and 10 cc. of 30% sodium hydroxide added. The solution is then neutralized with phosphoric acid and the iodine determined as in the method here outlined.

The thiosulfate solution may also be standardized by pipetting into a beaker or flask 25 cc. of a solution containing 0.1308 g. of potassium iodide per liter, adding 200 cc. of water, 5 cc. of 20% sodium bisulfite and 2 or 3 g. of sodium hydroxide. This is neutralized with phosphoric acid, adding 1.0 cc. of the concentrated acid in excess and proceeding further as in the regular determination described above. To calculate the milligrams of iodine to which 1 cc. of the thiosulfate solution is equivalent, the following formula is used

$$\frac{2.5}{\text{cc. of } Na_2S_2O_3 \text{ soln.}} = \text{mg. I equiv. to 1 cc. of } Na_2S_2O_3 \text{ soln.}$$

It is well to keep the volume of the solution used in standardization down to about 200 cc. for better and more comparable end-points in the final titration.

TABLE I

ANALYSIS OF MINERAL MIXTURE SAMPLES OF KNOWN IODINE CONTENT

Iodine added, mg.	Recovered, mg.	Remarks	Iodine added, mg.	Recovered, mg.	Remarks
2.0	1.96	10 g. of KNO_3 used	1.0	1.04	10 cc. of $NaHSO_3$ soln.
2.0	2.07	10 g. of KNO_3 used	2.0	1.99	15 cc. of $NaHSO_3$ soln.
2.0	1.97	10 g. of KNO_3 used	2.0	1.93	15 cc. of $NaHSO_3$ soln.
2.0	1.86	10 g. of KNO_3 used	2.0	2.01	15 cc. of $NaHSO_3$ soln.
2.0	1.96	3 g. of KNO_3 used	2.0	2.03	20 cc. of $NaHSO_3$ soln.
2.0	1.96	3 g. of KNO_3 used	2.0	2.03	20 cc. of $NaHSO_3$ soln.
2.0	2.00	3 g. of KNO_3 used	2.0	1.99	20 cc. of $NaHSO_3$ soln.
2.0	1.89	5 cc. of $NaHSO_3$ soln.	2.0	2.01	20 cc. of $NaHSO_3$ soln.
2.0	1.87	10 cc. of $NaHSO_3$ soln.	2.0	2.03	20 cc. of $NaHSO_3$ soln.
2.0	1.87	10 cc. of $NaHSO_3$ soln.	2.0	2.06	20 cc. of $NaHSO_3$ soln.
1.0	1.05	10 cc. of $NaHSO_3$ soln.	2.0	2.02	20 cc. of $NaHSO_3$ soln.
1.0	1.05	10 cc. of $NaHSO_3$ soln.	2.0	2.08	20 cc. of $NaHSO_3$ soln.
1.0	1.02	10 cc. of $NaHSO_3$ soln.			

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[7] Impurities in the phosphoric acid are reduced according to Kendall's method (*J. Biol. Chem.*, 43, 150 (1920)) by diluting the 85% acid with four volumes of water and boiling for some time with aluminum strips.

The table shows some typical results obtained by this method with samples containing known amounts of iodine. The iodine was added in the form of potassium iodide to samples of mineral mixture containing no iodine or a very slight trace. Blanks were always run on the samples used and on the reagents.

Samples which contain no charcoal or bone meal may be fused with 20 g. of sodium hydroxide alone, omitting the potassium nitrate except for the addition of a few small crystals at the end of the fusion.

Summary

A method is described for the quantitative determination of small amounts of iodine in mixtures of mineral salts, charcoal, spent bone black, etc. The method is a modification of Kendall's and involves fusion with sodium hydroxide and potassium nitrate, removal of interfering substances, oxidation with bromine and determination of the iodine iodimetrically. Necessary conditions are outlined. Other methods were found very unsatisfactory for complex mixtures except when the samples were freshly prepared.

QUINCY, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

THE ANTIMONY–ANTIMONY TRIOXIDE ELECTRODE AND ITS USE AS A MEASURE OF ACIDITY[1]

BY E. J. ROBERTS[2] AND F. FENWICK

RECEIVED MAY 2, 1928 PUBLISHED AUGUST 4, 1928

Increased realization of the importance of a knowledge of acidity in the control of chemical reactions has aroused a general interest in methods by which the activity of the hydrogen ion may be measured. If we dismiss from consideration the numerous and widely used color indicators, whose applicability rests upon comparative measurements with the hydrogen electrode, the latter at present constitutes by far the most important means of determining acidity. Under strictly defined conditions, it possesses a very high degree of accuracy and reproducibility; the maximum accuracy of the hydrogen electrode is not easy to attain, however, even approximately. The proper functioning of the platinum (or iridium) coating of the electrode is readily affected by traces of many substances not unlikely to be present in the system; reactions catalyzed by the platinum black may affect the hydrogen ion activity of the solution; the necessity of employing a gas phase of known partial pressure of hydrogen is awkward and presents serious difficulties in the investigation of

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[1] From the dissertation presented by E. J. Roberts to the Graduate School of Yale University, June, 1928, in candidacy for the degree of Doctor of Philosophy.

[2] Loomis Fellow, 1926–1927.

solutions in equilibrium with a dissolved gas. In this case the gas surrounding the electrode must be such that the equilibrium conditions of the original solution are not disturbed. Solutions containing carbonates, which are of especial interest to the physiological chemist, are but one example of a case in which the gas phase must consist of a mixture of gases of known partial pressure.

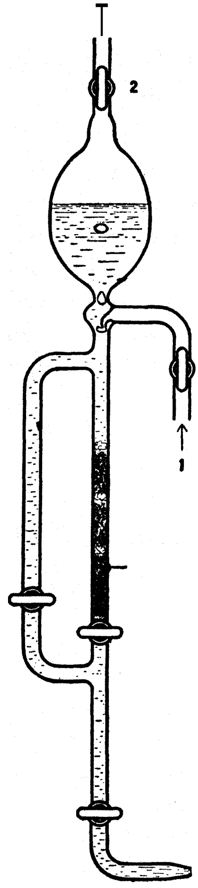

Fig. 1.—Antimony–antimony trioxide electrode for use with nitrogen. 1. Nitrogen inlet. 2. Nitrogen outlet.

The quinhydrone electrode and its several modifications are used quite extensively. The independence of a gas phase is a marked advantage of this electrode but its stability falls far short of that of the hydrogen electrode and it is not usable in solutions of appreciable alkalinity.

Another class of electrodes closely related to the hydrogen in principle but employing no gas phase is the metal oxide electrode, more particularly an electrode made up of a pure metal in contact with a solution saturated with respect to its oxide. Probably the best known example of this type is the mercuric oxide electrode; but, because of the solubility of the oxide, this electrode does not function as a measure of the activity of hydrogen ion except in alkaline solution and in absence of ammonia and of the anions of the slightly soluble mercurous salts, notably the chloride.

The first suggestion for a metal oxide electrode composed of a metal which does not displace hydrogen, whose salts are readily hydrolyzed and whose oxide possesses a low solubility in both acids and bases, was made by Uhl and Kestranek.[3] These authors pointed out that antimony and its amphoteric trivalent oxide meet the requirements over a presumably wide range in acidity. Their working electrode, which was used only as an end-point indicator in acidimetric titrations, was somewhat crude, consisting of a bar of massive antimony standing in the solution in which had been suspended several milligrams of antimony trioxide prepared by treating antimony with nitric acid.

The obvious advantages of such an electrode for measuring acidity led us to make an intensive investigation of the electromotive behavior of antimony and its trivalent oxide. Kolthoff and Hartong[4] have published the results of a brief study of the potential of the antimony–

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[3] Uhl and Kestranek, Monatsh., 44, 29 (1923).

[4] Kolthoff and Hartong, Rec. *trav. chim.*, 44, 113 (1926).

antimony trioxide electrode in various solutions of known acidity. Their electrode arrangement was that of Uhl and Kestranek; the relation between potential and PH was shown to be nearly linear, although the change in potential for each Sørensen unit was always less than that required by theory, diverging more in acid than in alkaline solution. Similar results were obtained in a rather more detailed research by Vlès and Vellinger.[5] After our work was practically complete, Franke and Willaman[6] described a form of antimony electrode for use in the control of pulp and paper manufacture; their electrodes, bars of metal cast with more care than those of previous authors, gave potentials which, at 25°, differed by only 54 mv. for a tenfold ratio of the hydrogen ion activities over the range 1 to 12 *P*H.

In the following we have attempted to define the conditions under which the behavior of the antimony–antimony trioxide electrode approaches the ideal, and also to describe a practical form of the electrode which may be used as a substitute for the hydrogen electrode with no essential decrease in accuracy and a considerably increased field of applicability over the latter. This has involved a study of the condition of both metal and of oxide stable at ordinary temperatures, the effect of oxygen upon the system, the time required for equilibrium to be established and the direction from which it must be approached. Moreover, it has necessitated a detailed examination of the validity of the accepted *P*H values of certain buffer solutions at 25° and, because of the uncertainty of some of the corrections involved, the direct measurement of some of them at 25°.

The Antimony–Antimony Trioxide Electrode at 25°

Corresponding to the electrode reaction $\mathrm{Sb(s)} \qquad \mathrm{Sb}^{+++} + 3\ \ominus$, the potential of an antimony electrode at 25° may be written

$$E_{\mathrm{Sb}} = E_0' - (0.05915/3) \log (\mathrm{Sb}^{+++}) \qquad (1)$$

In a solution saturated with respect to the trioxide, the following equilibrium may be considered to exist: $\mathrm{Sb_2O_3(s)} + 3\mathrm{H_2O} \qquad 2\mathrm{Sb}^{+++} + 6\mathrm{OH}^-$, wherefore, substituting in Equation (1) the value for the activity of Sb^{+++}, we have

$$\begin{aligned} E_{\mathrm{Sb}} &= E_0 + 0.05915\,[-\log(\mathrm{H}^+) - \log(\mathrm{Sb_2O_3})^{1/6} + \log(\mathrm{H_2O})^{1/2}] \\ &= E_0 + 0.05915\left[\mathrm{P_H} - \frac{1}{6}\log(\mathrm{Sb_2O_3}) + \frac{1}{2}\log(\mathrm{H_2O})\right] \qquad (2) \end{aligned}$$

Thus, if the last two terms in the equation are disregarded, E_0 is the difference in potential between an antimony–antimony trioxide and a hydrogen electrode in solutions of the same acidity. This cell was measured by Schuhmann[7] in three concentrations of perchloric acid ranging from 0.23 to 1.13 M, who demonstrated that in acid solution trivalent

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[5] Vlès and Vellinger, Arch. phys. *biol.*, *6*, 38 (1927); Vlès, *ibid.*, 6, 92 (1927).

[6] Franke and Willaman, *Ind.* Eng. Chem., 20, 87 (1928).

[7] Schuhmann, THIS JOURNAL, 46, 52 (1924).

antimony is present mainly in the form of SbO^+. The ions Sb^{+++}, $SbOH^{++}$, SbO^+, SbO_2^-, SbO_2OH^{--} and SbO_3^{---} may be regarded as capable of existence under different conditions of acidity. However, provided the system is in equilibrium, Equation (2) is independent of the form of the ion in which the antimony may occur; indeed, it may be very simply derived from the reaction expression $2Sb(s) + 3H_2O \quad Sb_2O_3(s) + 6H^+ + 6\ominus$.

The term in Equation (2) which involves the activity of the solid oxide disappears if the oxide is in its standard state (that is, the stable crystalline form), and this condition must hold if the antimony trioxide electrode is to attain its highest accuracy in acidimetric measurements. Other authors have paid no attention to this point, which has proved to be of major importance.

The term involving the activity of water is not altogether desirable from the standpoint of the applicability of the electrode for determining P_H. It is not always easy to evaluate this term with absolute accuracy but, since the activity of water decreases slowly with increasing concentration of dissolved salts, an approximation can usually be made that is within the experimental accuracy. For instance, even with solutions saturated at 25° with potassium chloride, sodium chloride, and potassium sulfate, respectively, the correction for the activity of water[8] amounts to 2.2, 3.7 and 0.4 mv.; in the case of the buffer solutions used in our experiments this term, being of the order of 0.01 mv., may be entirely neglected.

Since E_0 at 25° for the antimony–antimony trioxide electrode is essentially the potential of the electrode in a solution containing hydrogen ions at unit activity referred to a hydrogen electrode under a partial pressure of hydrogen of 1 atmosphere at 25° in a similar solution, the value of E_0 must be determined by making such a measurement either directly or indirectly, the direct measurement being obviously the more reliable method. However, owing to the fact that previous investigators have found that the coefficient of the second term of the right member of Equation (2) may deviate from theory as much as 10%, the indirect method promised distinct advantages in the study of the electrode under varied, but strictly defined, conditions. Accordingly, if the potential of the antimony electrode in a buffer solution, whose P_H has been determined by means of a hydrogen electrode measurement, is measured against reference electrodes corresponding to those used in the standardization of the buffer, the value for E_0 may be determined provided that (a) the conventions adopted with regard to the liquid junction potentials in the two systems correspond, (b) the reference electrodes in the two cases have the same thermodynamic properties. Since the slope of the E vs. P_H curve

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[8] Leopold and Johnston, THIS JOURNAL, 49, 1974 (1927).

of the antimony electrode is altered by 1 mv. per PH (that is, by almost 2%) by a change of as little as 0.12 in the difference attributed to a pair of buffers of PH 3 and 10, respectively, and since an uncertainty of this magnitude may easily enter when the buffers are used at a temperature other than that at which the values were set, we were forced to consider very carefully the *PH* of the standard buffers which we used. Furthermore, it is necessary to establish that the liquid junction potentials in our reference system correspond to those used in the standardization of the buffers and to choose the proper potentiai of our reference electrode.

The PH of the Standard Buffer Solutions at 25°

The buffers used in this investigation were those described by Clark and Lubs,[9] the PH of which was fixed by means of the hydrogen electrode at 20°, thus rendering a temperature correction to 25° necessary. Table I lists the several buffers with corresponding temperature corrections obtained from a number of sources (Col. 3). In the case of the two potassium chloride–hydrochloric acid buffers, the measurements were made at 25°; the next five were corrected on the basis of the work of Kolthoff and

TABLE I

THE TEMPERATURE CORRECTION AND BJERRUM EXTRAPOLATION FOR THE CLARK AND LUBS BUFFERS

Buffer	C. and L. PH at 20°	Temp. corr. to PH at 25°	Calcd. PH at 25°	Measured PH at 25°	Bjerrum, extrapolation, mv.
KCl, HCl	..	...	...	1.2	..
KCl, HCl	..	...	...	2.2	..
KHPhthalate, HCl	2.2	0.008	2.208	....	−0.21
KHPhthalate, HCl	3.0	.008	3.008	3.008	.31
KHPhthalate, NaOH	4.0	.010	4.010	....	.38
KHPhthalate, NaOH	4.4	.010	4.410	....	.43
KHPhthalate, NaOH	5.0	.012	5.012	....	.48
KHPhthalate, NaOH	5.6	.012	5.612	....	.48
KHPhthalate, NaOH	6.0	.013	6.013	6.018	.49
KH_2PO_4, NaOH	6.0	...	6.0	....	.32
KH_2PO_4, NaOH	6.4	...	6.4	....	.36
KH_2PO_4, NaOH	6.6	...	6.6	....	.38
KH_2PO_4, NaOH	7.0	...	7.0	6.975	.41
KH_2PO_4, NaOH	7.4	...	7.4	....	.42
KH_2PO_4, NaOH	8.0	...	8.0	....	.48
H_3BO_3, KCl, NaOH	8.0	−0.02	7.98	7.960	.00
H_3BO_3, KCl, NaOH	9.0	.04	8.96	(8.933)[a]	.05
H_3BO_3, KCl, NaOH	10.0	.06	9.94	9.905	.11
Na_2HPO_4, NaOH	11.29 (18°)	...	...	11.14	..
Na_2HPO_4, NaOH	12.06 (18°)	...	...	(11.91)[b]	..

[a] Interpolated from the preceding and following measurements.

[b] Calculated from direct measurements.

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[9] Clark and Lubs, *J. Biol. Chem.*, 25, 479 (1916).

Tekelenburg[10] on the change of *PH* in buffer mixtures at varying temperatures. Walbaum[11] found the *PH* of the phosphate buffers of the Sørensen series independent of the temperature over a wide interval, therefore the same conclusion was drawn with respect to the similar Clark and Lubs buffers; the corrections adopted for the borate buffers were also taken from Walbaum's work on the Sørensen solutions. The two most alkaline buffers are not from the Clark and Lubs series but were calculated from Ringer's[12] data by Kolthoff. The *PH* at 25° for the supposed *PH* 12.06 buffer is calculated from our own direct measurement on the preceding solution, assuming Kolthoff's difference to be correct. In some instances we determined the *PH* of the buffer directly with a hydrogen electrode; these values, discussed later, are given in the fifth column of the table and are used in subsequent calculations in preference to the computed values (Col. 4), as each of these involves a consideration of the work of more than one author.

Liquid Junction Potentials

Clark and Lubs measured the cells Pt, H_2 | buffer | 1.75 N KCl followed by 3.5 N KCl | KCl (saturated), Hg_2Cl_2 | Hg and Hg | Hg_2Cl_2, KCl (saturated) | 0.1 N KCl, Hg_2Cl_2 | Hg, employing the Bjerrum extrapolation indicated as a correction for the liquid junction potential between the buffer and the saturated potassium chloride, and "neglecting the liquid junction potential between saturated and 0.1 N potassium chloride." However, Scatchard[13] showed that in using a flowing junction apparatus in measuring the cell Hg | Hg_2Cl_2, KCl (saturated) || 0.1 M KCl, AgCl | Ag[14] the electromotive force did not change on stopping the flow, indicating that the junction potential was independent of the nature of the junction in the case of two potassium chloride solutions, and, therefore, that the combination of liquid junctions 3.5 N KCl | KCl (sat.) | 0.1 N KCl is exactly equivalent to the junction 3.5 *N* KCl | 0.1 N KCl; also that the combination 1.75 N KCl | KCl (sat.) | 0.1 N KCl is equivalent to 1.75 N KCl | 0.1 N KCl. This conclusion is still further verified by the fact that Clark found no Bjerrum extrapolation in the measurements on the borate buffers at low sodium ion content, that is, when the ions in the buffers were chiefly potassium and chloride ions. This means that the junction potential 0.1 N KCl | 1.75 N KCl plus 1.75 N KCl | KCl (sat.) equals 0.1 N KCl | 3.5 N KCl plus 3.5 N KCl | KCl (sat.) which may be extrapolated to equal 0.1 N KCl | KCl (sat.). Therefore 3.5 N KCl | 0.1 *N* KCl equals 3.5 N KCl | KCl (sat.) plus KCl (sat.) | 0.1 N KCl.

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[10] Kolthoff and Tekelenburg, *Rec. trav. chim.*, *46*, **33** (1927).

[11] Walbaum, *Biochem.* Z., 107, 219 (1920).

[12] Ringer, *Verslag. Physiol. Lab. te Utrecht*, 10, 109 (1909).

[13] Scatchard, THIS JOURNAL, 47, 696 (1925).

[14] The symbol || indicates a flowing junction.

If this is the case, Clark's liquid junction train is reduced in effect to Bjerrum's original train, solution | 3.5 N KCl followed by 1.75 N KCl | 0.1 N KCl, and the extrapolation tends to reduce the sum of all the liquid junction potentials to zero rather than merely that between the buffer and the saturated potassium chloride solution.

Our measurements were made with the liquid junction system buffer | 3.5 *N* KCl | 0.1 *N* KCl; since this corresponds to Bjerrum's train, it, in effect, is equivalent to Clark's train; therefore Clark's determined values for the Bjerrum extrapolation on the several buffers (Table I, last column) may be applied to our readings, thus bringing them into concordance with Clark's corrected potentials. It is to be noted that this correlation of our junction potentials with Clark's and our use of his Bjerrum extrapolations are necessary if we are to use his calculated values for the P_H of the solutions; but it must be emphasized that our derived value for E_0 is independent of any theory of the liquid junction since the corrections applied merely cancel those introduced by Clark in calculating the P_H of the solution.

Potential of Reference Calomel Electrodes

Clark used for the value of the decinormal calomel electrode —0.3355 v. referred to a platinized electrode immersed in a solution normal with respect to hydrogen ions and under an atmosphere of water vapor and pure hydrogen gas at a partial pressure of the latter of 760 mm. at 0°. In order to obtain the value of E_0 for the antimony–antimony trioxide electrode at 25° referred to a hydrogen electrode under 1 atmosphere partial pressure of hydrogen at 25°, now the generally accepted standard, by comparison with a 0.1 M calomel electrode, through the medium of a 3.5 N KCl, silver–silver chloride electrode, it is necessary to correct Clark's value for the 0.1 N calomel electrode for (1) the difference in concentration of hydrogen at a partial pressure of 760 mm. at 0° and 760 mm. at 25°, or 0.89 mv.; (2) the temperature coefficient of the electrode, giving rise to a potential change from 20 to 25° of 0.30 mv.;[15] (3) the difference in concentration between 0.1 N and 0.1 M potassium chloride, or —0.15 mv. The resulting value, -0.3374_6 v., refers our measurements to the desired hydrogen standard and to Clark's P_H scale, which, in turn, depends upon the absolute accuracy of his adopted value and his liquid junction corrections. The validity of the scale comes into question later when 0.1 M and 0.01 M hydrochloric acid solutions were used in some of the electrodes and the P_H values calculated on the basis of Scatchard's[13] values for the activity coefficients of hydrogen ion.

On the basis of the activity coefficients for hydrochloric acid[16] from

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[15] Clark, "The Determination of Hydrogen Ions," Williams and Wilkins Co., Baltimore, Maryland, 1925, Chap. XIX.

[16] Scatchard, THIS JOURNAL, 47, 641 (1926).

which those for hydrogen ion were derived, Scatchard finds the absolute value of the 0.1 M calomel electrode, including no junction potentials, to be —0.3353 v.[13] This calculation, however, is based on the value 0.3989 v. (average of best existing values in the literature, as judged by Scatchard) for the electromotive force of the cell Pt, H_2 | 0.1 *M* HCl, Hg_2Cl_2 | Hg which leads to 0.0466 v. for the difference between the calomel and the silver–silver chloride electrodes. In view of the fact that our direct measurements of this potential[17] using 0.1 M potassium chloride gave 0.04530 v. ± 0.05 mv. and that the calomel electrode is known to behave erratically in dilute hydrochloric acid solutions, we prefer to calculate the value of the calomel from Scatchard's measurements of the cell Pt, H_2 | HCl, AgCl | Ag[16] and our own value[18] for the difference between the silver chloride and calomel electrodes. Calculation of Scatchard's results to exactly 0.1 M hydrochloric acid gives 0.35230 v.; adding our value of 0.04535 v. we arrive at a result of 0.39765 v. for the potential of the hydrogen–calomel cell in 0.1 M hydrochloric acid. A value almost identical with this may be calculated from measurements presented later in Tables IV and V; that is, the electromotive force of the cell Pt, H_2 | 0.1 M HCl, Sb_2O_3 | Sb is 0.14436 v.; that of the cell Sb | Sb_2O_3, 0.1 M HCl || 3.5 N KCl, AgCl | Ag is 0.1259 v.; and for the cell Ag | AgCl, 3.5 N KCl || 0.1 M KCl, Hg_2Cl_2 | Hg the electromotive force is 0.13135 v.; from this it is evident that the electromotive force of the combination Pt, H_2 | 0.1 M HCl || 3.5 N KCl || 0.1 M KCl, Hg_2Cl_2 | Hg is 0.4016 v. In a paper to be published shortly, we will show that the difference between the two flowing liquid junction potentials indicated is 3.9 mv., which gives 0.3977 v. for the electromotive force of the cell Pt, H_2 | 0.1 M HCl, Hg_2Cl_2 | Hg if the activity of chloride ion in 0.1 M HCl and 0.1 M KCl is the same. Both of these values lead to an E_0 for the electrode Hg | Hg_2Cl_2, Cl^- of —0.2680 v., and —0.3341 v. for the potential of the decimolal calomel electrode, using Scatchard's values for the necessary activity coefficients.[19]

Thus, since the correct value for the potential of the decimolal calomel

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[17] Roberts and Fenwick, **THIS JOURNAL**, 49, 2787 (1927).

[18] In view of later measurements in connection with liquid junction potentials soon to be published, the highest of the possibilities indicated above, 0.04535 v., is judged to be more nearly accurate.

[19] Randall and Young, in a paper appearing just after the writing of this paper had been completed, **THIS JOURNAL**, 50, 989 (1928), give the following values:

	Randall and Young	Our values
Pt, H_2 | 0.1 M HCl, Hg_2Cl_2 | Hg, E	0.3976 v. (p. 990) 0.3977 v. (p. 993)	0.3977 v.
Hg | Hg_2Cl_2, Cl^-, E_0	—0.2676 v.	—0.2680 v.
Hg | Hg_2Cl_2, 0.1 M KCl, E	—0.3341 v.	—0.3341 v.

The agreement between the two sets of results is remarkable, the difference in the second value in the two cases being due to the use of different activity coefficients in the calculations.

electrode, corresponding to Scatchard's activity coefficients of hydrogen ion, is **–0.3341** v., and we are using -0.3374_6 v., we must either make a special case of the two hydrochloric acid solutions and use **–0.3341** v. for the potential of this cell in our calculations in these two instances, or else modify the calculated PH by an amount equivalent to the difference between the two calomel values, this being 3.3_6 mv. $(0.3374_6-0.3341)$ or **0.0568 PH,** which must be subtracted from the given calculated values **(1.075** and **2.036)** in order to make them conform to Clark's scale and our own working value for the calomel electrode; these computed values for **0.1** M and **0.01** M hydrochloric acid solutions become **1.018** and 1.979 **PH,** respectively, upon applying the above adjustment.

From this it is clear that our value for the E_0 of the antimony–antimony trioxide electrode is independent of any PH scale, since in both cases we have in effect used a value for our reference electrode which corresponds to that of the author from whose work the PH of our solution was derived. The absolute value of the hydrogen ion activity, as derived from measurements with this type of electrode as well as the hydrogen electrode, depends, of course, upon the value attributed to the reference electrode. For this the value **–0.3341** v. for the potential of the **0.1** M calomel seems to be preferable, while if the relative activity of hydrogen ion is desired, the value -0.3374_6 v., corresponding to that used by Clark, may be used as this leads to results in concordance with the generally accepted PH scale.

Preparation of Solutions and Materials

Buffer Solutions.—The standard buffer solutions were made up much as directed by Clark;[20] potassium chloride, potassium acid phthalate, potassium dihydrogen phosphate and boric acid were recrystallized as advised but the buffers were prepared as needed from weighed samples of the salts rather than from stock solutions. A special grade of disodium hydrogen phosphate ($Na_2HPO_4 \cdot 2H_2O$) was purchased ready for use.[21] A solution of constant boiling hydrochloric acid, analyzed gravimetrically, was used in the most acid buffers, and for the standardization of carbonate-free sodium hydroxide obtained by diluting a stronger hydroxide solution prepared by dropping metallic sodium into a deep ether layer above water.[22] All of the water used for the solutions was freshly distilled and collected in a current of escaping steam.

Antimony.—Pure crystalline antimony was prepared by the rapid electrolysis of antimony trifluoride solution, as described by Schuhmann;[7] however, the product was not allowed to dry but was kept under water until needed, treated with hot, dilute hydrofluoric acid and washed. The trifluoride solution was obtained by dissolving specially purified precipitated oxide in pure hydrofluoric acid.

Antimony Trioxide.—The oxide required for the antimony electrode was obtained from the hydrolysis of antimony trichloride, which was prepared in a very high state

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[20] Clark, ref. 15, Chap. VI.

[21] From LaMotte Chemical Products Co., Baltimore, Md.

[22] Cornog, THIS JOURNAL, 43, 2573 (1921). The sodium carbonate content of our solution was shown by nephelometric comparison to be less than 0.01% of the sodium hydroxide present; no cloudiness developed on the addition of barium chloride.

of purity by distilling the hydrochloric acid solution of commercial "C. P." antimony trioxide[23] in an all-Pyrex apparatus. The high boiling point of antimony trichloride (above 220°) renders an elaborate still unnecessary; a 1-liter distilling flask with the neck drawn down to about 8 mm. in diameter, stoppered with a flanged rod and a 70–80-cm. length of tubing slipped over the side arm for a condenser serves excellently. The distillate was discarded until a test drop of the dense, highly refractive liquid solidified on striking a cold glass surface. The collected product was melted, poured into about 15 times its volume of water and allowed to stand overnight at 80°. The initial voluminous flocculent precipitate of basic chloride became coarsely crystalline; it was washed with distilled water, digested twice for eighteen hour periods at 80° with a strong solution of carefully recrystallized sodium carbonate and then with hot distilled water for three weeks, the water being changed daily. The resulting very finely divided oxide, which will be termed "precipitated oxide," was filtered and dried at 110°; it was easily and completely soluble in hydrochloric acid and gave no chemical test for pentavalent antimony.

Consideration of the behavior of the electrodes containing this precipitated oxide as a solid phase (Nos. 1 and 2) led us to undertake a study of the allotropy of antimony trioxide with the view of obtaining definitely stable, crystalline material.

The Allotropic Forms and Transition Temperature of Antimony Trioxide

A cubic form of antimony trioxide occurs naturally as Senarmontite, and an orthorhombic form as Valentinite. The literature with regard to the form stable at 25° is indefinite.

Small amounts of our pure precipitated oxide were placed in a platinum boat in a sealed, evacuated Pyrex tube, heated in a small electric furnace, cooled quickly and the products examined under a petrographic microscope. A platinum–platinum-rhodium thermocouple with direct reading galvanometer, calibrated at the sulfur point, was used to measure the temperature of the furnace. A sample heated at 550° for twelve hours gave as a product cubic crystals only, 0.005 mm. to 0.02 mm. in diameter, octahedra and octahedra truncated by the cube, dodecahedron, or both. A sample heated at 590° for twelve hours gave orthorhombic crystals only; the orthorhombic form also separates from the molten material when it is allowed to crystallize. On heating these orthorhombic crystals at 550° for twenty-four hours, no trace of the original crystal form remained, transformation to the cubic being complete. At 380° no crystallization of the original oxide took place in twenty-four hour-, while at 470° cubic crystals were formed from all samples in twenty-four hours. This was chosen as a safe temperature at which to heat the oxide for future use in the electrodes.

The transition point of antimony trioxide, which must lie between 550 and 590°, was found by a series of successive trials. A final run was made

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[23] Every sample of antimony trioxide that we were able to procure contained considerable quantities of sulfide, which made drastic methods of purification an obvious necessity.

at 573°, as recorded when the thermocouple extended to within 2 cm. of the front of the platinum boat, which did not rest on the bottom of the furnace. At the end of six hours the tube was removed and allowed to cool. The material in the boat was found to consist of orthorhombic crystals only in the rear end, a mixture of orthorhombic and cubic in the middle section and cubic crystals only for the first centimeter. The temperature gradient of the furnace, although not extreme, was positive toward the rear, therefore 570 ± 10° was adopted as the temperature at which cubic and orthorhombic crystals of antimony trioxide are in equilibrium under the pressure of their own vapor, the cubic being the stable form below this temperature.

In order to ascertain the structure of the unheated precipitated oxide, powder photographs were taken of this material, a similar product obtained by treating antimony trichloride over a period of months with water only and which showed a positive orthorhombic structure under the microscope,[24] cubic crystals prepared by heating at 525°, and orthorhombic crystals prepared by sublimation at 600'. The lines from the water hydrolyzed material checked the lines of the orthorhombic control perfectly, while the lines from our oxide prepared by sodium carbonate hydrolysis differed from the orthorhombic control only in that the principal line was broader, extending from 3.14 Å. to 3.21 Å. The principal line of the orthorhombic is 3.13–3.15 Å., of the cubic 3.22 Å., indicating that our precipitated oxide consisted of a mixture of both crystal forms with the orthorhombic greatly predominating.

Preparation of Electrodes and Method of Measurement

Antimony–Antimony Trioxide Electrode.—The electrode vessel used was a modification of the type described by Brönsted[25] in which the solution flows slowly down through a deep layer of the saturating substance, past the electrode proper, to the junction. The modified vessel and the mica-plate flowing junction arrangement have been discussed in an earlier paper.[17] The addition of the by-pass so that there is no flow of electrolyte past the electrode metal while the potentials are being measured is of the utmost importance in this work. In setting up an electrode, the vessel was first filled with water to prevent the entrainment of air bubbles and the main arm was then packed with antimony crystals (or a mixture of metal and oxide) using cotton plugs to prevent clogging of the stopcock and to break the column into several sections. This insures a sufficiently rapid flow of electrolyte for thorough washing when the solution is being changed and also assists in equilibrating the flowing solution with metal or metal and oxide before it reaches the electrode proper.

Hydrogen Electrode.—The hydrogen electrode vessel adopted was of the type described by Lewis, Brighton and Sebastian.[26] The electrode consisted of a section of

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[24] This material was very kindly supplied by Mr. J. E. Cavelti, Wesleyan University, together with many valuable suggestions with regard to the preparation of pure antimony trioxide.

[25] Brönsted, Kgl. *Danske Videnskab. Selskab, Math.-fys. Medd.*, **3,** No. **9 (1920).**

[26] Lewis, Brighton and Sebastian, THIS JOURNAL, **39,** 2245 **(1917).**

gold plated platinum foil coated with a thin layer of platinum black. Tank hydrogen was purified for use by passing through a strong solution of sodium hydroxide, over phosphorus pentoxide and through two 75-watt tungsten filament bulbs before entering the presaturator.[27]

Reference Electrodes.—The antimony-antimony trioxide and hydrogen electrodes were measured against a silver–silver chloride electrode in 3.5 N potassium chloride[28] as a reference; this in turn was checked against a decimolal calomel electrode as the ultimate standard. The silver and calomel electrodes were made up as outlined in the former investigation[17] except that the mercury for the calomel electrodes was even more carefully purified. After spraying many times through dilute nitric acid, it was distilled several times under diminished pressure in air as described by Hulett,[29] followed by a double distillation in *vacuo*.[30]

The electrode system was maintained at 25 ± 0.02° in an air thermostat. A Leeds and Northrup Type K potentiometer was used and the working standard Weston cell was checked at frequent intervals against two newly calibrated cells purchased from well-known makers.

The Measured Electromotive Force of the Cell Sb | Sb_2O_3, Solution || 3.5 N KCl, AgCl | Ag at 25°

A. Precipitated Oxide, Air Substantially Excluded (Electrodes Nos. 1 and 2).—The first measurements of the potential of the antimony–antimony trioxide electrode were made with precipitated oxide. In the preparation of duplicate electrodes (Nos. 1 and 2 of Col. 2, Table 11), the platinum lead-wires were given a very thin electroplate of antimony from a trifluoride solution and the columns filled with antimony alone, the only oxide introduced being that suspended in the saturated solutions. Each electrode solution was saturated with the respective soluble constituents of the electrode by shaking in the thermostat with an excess of the solids over a period of at least twelve hours. In the case of the solutions for the antimony electrodes, both oxide and metal were used, the metal being introduced to reduce any pentavalent antimony that might be present. The equilibrating solutions completely filled the containing bottles to avoid the presence of air; after equilibration, they were siphoned quickly into the electrode vessels until the bulb was completely filled and an Orsat bulb containing hydrogen was connected to the top. Immediately before the introduction of the equilibrated solution, the electrodes were thoroughly washed with a similar unequilibrated solution and, immediately after, thoroughly washed again. Readings were taken at various intervals over a period of from seventy-two to ninety-six hours, at the end of which time the next solution was intro-

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[27] Clark, ref. 15, Chap. XV.

[28] The electrode solution contained 3.5 moles (air weight) of potassium chloride per liter at 20°; $d_4^{20} = 1.1526_5$, or the solution was 3.927 molal (vacuum weight).

[29] Hulett, *Phys. Rev.*, 33, 307 (1911).

[30] The additional precautions were evidently unnecessary since the electromotive force found for the cell Ag | AgCl, 3.5 N KCl || 0.1 M KCl, Hg_2Cl_2 | Hg checked our former result precisely.

duced. The metal was rinsed with fresh solution from the reservoir bulb after every reading during the first forty-eight hours and occasionally during the rest of the run. The potential difference showed an upward trend with time, the increase during the first twenty-four hours after the introduction of a new solution normally amounting to from 3 to 6 mv., disregarding erratic changes during the first hour or so. After twenty-four hours, further change was very slow. For example, after the first forty-eight hours, the potential with the buffer of PH 1.2 remained constant to within 0.5 mv. for forty-eight hours, at the end of which the experiment was closed. The deviations during this period showed no definite trend.

The observed potentials given in the third column of Table II were read at least twenty-four hours after setting up the cell. The fourth column contains the observed potential difference corrected for the liquid junction potential by means of the Bjerrum extrapolation given in the last column of Table I. These values were plotted against the corrected PH of the buffers (Col. 1) and a straight line with slope 0.05915 was drawn through the points. The line fitted the data within the limit of experimental accuracy from PH 5 to PH 10. The rate of change of potential with *P*H thus being fixed, E_0 was calculated from the equation E_0 =

TABLE II

THE MEASURED ELECTROMOTIVE FORCE OF THE CELL Sb | Sb_2O_3, SOLUTION || 3.5 N KCl, AgCl | Ag AT 25° (ELECTRODES NOS. 1 AND 2)

PH of soln.	Elect. Nos.	E (obs.), volts	E' (E corr. for j.p.), volts	E_{Sb} (E' − 0.2061), volts	E'' (0.05915 *P*H), volts	E_0 ($E_{Sb} - E''$), volts	Dev. from $E_0 = -0.1512$ millivolts
1.2	1	0.1331	....	**−0.0730**	0.0710	−0.1440	...
2.2	1	.1954	....	**−0.0107**	.1301	.1408	...
3.008	1	.2315	0.2312	+0.0251	.1779	.1528	...
4.010	2	.2978	.2974	.0913	.2372	.1459	...
5.012	1	.3531	.3526	.1465	.2965	.1500	−1.2
5.612	2	.3892	.3887	.1826	.3319	.1493	−1.9
6.0	1	.4090	.4087	.2026	.3549	.1523	+1.1
6.0	1	.4070	.4067	**2006**	.3549	.1543	+3.1
6.0	2	.4072	.4069	.2008	.3549	.1541	+2.9
6.4	1	.4309	.4305	.2244	.3786	.1542	+3.0
6.4	2	.4335	.4331	.2270	.3786	.1516	+0.4
6.6	2	.4471	.4467	.2406	.3904	.1498	−1.4
6.975	2	.4705	.4701	.2640	.4126	.1486	−2.6
7.4	1	.4930	.4926	.2865	.4377	.1512	0.0
8.0	2	.5298	.5293	.3232	.4732	.1500	−1.2
7.960	1	.5250	.5250	**,3189**	.4708	.1519	+0.7
8.933	2	.5849	.5848	.3787	.5284	.1497	−1.5
9.905	1	.6418	.6417	.4356	.5859	.1503	−0.9
11.14	2	.7161	.7161	.5100	.6589	.1489	...
11.91	1	.7656	.7656	.5595	.7045	.1450	...
				Mean (*P*H 5 − *P*H 10)		**− .1512**	**1.6**

E_{Sb} – 0.05915 PH (Equation (2) rewritten on the basis of our stated assumptions), where E_{Sb} is the potential of the antimony–antimony trioxide electrode alone, obtained by adding to E' the value for the potential of the reference half cell, –0.2061 v. This was derived from our measured electromotive force of the cell Ag | AgCl, 3.5 N KCl || 0.1 M KCl, Hg_2Cl_2 | Hg, 0.13135 v., and the value for the decimolal electrode at 25° corresponding to that employed by Clark and Lubs in the standardization of their buffer solutions, –0.33746 v. The mean value of E_0 over the range in PH stated was –0.1512 v., with a maximum deviation of 3.1 mv. and a mean deviation of 1.6 mv.; below *PH* 5 and above *PH* 10, the deviation was greater. If the computed values of *PH* (Col. 4, Table I) were used to the exclusion of any of our later determined values, the slope was less than the theoretical, about 0.0586. Schuhmann[7] found 0.1524 v. for the electromotive force of the cell Pt, H_2 | $HClO_4$, aq., Sb_2O_3 | Sb with a maximum deviation from the mean of his three cells of 2.5 mv., a result which compares favorably with our own.

Thus far the antimony–antimony trioxide electrode had exhibited two distinct peculiarities; the "best" E *vs.* *PH* curve is not linear except from *PH* 5 to PH 10, the slope, based on the most reliable published values for the buffers, tending to be rather less than the theoretical, and the approach to a constant potential being very slow, sometimes requiring days. In the case of our measurements the first abnormality is not large, but it is in the same direction as the much larger deviations found by other workers.[4,6] Several explanations for the erratic behavior of the electrode suggest themselves. (1) The assumption that the term in Equation (2) involving the activity of the solid oxide drops out may not be valid because the oxide used was not in its stable state and a virtual supersaturation of the solution with antimony trioxide persisted. This would not only explain the slow change of the potential with time but it is a plausible reason for the departure of the curve from linearity and from the ideal slope, since it is easy to believe that the rate of approach to equilibrium might always be slow and yet vary considerably with the acidity. (2) Extreme precautions to exclude air were not taken. It is possible that the system is more susceptible to oxidation than supposed, pentavalent antimony ions forming so readily that the equilibrium $Sb^{+++++} + Sb \qquad Sb^{+++}$ is attained with difficulty.[31] (3) The derived *PH* values assigned to the buffer solutions may not be actually correct. Although suspicion of the accuracy of the temperature corrections employed for the buffers is justifiable, this last reason for inconsistency will, for the present, be disregarded; in view of the facts that two crystal forms of antimony trioxide are known and the material used showed no definite crystal structure at a magnifi-

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[31] Franke and Willaman report serious drifts in potential on bubbling air through their solutions.

cation of 1000 diameters, the first explanation seemed most likely. Consequently the study of the allotropy of antimony trioxide was made and a supply of definitely pure cubic oxide prepared.

B. Cubic Oxide, Air not Excluded (Electrodes **Nos.** 3 and 4).—Two new electrodes were made up with cubic antimony trioxide in order to investigate its electromotive behavior and to compare it with the precipitated oxide in electrodes Nos. 1 and 2. In keeping with the precautions with regard to the exclusion of any unstable oxide, the subject of the constant activity of the metal was considered. Although the presence of a large number of unstrained crystals of metal in contact with strained metal is supposed to dissipate the strain, electroplating of the platinum lead-wire was discontinued. Instead, it was pretreated with a strong solution of stannous chloride in hydrochloric acid, washed, and a solution of antimony trifluoride introduced to adjust the potential of the wire to that of antimony,[32] before the electrode column was filled, in this case with an intimate mixture of metal and oxide. Crystals of antimony prepared as described for the first two electrodes were used in electrode No. 3; for No. 4 the metal was annealed by heating to 500° in a vacuum, followed by slow cooling. Before use, the annealed metal was treated with boiling hydrofluoric acid for several minutes and washed thoroughly. No precautions were taken to exclude air beyond a soda-lime guard tube in the top of each electrode to avoid the absorption of carbon dioxide, and the solutions were unequilibrated with either metal or oxide before their introduction into the electrode reservoirs.

The pair of electrodes was read over a period of from forty-eight to ninety-six hours after introduction of the buffers. In most cases, the final value was reached within fifteen or twenty-four hours, the potential thereafter remaining constant within 0.2 mv. or less. Upon rinsing the metal with fresh solution from the bulb, a drop of 2 to 3 mv. occurred; after a lapse of ten hours, the electrode had always returned to constant potential. In all cases in which the change of potential with time at the beginning of an experiment was studied, the readings at the end of the first thirty minutes were never more than 6 mv. lower than the final value. Table III shows the behavior of these electrodes. The column headings are self-explanatory and the calculated values given in the table were arrived at in a manner similar to those in Table II, except for Col. 6, in which the value 0.05835 for the slope was determined analytically on the basis of the values for electrode No. 3. The average value for E_0 was also based on the values for electrode No. 3, excluding the widely divergent value at PH 6.018. The final column indicates the direction

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[32] A similar procedure was found of great value in the preparation of noble metal electrodes for use in the electrometric determination of silver by precipitation as silver chloride, Van Name and Fenwick, THIS JOURNAL, 47, 9 (1925).

of approach to equilibrium, that is, whether the preceding solution in the electrode had been more alkaline or more acid; *U* signifies that this solution had been more acid and D the reverse. It will be noticed that electrode No. 3 is the more consistent of the two, the mean deviation being but 0.17 mv. if the value at PH 6.018 is excluded, and that in this case the equilibrium was always approached from the more alkaline side; this peculiarity was also noticed in later work. The values for E_0 for electrode No. 4 are in general more negative than those for No. 3 (the mean being —0.1513 v.), indicating greater mobility and therefore less strain; nevertheless, no significance was attached to the fact that the metal was annealed, since the individual deviations from the mean are considerably greater than for No. 3, and since later work showed that approach to equilibrium from the acid side, as was the case with No. 4, always tended to give slightly low and varying readings.

TABLE III

THE MEASURED ELECTROMOTIVE FORCE OX THE CELL Sb | Sb_2O_3, SOLUTION || 3.5 *N* KCl, AgCl | Ag AT 25° (ELECTRODES NOS. 3 AND 4)

Pa of soln.	Elect. Nos.	*E* (obs.), v.	*E'* (*E* corr. for j.p.), v.	E_{Sb} (E' − 0.2061), v.	*E''* (0.05835 PH), v.	E_0 (E_{Sb} − E''), v.	Dev. from E_0 = 0.1504, mv.	Dir. of app. to equilib.
2.2	3	0.1846	0.1844	—0.0217	0.1284	—0.1501	−0.3	D
2.2	4	.1832	.1830	—0.0231	.1284	.1515	+1.1	U
3.008	3	.2315	.2312	+0.0251	.1755	,1504	+0.0	D
3.008	4	.2322	.2319	.0258	.1755	.1497	−0.7	U
4.01	4	.2868	.2864	.0803	.2340	,1537	+3.3	D
4.41	4	.3148	.3144	.1083	.2573	.1490	−1.4	U
6.018	3	.4047	.4042	.1981	.3502	.1521	+1.7	D
6.018	4	.4025	.4020	.1959	.3502	.1543	+3.9	U
6.975	3	.4630	.4626	.2565	.4070	.1505	+0.1	D
6.975	4	.4589	.4585	.2524	.4070	.1546	+4.2	U
7.960	3	.5200	.5200	.3139	.4645	.1506	+0.2	D
7.960	4	.5188	.5188	.3127	.4645	.1518	1.4	U
8.933	3	.5770	.5769	.3708	.5213	,1505	+0.1	D
8.933	4	.5815	.5814	.3753	.5213	.1460	−4.4	U
9.905	3	.6341	.6340	.4279	.5780	.1501	−0.3	D
					Mean (No. 3)	−0.1504		

The use of cubic instead of precipitated oxide, therefore, resulted in smaller deviations from a straight line relationship between the potential and PH, over a wider range in PH (2.2–10); but the slope of the straight line was now further from the theoretical than before. Hence only a part of the abnormal behavior of the electrodes could be ascribed to the presence of an unstable solid phase and the effect of complete elimination of dissolved oxygen from the electrolyte was next investigated.

C. Cubic Oxide, Air Completely Eliminated (Electrodes Nos. 3a, 4a and 5).—New reservoir bulbs of 150-cc. capacity were sealed onto electrodes Nos. 3 and 4 without disturbing the metal and oxide, making the completed electrodes (Nos. 3a and 4a) appear as shown in the figure. The electrolyte was drawn up into the bulb through the nitrogen inlet tube by applying suction at the outlet tube. After washing the entire electrode thoroughly with the unequilibrated solution, the bulb was filled, a rubber tube, connected to a nitrogen supply,[33] was attached to the inlet tube and nitrogen bubbled through the solution for three or four hours; the solution in the by-pass was displaced by the oxygen-free solution, and the metal was then washed slowly with the deoxygenated solution for ten to twenty minutes. After twelve hours the nitrogen was again started; an hour later a reading was taken and the metal again washed. Twelve

TABLE IV

THE MEASURED ELECTROMOTIVE FORCE OF THE CELL Sb | Sb_2O_3, SOLUTION || 3.5 *N* KCl, AgCl | Ag AT 25° (ELECTRODES NOS. 3a, 4a AND 5)

*P*H of soln.	*Elect. Nos.*	*E* (obs.), v.	*E'* (*E*, corr. for j p.), v.	E_{Sb} (E' − 0.2061), v.	E'' (0.05915 *P*H), v.	E_0 (E_{Sb} − E''), v.	Dev. from E_0 = −0.1445, mv.	Dir. of app. to equilib.
1.018	5	0.1259	0.1220[a]	−0.0841	0.0602	−0.1443	− 0.2	D
1.979	5	.1826	.1787	−0.0274	.1171	.1445	0.0	U
3.008	3a	.2391	.2388	+0.0327	.1779	.1452	+0.7	D
3.008	4a	.2395	,2392	.0331	.1779	.1448	+0.3	D
3.008	5	.2396	.2393	.0332	.1779	.1447	+0.2	D
3.008	5	.2384	.2381	.0320	.1779	.1459	+1.4	U
6.018	3a	.4149	.4144	,2083	.3560	,1477	+3.2	U
6.018	4a	.4170	.4165	.2104	.3560	,1456	+1.1	U
6.975	4a	.4731	.4727	.2666	.4126	.1460	f1.5	D
6.975	5	.4747	.4743	.2682	.4126	.1444	− 0.1	D
9.905	3a	.6454	.6453	.4392	.5859	.1467	+2.2	D
9.905	4a	.6474	.6473	.4412	.5859	.1447	+0.2	D
9.905	5	.6461	.6460	.4399	.5859	.1460	+1.5	U
9.905	5	.6468	.6467	.4406	.5859	.1453	+0.8	D
11.14	5	.716	.716	.510	.6588	.1488	+4.3	U
12.561[b]	5	.8032	.8032	.5971	.7430	.1459	+1.4	D
12.889"	3a	.8225	.8225	.6164	.7624	.1460	f1.5	U
12 889	4a	,8224	.8224	.6163	.7624	.1461	+1.6	U

[a] The correction of 3.9 mv. for the liquid junction potential in this case was derived from measurements, to be published soon, on silver-silver chloride electrodes using 0.1 M HCl, 0.1 KCl and 3.5 N KCl solutions.

[b] The *P*H of this sodium hydroxide solution (0.05979 *M*) was calculated from hydrogen electrode measurements on the basis of no liquid junction potential correction.

[c] This value for 0.1330 M sodium hydroxide was derived from the preceding one using activity coefficients for hydroxide ion calculated from activity coefficients of potassium chloride and hydroxide given by Scatchard, THIS JOURNAL, 47, 648 (1925), from the molalities of the two solutions, and on the assumption of equal junction potentials in the two cases: $\Delta P_H = \log (0.1330 \times 0.776)/(0.05979 \times 0.811) = 0.328$.

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[33] Tank nitrogen was used, purified by passing over hot copper (prepared by reducing the oxide with hydrogen) and washing with strong sodium hydroxide solution, pure water and, finally, a portion of the same solution contained in the electrodes.

hours later the operation was repeated and in most cases the reading was the same as before. If not, this procedure was repeated until two consecutive readings checked within 0.2 mv. The potentials always rose with rinsing and standing. Later on in the work Electrode No. 5 was made up, differing from No. 4a only in that the cubic oxide was prepared from material obtained from the trichloride by water hydrolysis alone and heated in the presence of metallic antimony at 500°. This was to obviate any contamination from sodium salts used in the hydrolysis of the trichloride by the other method, or from pentavalent antimony. The final values in every case are listed in Table IV. After several readings of this series had been taken, it was apparent that, on the basis of the temperature corrections to the buffers which we were able to glean from the literature, the slope would still be slightly less than the theoretical from *P*H 3 to PH 10. The last possibility previously mentioned, that the reported temperature coefficients of the buffers are not correct, seemed the only explanation of this deviation. The simplest solution to this problem was to measure directly the difference in potential between the antimony–antimony trioxide electrode and a hydrogen electrode immersed in solutions of the same acidity.

The Measured Electromotive Force of the Cell Pt, H_2 | Solution Sb_2O_3 | Sb at 25°

In determining E_0 directly, the general procedure was to measure electrode No. 4a or 5 (the preceding solution always having been more alkaline) against the reference electrode for a period of two to three days until the potential had definitely become constant. The hydrogen electrode vessel was then filled with a portion of the same solution which had been used in filling the antimony electrode, and hydrogen was passed through for at least two hours before any measurement was taken. Junction was made in the following manner. The outlet cock on the antimony electrode was closed and a slight excess pressure of nitrogen allowed to develop; the cock on the intake side was closed, the nitrogen supply disconnected and the cock opened slowly, allowing solution to fill the intake tube to the orifice; the volume of solution escaping was sufficient to decrease the pressure inside the bulb enough to balance the hydrostatic pressure of the solution. A short length of carefully cleaned rubber tubing was attached to the hydrogen electrode vessel and filled with solution from the reservoir of this vessel; this was slipped over the intake tube of the antimony electrode making contact; the two cocks on the hydrogen electrode vessel were now opened for the reading, the hydrogen still bubbling. No change in level of the electrolyte on the hydrogen electrode took place, due to the hydrostatic balance previously set up in the antimony electrode.

After the reading had been taken, the electrodes were disconnected and the nitrogen supply reattached to the antimony electrode. From two to four hours later another reading was taken. In two instances the procedure was repeated the following day. Barometric readings were taken coincident with all measurements and the potentials were corrected to 1 standard atmosphere partial pressure of hydrogen at 25°. The maximum deviation from the mean of the two or four corrected readings was 0.16 mv. The measurements are presented in Table V. These results clearly indicate that any previous apparent departure from the theoretical slope was due entirely to errors in the reported temperature coefficients of the buffers; therefore, hydrogen electrode measurements were made on buffers of PH 3, 6 (phthalate), 7, 8 (borate), and 10 of Clark and Lubs, Ringer's buffer of PH 11.29, and 0.05979 M sodium hydroxide solution directly against the reference electrode, using a flowing junction. The correct PH of these buffers at 25° was calculated (Table I, Col. 5) and used in the rest of the tables. In these calculations the Bjerrum extrapolations found by Clark and the value -0.3374_6 v. for the potential of the 0.1 M calomel electrode were used.

TABLE V

THE MEASURED ELECTROMOTIVE FORCE OF THE CELL, PT, H_2 | SOLUTION, SB_2O_3 | SB AT 25°

Solution	E (obs.), v.	Dev. from mean, mv.
0.1000 M HCl	**0.14436**	**– 0.13**
0.0100 M HCl	.14449	.00
C. and L. buffer, PH 7	.14436	– .13
C. and L. buffer, PH 10	.14474	+ .25
Mean	.14449	Mean .13

The results of Table IV may now be considered. The correct value of E_0 was taken as –0.1445 v., the directly determined result. The maximum deviation of the D values of electrodes Nos. 4a and 5, between PH 1 and 10, from this value for E_0, is 1.5 mv. and the mean deviation, 0.5 mv. U values are consistently lower than D by more than 1 mv., except in 0.01 M hydrochloric acid. This bears out the results of Table III with regard to the necessity of approaching equilibrium from the alkaline side for the best results.

Discussion of Results

Our results point definitely to the conclusion that the potential of the antimony–antimony trioxide electrode attains its maximum accuracy only provided that: the presence of any unstable solid phase in the system, notably orthorhombic antimony trioxide, is carefully avoided; dissolved oxygen is eliminated from the solution; and the equilibrium is approached from the alkaline side, a circumstance for which we are unable to offer an adequate explanation. Under these conditions the potential of the electrode is a linear function of the logarithm of the activity of hydrogen ion, with the theoretical slope, from *P*H 1 to 10. It seems conservative to claim a probable accuracy of less than 0.6 mv. or about 0.01 P_H. This compares very favorably with the hydrogen electrode under ordinary conditions. Schuhmann's investigation of the molal electrode potential of antimony provides excellent evidence that our range of applicability may be extended on the acid side to P_H 0 with at least some acids; our own measurements in the two most alkaline solutions indicate that the error at P_H 13 is not more than 2 mv. and with careful pretreatment with a stronger sodium hydroxide solution it may be reduced to 0.5 mv.

Although our results prove that cubic antimony trioxide is the stable solid phase over the range in acidity in which precise activity measurements are ordinarily required, the question may be raised as to the probable extent of its region of stability. Van Bemmelen and other workers[34] have asserted that the stable solid phase in the presence of hydrochloric acid at any dilution contains chloride, but their claims are without adequate support. Lea and Wood[35] found that very finely divided Sb_2O_3 was slowly transformed into $Sb_4O_5Cl_2$ in 0.125 N HCl. However, their material is not comparable with our definitely crystalline oxide; accordingly, to make a direct test of the stability of cubic antimony trioxide, certain acid and alkali solutions were shaken with an excess of the trioxide and the final systems analyzed, with the following results.

Soln.	Concn. of soln. at invariant point at 25°	Soln.	Concn. of soln. at invariant point at 25°
HCl	Approx. 0.10 M	HNO_3	Above 1
H_3PO_4	Approx. 0.06	NaOH	Above 2
H_2SO_4	Approx. 1		

In the last three cases solutions of the concentrations stated produced no new solid phase detectable under the petrographic microscope and underwent no determinable change in concentration after shaking for four days. In the sulfuric acid solution, however, a small amount of a new solid phase was detected after a lapse of one month. The first two invariant points were determined by starting with solutions of different initial strengths, slightly above the concentrations stated, containing a large excess of both solid phases, and analyzing the solutions by titration at one-week intervals for three weeks. The change was very slow after the second week and the results given are very probably within 0.01 M of the true invariant concentration. Above 0.10 *M* HCl and 0.06 *M* H_3PO_4, therefore, antimony trioxide is not the stable solid phase and the

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[34] Van Bemmelen, Meerburg and Noodt, *Z. anorg. Chem.*, 33,272 (1903); Le Chatelier, *Compt. rend.*, 100, 737 (1885).

[35] Lea and Wood. *J. Chem. Soc.*, 125, 137 (1924).

antimony–antimony trioxide electrode cannot be subjected to such solutions for long periods of time without injury. However, in solutions as concentrated as 0.16 M HCl or 0.15 M H_3PO_4, initially containing the trioxide only, no new solid phase is formed in a week or more and the solutions undergo no change in concentration; therefore, solutions as strong as these may be safely used in the electrodes for short periods of time (three to four days). This was actually done in the case of hydrochloric acid and the electrode behaved perfectly normally afterward. We are not prepared to state positively that cubic antimony trioxide is stable in all moderately dilute acids; exceptional cases may exist but in any event there need be but little difficulty in their detection.

On comparing the several values for the difference in potential between a hydrogen and an antimony–antimony trioxide electrode in solutions of the same acidity, or E_0, it is interesting to observe that our value obtained with precipitated antimony trioxide checks that found by Schuhmann, who used oxide of the same character, to 1.2 mv., or within the limit of error of both investigations. Our final value, using cubic crystals of the trioxide, is 6.7 mv. more positive than this preliminary result, or —0.1445 v. The work of former authors who used massive metal electrodes is so uncertain and irregular that it provides no reasonable basis for comparison with our own and Schuhmann's.

The use of nitrogen as a gas phase for the antimony electrode has distinct disadvantages for its practical application. However, our results in air so closely approached those in nitrogen as regards the magnitude of the deviations from linearity that the former electrode may be safely recommended for general use, provided that the value of E_0 is fixed by means of two or more buffers in the range desired.

Although the necessity for the very careful preparation of the materials comprising the antimony trioxide electrode has been stressed, emphasis has not been laid on its superior permanency to the hydrogen electrode. With a reasonable amount of care there is no reason why it should not remain in service for an indefinite period, merely displacing one solution with another, with the proper precaution that each is more acid than its immediate predecessor. The electrode is undoubtedly slower than the hydrogen electrode in attaining actual equilibrium but the P_H calculated about thirty minutes after the solution has been introduced is normally within 0.1 P_H of the equilibrium value and, since the error is always on the acid side, the true P_H can probably be estimated to within 0.05 P_H. In order to attain an accuracy of the order of 0.01 P_H or greater, twenty-four hours may be required, as compared with two hours for the hydrogen electrode; however, the relative lack of attention demanded and the inert character of the electrode as regards its effect upon the acidity of the solution itself more than compensate for the required wait.

The Free Energy of Formation of Cubic Antimony **Trioxide** and the Free Energy Change for the Transformation: Sb_2O_3 (orthorhombic) $\longrightarrow$ Sb_2O_3 (cubic) at 25°

If 0.1445 v. is accepted as the best mean value for the electromotive force of the cell Pt, H_2 | Solution, Sb_2O_3 (cubic) | Sb, the free energy change for the cell reaction $3H_2(g) + Sb_2O_3$ (cubic) $\longrightarrow 2Sb + 3H_2O(l)$, ΔF_1, $= -6 \times 0.1445 \times (96{,}500/4.185) = -19{,}992 \pm 20$ cal. If the change in free energy for the reaction $3(H_2(g) + 1^1/_2O_2(g) \longrightarrow 3H_2O(l)$, ΔF_2, $= -169{,}680$ cal. (probable accuracy about 0.1%),[36] the free energy of formation at 25° of cubic antimony trioxide is equal to the difference $\Delta F_2 - \Delta F_1 = -149{,}690 \pm 200$ cal. This value is recommended in place of Schuhmann's $-148{,}600$ cal. because of the indefinite crystalline characteristics of his oxide.

The free energy change for the transformation of orthorhombic to cubic antimony trioxide may be calculated from the electromotive force of the cell Sb | Sb_2O_3 (orthorhombic), Solution, Sb_2O_3 (cubic) | Sb. For this purpose two electrodes similar to Nos. 3a and 4a were made up, using orthorhombic antimony trioxide which had been freshly prepared by fusing precipitated oxide in a platinum boat in an evacuated Pyrex tube and cooling quickly after solidification had taken place. Immediately after setting up, the electrodes were washed, filled with buffer, the nitrogen was turned on and the usual procedure followed. Readings against the same reference electrode as used previously were continued for twenty-four hours; constant potentials were not attained. The final values of the two electrodes containing the two buffers PH 9.905 and PH 3.008 were 0.6350 v. and 0.2255 v., respectively. The best values on these same buffers for cubic oxide were 0.6474 v. and 0.2395 v., giving differences of 12.4 mv. and 14.0 mv., respectively. The average value, 13.2 mv., is judged to be accurate to 10% on the basis of these measurements. The free energy change for the transformation Sb_2O_3 (orthorhombic) $\longrightarrow$ Sb_2O_3 (cubic) at 25° is, therefore, equal to $-6 \times 23{,}059 \times 0.0132 = -1826$ cal., or -1800 ± 200 cal. We can claim this only as a minimum negative value since the work with the precipitated oxide showed that even if the oxide saturating the solutions is mainly orthorhombic, if a certain amount of cubic is present, the electrode tends to assume a potential between that characteristic of the cubic and of the orthorhombic. Thus the difference in E_0 of both Schuhmann's and our precipitated oxide electrodes and of our cubic oxide electrodes is only about half the measured electromotive force of the cell under consideration.

In conclusion, the authors wish to express their gratitude to Dr. John Johnston for the suggestions and help he has given in connection with this work.

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[36] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, 1923, p. *485*.

Summary

1. The potential of the electrode Sb | Sb_2O_3, Solution has been shown to depend on three main factors: (a) the crystalline character of oxide used, (b) presence or absence of air in the electrolyte, (c) direction of approach to equilibrium; the best results are obtained with cubic oxide, air-free electrolyte, and by pretreatment with a solution more alkaline than the one being studied. Under these conditions, the potential is a linear function, with theoretical slope, of the PH of the solution; the difference between it and a hydrogen electrode in a solution of the same acidity is 0.1445 v. ± 0.2 mv. at 25°.

2. Equal accuracy may be secured without the necessity of excluding air, provided that the electrode is standardized by the use of two or more solutions of known acidity. Such an electrode is superior to the hydrogen electrode in that once set up it requires little further attention, is permanent and may be readily used for solutions the acidity of which is affected either by hydrogen alone or by hydrogen in combination with platinum black. Hydrochloric acid (and probably hydrobromic and hydriodic acids) may not be used in the electrode in a concentration exceeding 0.16 M, phosphoric acid in a concentration not exceeding 0.15 M and sulfuric acid in a concentration not exceeding 1 M, due to the formation of new solid phases. Nitric acid and sodium hydroxide may be used up to 1 M and 2 M, respectively, and perhaps further.

3. Because the behavior of the antimony–antimony trioxide electrodes indicated that previously determined temperature coefficients applied to the Clark and Lubs buffers were somewhat in error, the *P*H of certain of these solutions (the accepted standards at 20°) were measured at 25° with the hydrogen electrode (Table I, Col. 5).

4. Antimony trioxide formed by the hydrolysis of antimony trichloride has been demonstrated to consist chiefly of orthorhombic crystals; the transition temperature of antimony trioxide has been found to be 570 ± 10°, the cubic form being stable below this temperature.

5. The free energy of formation of cubic antimony trioxide at 25° was found to be −149,690 ± 200 cal. and the free energy of transformation, Sb_2O_3 (orthorhombic) $\longrightarrow$ Sb_2O_3 (cubic), −1800 ± 200 cal.

6. The potential of the decimolal calomel electrode has been derived from two different sources and found to be −0.3341 v.

NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE FERTILIZER AND FIXED NITROGEN LABORATORY OF THE UNITED STATES BUREAU OF CHEMISTRY AND SOILS]

AN APPARATUS FOR CONTINUOUS GAS ANALYSIS

BY ERNEST C. WHITE

RECEIVED MAY 7, 1928 PUBLISHED AUGUST 4, 1928

The apparatus herein described is designed to afford a continuous determination of moderate concentrations of a given constituent in a flowing gas mixture, and to register the concentration automatically by electrical means. The principle is to scrub a definite proportion of the gas with a definite proportion of a suitable absorbent and to determine the titer of the resulting solution by measuring its electrical conductivity.

Apparatus

From a large reservoir R (Fig. 1) the absorbent is fed slowly through a tube terminating in a small bore capillary A[1] of 7 mm. outside diameter, whose flat, fine-edged tip[2] is horizontally disposed. The rate of flow is maintained fairly constant by means of the constant level device S, so that the liquid falls from the tip of the capillary in drops of uniform volume at intervals of about eight seconds.[3] Each drop falls freely through the bulb B upon the aperture C, forming a thick film which traps the gas in the tube CD, of about 4 mm. bore, and forces it along in descending by gravity to the goose-neck at D. The latter is a capillary constriction of about 1.5 mm. bore, suitably bent so as to arrest each droplet until it is displaced by the impact of the succeeding drop.[4] From this it results that the same volume of gas, namely, the volume of the tube between the points G and D, is aspirated by each drop of the liquid.

The temperature is kept constant by immersion in a thermostatic bath contained in the receptacle U, so that the quantity of gas in each sample is assumed to vary only with the barometric pressure. The gas is introduced-at N at a rate slightly in excess of that at which it is being drawn through the coil O by the pump action, the overflow escaping through the side arm P of sufficient length to prevent air from entering the coil. All of these tubes should be of sufficient bore to afford an easy flow of gas.

After having been thus brought into contact in a definite proportion by volume, the liquid and the gas traverse the coiled tube E, which should be long enough to insure practically complete absorption of the desired constituent of the gas. They are separated at the widened lower end F of the coil, where the films are disrupted and the liquid flows into the cell GIJ, the spent gas escaping through the tube Q. The overflow from the cell passes out through the siphon L, the outer arm of which is bent upward at its lower end, the tip M being level with a point just above the electrode H.

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[1] A bore of about 1 mm. is adequate and the length of the capillary is selected so as to give the desired rate of flow when the liquid is under a pressure head equal to that maintained by the constant level device.

[2] The fine edge may be obtained by grinding the tip in a Wood's metal sleeve, as described by Harkins and Brown, THIS JOURNAL, 41, 499 (1919), and later by Whitman, Young and Wang, Ind. *Eng. Chem.*, **18**, 363 (1926).

[3] At this rate of formation the size of the drop varies by less than 0.3% for a difference of one second in its time of formation; see Whitman and others, ref. 2. A more rapid rate could be used if desired, since the constant level device is capable of maintaining a high degree of uniformity.

[4] No great difficulty is inherent in the correct adjustment of the goose-neck, whose shape can be altered by bending the softened glass until found satisfactory by trial.

In the cell illustrated, the tube I, having an internal diameter of about 2 mm., is bent upward at the ends so as to prevent small gas bubbles from collecting in it. The electrode compartments G and J are similar in shape to an oblique cone, and the electrodes H and K are disks of platinized platinum, each of which is welded to a stout platinum wire about an inch in length. A portion of this wire is imbedded in a glass knob sealed to the wall of the vessel and the upper end is attached to a finer wire leading out of the apparatus. The wire leading through the siphon tube L is of platinum and requires a gas tight seal at V where it emerges. The dimensions and shape of the cell are designed to afford rapid and complete flushing, so as to diminish the time lag attending changes in the composition of the solution.

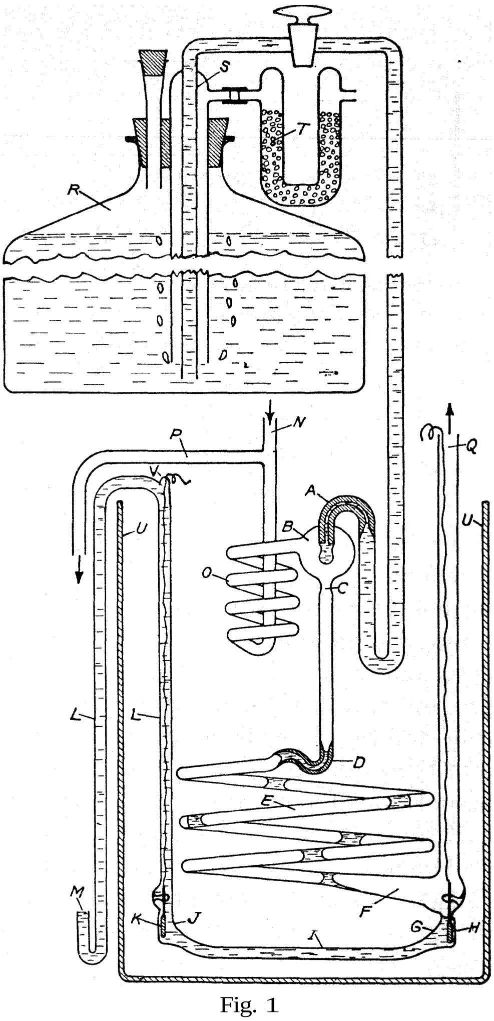

Fig. 1

The long, narrow tube I permits the determination of the conductivity by a method using direct current and possessing the advantages of rapidity and adaptability to recording instruments. This method requires a cell resistance of the order of 10^5 ohms. The cell is connected in series with a low resistance galvanometer in a direct current circuit of about 100 volts, in which the potential is constant or readily adjustable. For this purpose radio "B" batteries have been found very serviceable, if the circuit is closed only for brief intervals. Fig. 2 illustrates an arrangement for detecting and compensating any slight changes in the voltage of the "B" battery. Here the current that flows through a standard fixed resistor, of about the same resistance as that of the cell, is made a measure of the potential and the latter is capable of minor adjustment by means of a variable potential unit, consisting of a 1.5-volt dry cell around which is shunted a rheostat of about 200 ohms. With this arrangement the conductivity of the solution may be assumed to be directly proportional to the current, since variations of the polarization at the electrodes will be only a negligible fraction of the applied voltage, and the total resistance of the circuit will not differ appreciably from that of the cell alone. With a current of about one milliampere the effect of electrolysis is scarcely perceptible.

If a recording instrument is used in place of the simple galvanometer, its timing mechanism should be made to close the circuit a few seconds before registering and open it immediately afterward. An instrument of the self-balancing potentiometer type, such as a Leeds and Northrup recording pyrometer, would have to be shunted with a suitable fixed resistance and might require modification of its range by altering the zero offset.

Calibration

Method I.—An empirical calibration of the apparatus can be obtained by operating with gas mixtures of known composition, and plotting these compositions against the corresponding conductivities observed for the resulting solutions. This method is perhaps preferable for mixtures with a fairly high content, say 5% and above, of the gas sought, or in cases where absorption is incomplete.

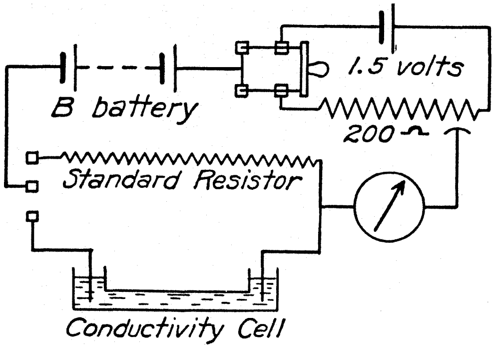

Fig. 2.

Method II.—If the apparatus is to be used for low concentrations of a readily absorbed gas, it is possible to derive a calibration curve where conductance data are available. This second method consists in making careful determinations of the liquid drop size, which will be referred to as a, and of the capacity of the cylinder CD, which will be referred to as b. The former measurement may be obtained by collecting the liquid that overflows at M resulting from the fall of a counted large number of drops during operation at a steady state. The determination of b is best made under similar conditions, using an inert gas and measuring the quantity delivered from the tube Q. If this gas is collected by water displacement, a little care is necessary in order to maintain the pressure at the exit exactly equal to that at the intake, namely, barometric; for otherwise the apparatus will not function properly.

If, during the fall of n drops, an observed volume V cm.^{3} has been collected over water at the room temperature T_r, under barometric pressure P and saturated vapor pressure p_r, while T and p are, respectively, the thermostat temperature and the corresponding aqueous vapor pressure in the tube CD, the capacity b may be calculated as follows:

$$b = \frac{VT(P - p_r)}{nT_r(P - p)} \text{ cm.}^3$$

Although b is a constant for the apparatus, the number of moles m of dry gas aspirated by each drop will vary, of course, with barometric pressure. Assuming perfect gases and expressing pressures in mm. of mercury, the value of m would be

$$m = 273(P - p)b/22{,}420 \times 760\,T = 1.602 \times 10^{-5}(P - p)b/T.$$

From the values thus obtained for a and m it is a simple matter to calculate the relationship of the gas composition to the concentration of the resulting solution, and hence to the conductivity of the latter as computed from conductance data. An example will be given in a later section. In regard to this method of calibration, which is capable of great accuracy for concentrations less than 2%, it must be admitted that it does not take into account the quantity of gas absorbed by a liquid drop before the latter reaches the goose-neck D.[5]

Applications

For gases such as NH_3, HCl or SO_2, the most convenient absorbent would be distilled water, provided the other gases in the mixture are not very soluble. The conductivity of the water, which may be negligible but can be tested from time to time, will then correspond to zero gas concentration. With the aid of conductance data and a single determination of the cell constant, a calibration curve for low concentrations may be obtained by Method II.

Por gases requiring chemical absorption, for example, Cl_2, H_2S or CO_2, a carefully standardized reagent is required and the range of the apparatus is limited by the concentration of the reagent, if the upper limit is to be represented by complete neutralization of the solution. An absorbent should be chosen which does not yield a precipitate. In such cases the zero point corresponds to the conductivity of the unchanged solution; and the maximum gas concentration capable of absorption, as calculated from the known titer of the reagent and the apparatus constants a and b, corresponds to the conductivity of the equivalent salt solution at neutrality. According to the theoretical considerations discussed in a later paragraph, the intermediate concentrations should fall on a straight line when plotted against conductivity.

Adaptation for the Determination of Carbon Monoxide

The apparatus has been used successfully for the determination of small concentrations of carbon monoxide in the presence of hydrogen, methane and other gases.

After the removal of any carbon dioxide that may be present, the gas is passed through a tube containing iodine pentoxide at 140 to 150°, where the carbon monoxide is preferentially oxidized with the liberation of iodine. Vapors of the latter are removed in a tower of moist potassium iodide crystals, and the residual gas is analyzed for carbon dioxide in the apparatus illustrated, using a standard solution of carbonate-free potassium hydroxide as the absorbent.

A stock of 0.5 N potassium hydroxide was prepared in the following manner. To a 4% solution of C. P. caustic potash in which the carbonate content had been determined, the theoretical quantity of barium hydroxide was added to precipitate the

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[5] It can be shown that, even if absorption were complete in this brief interval of time, the calculated value of the mole fraction would exceed the actual value C only by the quantity $C^2 + C^3 + C^4 + \dots$, which is relatively small when $C < 0.02$.

carbonate. After the latter had settled, the solution was decanted and made up with freshly distilled water to exactly 0.5 N as standardized against benzoic acid, precaution being taken to prevent contact with air containing carbon dioxide. This stock solution was stored in a paraffin lined, tightly stoppered bottle. By means of a large pipet, of about 800 cm.^{3} capacity, a portion of the stock solution was transferred to the reservoir R, and then diluted with freshly distilled water measured from the same pipet. For use in determining carbon dioxide concentrations up to 2%, a supply of about 16 liters of an exactly 0.025 *N* potassium hydroxide solution was thus prepared from time to time without the necessity of repeated purifications and standardizations.

Referring to the diagram, Fig. 1, it will be seen that by connecting the tube P with the tube Q, for example with rubber tubing, the gas in the system will be caused to circulate through the apparatus, so that it will be purged and become inert toward the hydroxide solution. Eventually a pure sample of the latter will fill the cell and a determination of its conductivity can be made at the outset and also whenever desirable later. With the aid of this determination in addition to the measurements of the apparatus constants a and b, as indicated under Method II, the calibration of a particular apparatus was obtained at 25°, and it will be given here as an illustration.

Since the determinations of the conductivities, here indicated by k, were made by measuring the direct current flowing through the cell under a fixed voltage, which in this case was 92.5 volts, the values of k for the sake of simplicity will be given in milliamperes. The observed value of k for 0.025 N potassium hydroxide was $k_o = 1.440$ milliamperes. The equivalent conductances at 25° of potassium hydroxide and $^1/_2$ K_2CO_3 at 0.025 N, as derived from the data of Kohlrausch, were found to be 253 and 126, respectively. Hence the milliampere reading corresponding to 0.025 N K_2CO_3 should be $k_n = 1.440 \times 126/253 = 0.717$ milliamperes.

Readings corresponding to intermediate mixtures of hydroxide and carbonate resulting from partial neutralization, when plotted against the normality of the carbonate present, should fall on a straight line between k_o and k_n, in accordance with the principle introduced by Arrhenius, which may be stated: "In a mixture of two salts with a common ion, each salt has a degree of ionization equal to that which it would have when present alone in a solution in which its ions have a concentration equivalent to that of the common ion in the mixture." In testing this principle Bray and Hunt[6] found in the case of sodium chloride and hydrochloric acid mixtures that the observed values of the specific conductance agreed very closely with the values calculated on the assumption that the degree of ionization, and hence the equivalent conductance, of each substance depended on the total salt concentration. In the present case the total salt concentration, $C_{\text{KOH}} + C_{1/2\text{K}_2\text{CO}_3}$, remains unchanged throughout the series of mixtures, from which it follows that the equivalent conductance

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[6] Bray and Hunt, THIS JOURNAL, 33,781 (1911).

of each substance does not depart from the value at 0.025 N, and the specific conductance of any mixture in the series should be

$$L = 253\,C_{\mathrm{KOH}} + 126\,C_{1/2\mathrm{K_2CO_3}}$$

or the conductivities in the present calibration units should be

$$k = (1.440\,N_{\mathrm{KOH}} + 0.717 N_{\mathrm{K_2CO_3}})/0.025$$

and since $N_{\mathrm{KOH}} + N_{\mathrm{K_2CO_3}} = 0.025$, this may be simplified to

$$k = 1.440 - 28.92\,N_{\mathrm{K_2CO_3}}.$$

Experimental values for a and b were 0.0941 cm.^{3} and 1.43 cm.^{3}, respectively. For operation under a barometric pressure of 760 mm. of mercury, assuming aqueous vapor saturation, the number of moles m_{760} of dry gas per stroke would be

$$m_{760} = 1.602 \times 10^{-5}\,(760 - 23.5)b/298 = 5.67 \times 10^{-5} \text{ moles}$$

Hence the proportionality between the concentration $[\mathrm{CO_2}]_{760}$ mole fraction of carbon dioxide in the gas and the normality of carbonate in the resulting solution would be

$$[\mathrm{CO_2}]_{760} = aN_{\mathrm{K_2CO_3}} \times 10^{-3}/2m_{760} = 0.830\,N_{\mathrm{K_2CO_3}}.$$

By substituting in the expression for k above, there is obtained

$$[\mathrm{CO_2}]_{760} = 0.0287\,(1.440 - k)$$

an equation by means of which the carbon dioxide concentration can be calculated directly from the milliammeter reading, when the barometric pressure is exactly normal.

The coefficient for the increase of m per mm. increase in barometric pressure is 0.001359, so that the value of $[\mathrm{CO_2}]_P$ when the barometric pressure is P would be

$$[\mathrm{CO_2}]_P = 0.0287(1.440 - k)/[1 + 0.001359(P - 760)]$$

It is obvious that the maximum concentration of carbon dioxide here capable of measurement with 0.025 N alkali is about 2%. The sensitivity depends mainly upon that of the electrical measurements. Thus in the present instance 0.002 milliampere is the equivalent of about 0.006% of carbon dioxide. In a given apparatus the range of concentrations measurable could be varied in direct proportionality to the titer of the alkali employed; the resulting sensitivity, assuming the adoption of a voltage suitable for the same range of currents, would be inversely proportional to the titer. To obtain greater sensitivity without resorting to an extremely weak absorbent, the apparatus itself could be modified by lengthening the tube CD. It may also be worthy of mention that in actual practice the range of an apparatus has been approximately doubled by the very simple expedient of causing each drop of liquid to halt about midway between C and D, continuing its descent only after the fall of the next drop, which results in changing the gas/liquid ratio from b/a to $(b-a)/2a$. This is accomplished by increasing the pressure in the tube Q just enough to balance the increased pressure above the goose-neck, for instance, by making the emergent gas bubble through about 1 cm. depth of oil.

Practical Uses

Two apparatus of this type have been found very advantageous at the Fixed Nitrogen Laboratory in the pursuit of several investigations relating to processes for the removal of carbon monoxide from hydrogen prior to the synthesis of ammonia. The one whose calibration has been described above is used for the estimation of up to 2% of carbon monoxide with a sensitivity of about one volume of carbon monoxide in ten thousand of the mixture; the other, which is connected to a recording instrument is capable of a sensitivity of about one part in thirty thousand in the range up to 0.75% CO. A third apparatus has been used tentatively for the estimation of ammonia in the presence of nitrogen and hydrogen, the absorbent being distilled water. It appears to be satisfactory for experimental work in which the concentration does not change rapidly, and with modification it should be possible to reduce the time lag so as to improve its ability to register fluctuations.

Though somewhat fragile, due to the necessity of glass in its construction, it could be shielded by inclosure in a cabinet; and since it requires no expert attention beyond the occasional renewal of the standard solution and the few other chemicals required for preliminary purification, there are indications that an apparatus of this type could easily be adapted for industrial process control.

Summary

1. An apparatus is described for the continuous automatic analysis of certain gases, utilizing the change in electrical conductivity of a solution that has been exposed to the gas in a device for controlling the volume ratio.
2. Two methods of calibrating the apparatus are given.
3. Among the gases capable of estimation by this means NH_3, HCl, SO_2, Cl_2, H_2S and CO_2 are mentioned.
4. An actual adaptation for the determination of CO in the presence of H_2 and hydrocarbons is described in detail.
5. Possibilities of extended use are indicated.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE PORTLAND CEMENT ASSOCIATION FELLOWSHIP, BUREAU OF STANDARDS]

PHASE EQUILIBRIA IN THE SYSTEM $2CaO\cdot SiO_2$–MgO–$5CaO\cdot 3Al_2O_3$[1]

BY W. C. HANSEN

RECEIVED MAY 10, 1928 PUBLISHED AUGUST 4, 1928

Introduction

This investigation of the system $2CaO\cdot SiO_2$–MgO–$5CaO\cdot 3Al_2O_3$ was undertaken, in connection with researches on the constitution of Portland cement, to determine whether MgO and $2CaO\cdot SiO_2$ existed as individual compounds in this system or reacted to form other crystalline phases.

The system CaO–MgO–SiO_2 was investigated by Ferguson and Merwin[2], but a thorough study was not made of the region below the line $2CaO\cdot SiO_2$–$2MgO\cdot SiO_2$, Fig. 1.[3]

Klein and Phillips[4] studied two series of preparations in an effort to determine the manner in which MgO occurs in Portland cement. Their first series was prepared so as to have molecular replacements of CaO by MgO in the composition $2CaO\cdot SiO_2$. The compositions of the mixtures studied by them fall on the line $2CaO\cdot SiO_2$–$CaO\cdot MgO\cdot SiO_2$, Fig. 1. In the second series of preparations they made percentage replacements of CaO by MgO in the composition $2CaO\cdot SiO_2$. The compositions of this series of mixtures fall in the triangle $2CaO\cdot SiO_2$–$CaO\cdot MgO\cdot SiO_2$–MgO, Fig. 1. From a microscopic study of their preparations, Klein and Phillips concluded that β-$2CaO\cdot SiO_2$ and $CaO\cdot MgO\cdot SiO_2$ formed a limited series of solid solutions, and that a few per cent. of MgO could be combined with $2CaO\cdot SiO_2$ in this way in Portland cement.

The preparations studied by Klein and Phillips contained some SiO_2 in excess of that required to form $2CaO\cdot SiO_2$ with all of the CaO. In Portland cement there is more than sufficient CaO to convert all of the SiO_2 to $2CaO\cdot SiO_2$, and the compositions of Portland cements in terms of CaO, MgO and SiO_2 fall in the triangle $2CaO\cdot SiO_2$–MgO–$3CaO\cdot SiO_2$, Fig. 1. Therefore, if a solid solution of $CaO\cdot MgO\cdot SiO_2$ with $2CaO\cdot SiO_2$ exists in Portland cement, it is necessary that MgO be capable of combining with CaO and SiO_2 to form $CaO\cdot MgO\cdot SiO_2$ in products in which sufficient CaO is present to convert all of the SiO_2 to $2CaO\cdot SiO_2$. Whether MgO

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[1] Publication approved by the Director of the National Bureau of Standards of the U. S. Department of Commerce. Paper No. 18 of the Portland Cement Association Fellowship at the Bureau of Standards.

[2] Ferguson and Merwin, *Am. J. Sci.*, *48*, 81 (1919).

[3] The region below the line $2CaO\cdot SiO_2$–$2MgO\cdot SiO_2$ has been divided arbitrarily into a number of small triangles to simplify the discussion which is to follow.

[4] Klein and Phillips, *8th Int. Cong. Appl. Chem.*, **5**, 73 (1912).

has that ability or not should be shown by the behavior of $2CaO \cdot SiO_2$ and MgO in the system $2CaO \cdot SiO_2$–MgO–$5CaO \cdot 3Al_2O_3$. This system was chosen because the melting temperatures in a part of it are below 1600°, and because the results obtained in the presence of Al_2O_3 should be more nearly applicable to Portland cement than those obtained on mixtures of CaO, MgO and SiO_2 without Al_2O_3.

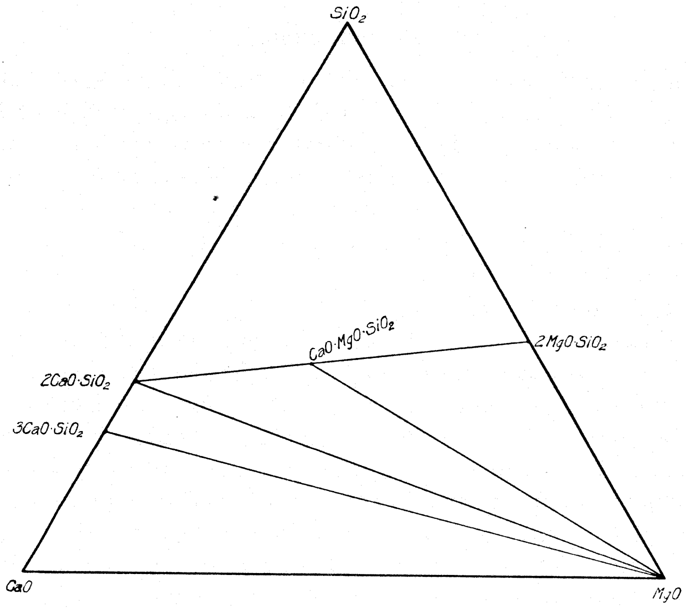

Fig. 1.—Triangular diagram representing a part of the system CaO–MgO–SiO_2.

Experimental Procedure

The results of the chemical analyses[6] of the raw materials used in this investigation are given below.

RESULTS OF ANALYSES

	Calcium carbonate	Magnesia	Silica	Alumina
CaO	55.55	0.50	0.02	0.02
MgO	.07	84.22	neg.	.08
SiO_2	.03	.08	99.37	neg.
Al_2O_3	.01	.02	.50	98.35
Fe_2O_3	neg.	.01	.03	.10
Cl	.04	.001	neg.	.01
SO_3	neg.	neg.	neg.	neg.
CO_2	43.63	...	...	...
Loss on ignition	43.97	15.31	.11	1.55

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[5] By H. C. Stecker.

The equipment used in these studies has been described in other papers[6,7] from this Laboratory.

The compositions studied are shown as dots in Fig. 2. Fifteen to twenty gram samples of each of the compositions were made up by melting, in platinum, a carefully prepared mixture of the components. The samples were crushed in a steel mortar and ground to fine powders in an agate mortar for use in the experiments described later.

Small charges of the above samples were wrapped in platinum and held at the temperatures and for the time periods given in Table I, and then quenched by dropping into water. The quenched charges were examined microscopically to determine the temperature and phase relations which are given in Table I and Fig. 2.

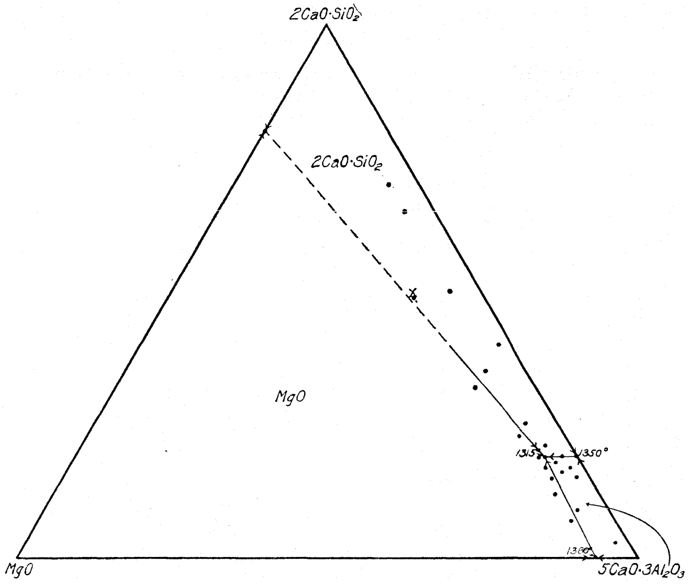

Fig. 2.—Diagram of the system $2CaO.SiO_2$–MgO–$5CaO.3Al_2O_3$, showing fields in which each component separates as a primary phase.

Similar charges were carefully annealed to allow complete crystallization, and these were studied microscopically to determine the optical properties of the crystalline phases. Indices of refraction were determined by the immersion method.

In all of the annealed samples the three compounds γ-$2CaO \cdot SiO_2$, $5CaO \cdot 3Al_2O_3$ and MgO were the only phases present. The indices of refraction of these compounds agreed with those given for them by Wright.[8]

[6] W. C. Hansen and R. H. Bogue, THIS JOURNAL, 48, 1261 (1926).

[7] W. C. Hansen and R. H. Bogue, *Ind. Eng. Chem.*, 19, 1260 (1927).

[8] (a) Wright, *Am. J. Sci.*, 28, 293 (1909); (b) 39, 1 (1915).

No optical evidence was obtained to show the formation of any solid solution of MgO with $5CaO \cdot 3Al_2O_3$ or with γ-$2CaO \cdot SiO_2$.

In all samples annealed below the eutectic temperature, 1315 ± 5°, the $2CaO \cdot SiO_2$ was present as the γ-form. It was necessary, therefore, to quench samples from above this temperature to prevent the inversion of the β-$2CaO \cdot SiO_2$ to the γ-$2CaO \cdot SiO_2$. By doing this, the β-form was obtained embedded in a glass. The microscopic examination of such samples requires that one obtain edges of the grain free from glass for index of refraction determination. The results obtained on such edges are not so reliable as those obtained on crystals entirely free from glass; however, the study of these β-$2CaO \cdot SiO_2$ grains did not give any evidence to indicate any solid solution of MgO with β-$2CaO \cdot SiO_2$.

TABLE I

BINARY EUTECTICS

Composition	Melting temp., °C.	Reference
6.5% MgO + 93.5% $5CaO \cdot 3Al_2O_3$	1380±5	Rankin and Merwin[9]
20% $2CaO \cdot SiO_2$ + 80% $5CaO \cdot 3Al_2O_3$	1350±5	Rankin and Wright[8b]

TERNARY EUTECTIC

Composition	Melting temp., °C.
5% MgO + 19% $2CaO \cdot SiO_2$ + 76% $5CaO \cdot 3Al_2O_3$	1315±5

QUENCHINGS WHICH DETERMINE THE ABOVE TERNARY EUTECTIC AND THE BOUNDARY CURVES, FIG. 2

	Composition[a]		Temp., ±5°C.	Time of heating minutes	Phases present
MgO	C_2S	C_5A_3			
2	3	95	1335	15	Glass + C_5A_3 + MgO
2	3	95	1370	30	Glass + C_5A_3
2	3	95	1290	240	$C_5A_3^+$, MgO + C_2S^+, trace glass
5	9	86	1290	240	$C_5A_3^+$, MgO, C_2S
5	9	86	1350	15	Glass + C_5A_3 + MgO
5	9	86	1360	15	Glass
10	32	58	1475	15	Glass + MgO
5	25	70	1380	15	Glass
7	23	70	1345	15	Glass + C_2S
7	23	70	1380	15	Glass
7	23	70	1330	15	Glass + C_2S + MgO
4	21	75	1325	15	Glass + C_2S + MgO
4	21	75	1350	15	Glass
4	21	75	1315	15	Glass + MgO + C_2S + C_5A_3
4	21	75	1345	15	Glass + C_2S
6	19	75	1335	15	Glass
6	19	75	1320	15	Glass + MgO
6	19	75	1315	15	Glass + C_2S + MgO + C_5A_3
5	*70*	75	1340	30	Glass + C_2S + MgO
11.2	48.1	40.7	1600	15	Glass + C_2S + MgO
11.2	48.1	40.7	1290	60	C_2S + C_5A_3 + MgO
2	15	83	1330	15	Glass + C_5A_3 + C_2S
2	15	83	1355	15	Glass

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[9] Rankin and Merwin, THIS JOURNAL, **38,** 568 (1916).

TABLE I *(Concluded)*

Composition[a]			Temp., ±5°C.	Time of heating, minutes	Phases present
MgO	C_2S	C_5A_3			
2	15	83	1345	15	Glass + C_5A_3
2	11	87	1340	15	Glass + C_5A_3
2	19	79	1340	15	Glass + C_2S + C_5A_3
4	18	78	1315	30	Glass + C_2S + C_5A_3 + MgO
4	18	78	1320	15	Glass + C_2S + C_5A_3
4	18	78	1330	15	Glass + C_5A_3
4	16	80	1325	15	Glass + C_5A_3 + C_2S
4	16	80	1340	15	Glass + C_5A_3
2	17	81	1330	15	Glass + C_5A_3 + C_2S
2	17	81	1340	15	Glass + C_5A_3
6	17	77	1330	15	Glass + C_5A_3 + MgO
6	17	77	1320	15	Glass + C_5A_3 + MgO
6	17	77	1310	15	Glass + C_5A_3 + MgO + C_2S
6	15	79	1340	15	Glass + MgO
6	15	79	1330	15	Glass + MgO + C_5A_3
7	12	81	1340	15	Glass + MgO
7	7	86	1350	15	Glass + MgO
5	19	76	1315	15	Glass + MgO + C_5A_3 + C_2S
5	19	76	1320	30	Glass + trace C_5A_3

[a] The formulas for $2CaO \cdot SiO_2$ and $5CaO \cdot 3Al_2O_3$ have been written C_2S and C_5A_3, respectively.

If MgO were capable of replacing a part of the CaO in $2CaO \cdot SiO_2$, the CaO replaced would be expected to react with either $5CaO \cdot 3Al_2O_3$ to form $3CaO \cdot Al_2O_3$ or with $2CaO \cdot SiO_2$ to form $3CaO \cdot SiO_2$. In none of the samples was it possible to identify either $3CaO \cdot Al_2O_3$, $3CaO \cdot SiO_2$ or free CaO.

It is necessary, therefore, to conclude, in the system $2CaO \cdot SiO_2 \cdot MgO$–$5CaO \cdot 3Al_2O_3$, that MgO does not form appreciable solid solutions with γ- or β-$2CaO \cdot SiO_2$, and that MgO is not capable of replacing CaO in $2CaO \cdot SiO_2$.

Discussion

These experiments demonstrate the inability of MgO to form $CaO \cdot MgO \cdot SiO_2$ in certain products in which there is sufficient CaO to convert the SiO_2 to $2CaO \cdot SiO_2$. This is brought out more forcibly if the composition x, Fig. 2, is considered. The composition of x may be expressed as $3(3CaO \cdot Al_2O_3) + 4(CaO \cdot MgO \cdot SiO_2)$ or as $5CaO \cdot 3Al_2O_3 + 4(2CaO \cdot SiO_2) + 4MgO$. A sample of this composition, after being fused, dusted completely, due to the formation of γ-$2CaO \cdot SiO_2$. A charge of it quenched from 1600° consisted of grains of β-$2CaO \cdot SiO_2$ and MgO embedded in a glass. A charge heated to 1600°, cooled slowly during several hours and then annealed for several hours at 1300°, dusted completely and consisted of γ-$2CaO \cdot SiO_2$, $5CaO \cdot 3Al_2O_3$ and MgO.

Further evidence of the inability of $CaO \cdot MgO \cdot SiO_2$ to exist in products where there is sufficient CaO to convert the SiO_2 to $2CaO \cdot SiO_2$ was obtained by fusing a mixture having the composition[10] $4CaO\cdot 2MgO\cdot Al_2O_3\cdot Fe_2O_3 + 2(CaO\cdot MgO\cdot SiO_2)$. This mixture dusted completely owing to the formation of γ-$2CaO\cdot SiO_2$. Also a sample having the composition $4CaO\cdot 2MgO\cdot Al_2O_3\cdot Fe_2O_3 + 2MgO\cdot SiO_2$ dusted completely after being fused.

Summary

1. A study has been made of the system $2CaO\cdot SiO_2$–MgO–$5CaO\cdot 3Al_2O_3$. A diagram is given showing the fields in which each of these compounds separates *as* primary phases.

2. No evidence was obtained to show that MgO formed solid solutions with either $2CaO\cdot SiO_2$ or $5CaO\cdot 3Al_2O_3$ or that MgO was capable of replacing CaO in these compounds.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY AT IOWA STATE COLLEGE]

REACTIONS IN LIQUID HYDROGEN SULFIDE. IV. THIOHYDROLYSIS OF ESTERS

BY A. W. RALSTON[1] AND JOHN A. WILKINSON

RECEIVED MAY 14, 1928 PUBLISHED AUGUST 4, 1928

Esters are well known to hydrolyze in water solutions, forming the free acids and alcohols. In a similar way the esters of the thio-organic acids should thiohydrolyze in liquid hydrogen sulfide to give the free acids and the mercaptans.

Of the several methods that are used to measure the degree of hydrolysis of esters in water solutions the one that is most applicable in the case of the thiohydrolysis in liquid hydrogen sulfide is that based on the determination of the conductance of the solutions.[2] The degree of hydrolysis is determined by measuring the conductance of the hydrogen sulfide solutions of the pure acid, the thiohydrolyzed ester and of the solution of the ester saturated with the base or mercaptan. It has been found that the solution of the mercaptan in liquid hydrogen sulfide does not conduct the current. Therefore, the conductance of the ester solution saturated with the mercaptan will be due to the unhydrolyzed ester alone.

The thiohydrolysis may be calculated from the expression

$$h = \frac{\lambda e - \lambda}{\lambda a - \lambda}$$

where h is the fraction of the ester thiohydrolyzed, λe is the equivalent

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[10] W. C. Hansen and L. T. Brownmiller, Am. J. *Sci.*, 15,225 (1928).

[1] This paper is from a portion of the work presented by A. W. Ralston to the Graduate Faculty at Iowa State College in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Walker, Z. *physik. Chem.*, 4, 333 (1889); Bredig, *ibid.*, 13, 214–321 (1894); Noyes, Kato and Sosman, THIS JOURNAL, 32, 159 (1910).

conductance of the solution of the ester at that dilution, λa is the equivalent conductance of the pure acid at the same dilution, λ is the conductance of the ester at this same dilution but after the solution has been saturated with the mercaptan.

Experimental

A number of the esters of thioacetic acid were prepared by the method Obermeyer[3] used for the preparation of methyl thioacetate. An alcoholic solution of lead acetate was added to an alcoholic solution of the mercaptan until no further precipitate of the lead mercaptide was formed. The lead mercaptide was filtered, washed with ether and dried in a vacuum desiccator. It was then treated with ice cold acetyl chloride, keeping the reaction flask immersed in an ice–salt mixture. After the reaction had completed itself, the excess of acetyl chloride was destroyed by water, the lead chloride was filtered out and the light oil distilled. The distillate was treated with calcium carbonate to remove any free acetic acid and then further purified by fractional distillation.

With the esters of higher molecular weight such as the *iso*butyl, the reaction took place much more slowly and it was necessary to reflux the mercaptide for several hours with acetyl chloride to obtain the ester.

TABLE I

THIOHYDROLYSIS OF ESTERS

Mol. vol., l.	$\lambda e \times 10^3$	$\lambda a \times 10^3$	$\lambda \times 10^3$	h
	Methyl Thioacetate			
50	0.110	1.450	0.004	7.33
20	.065	.917	.004	6.68
10	.035	.690	.004	4.52
5	.021	.614	.004	2.80
3.33	.018	.591	.004	2.38
2.5	.016	.580	.004	2.08
2	.011	.578	.004	1.22
	Ethyl Thioacetate			
50	.180	1.450	.008	12.55
20	.106	0.917	.008	10.80
10	.076	.690	.007	10.10
5	.059	.614	.007	8.56
3.33	.050	.591	.007	7.36
2.5	.044	.580	.006	6.62
2	.037	.578	.006	5.24
	n-Propyl Thioacetate			
20	.52	.917	.025	55.5
10	.35	.690	.020	49.3
5	.122	.614	.020	17.2
3.33	.096	.591	.020	13.3
2.5	0.089	0.580	0.020	12.3
2	.085	.578	.020	11.7
1.33	.075	.569	.020	10.0
1	.074	.565	.020	9.95
	Isopropyl Thioacetate			
10	.229	.690	.024	30.8
5	.146	.614	.024	20.5
3.33	.129	.591	.023	18.7
2.5	.122	.580	.020	18.2
2	.118	.578	.016	18.2
1.33	.113	.569	.011	18.2
1	.111	.565	.011	18.1
	n-Butyl Thioacetate			
10	.48	.690	-034	68.0
5	.395	.614	.025	56.7
3.33	.331	.591	.016	54.8
2.5	.327	.580	.012	55.5
2	.313	.578	.010	53.3

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[3] Obermeyer, Ber., 20, 292 (1887).

The esters of thioacetic acid that were made by this method and used had the following boiling points: methyl 95–96°, ethyl 115–116°, propyl 135–137°, *iso*propyl 122–123°, normal butyl 134–135° and phenyl 110–111° at 8 mm.

The conductances were determined in cells similar to those described and used by Quam and Wilkinson.[4] The cell constants were determined with 0.02 N potassium chloride at 25°. No correction was made for the change in the cell constant due to the fact that the cells were then used at −77°. Since the thiohydrolysis is calculated from a ratio this correction will be the same in both the numerator and the denominator and will be eliminated in the calculation.

The concentrations were determined by adding from a weight buret known weights of the ester to definite volumes of liquid hydrogen sulfide. The preceding tables give the data obtained and the percentage of hydrolysis calculated from them. The phenyl thioacetate was found to show no conductance when dissolved in liquid hydrogen sulfide.

Conclusions

1. Esters of thioacetic acid are shown to be thiohydrolyzed in liquid hydrogen sulfide. The degree of thiohydrolysis increases with the molecular weight of the ester.

2. The amount of thiohydrolysis of these esters in liquid hydrogen sulfide even at −77° is several times the value for the hydrolysis of esters of similar oxygen acids in water at room temperature.

AMES, IOWA

[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY, HARVARD UNIVERSITY]

THE ATOMIC WEIGHT OF CESIUM

BY THEODORE W. RICHARDS[1] AND MARCEL FRANÇON

RECEIVED MAY 24, 1928 PUBLISHED AUGUST 4, 1928

Introduction

A redetermination of the atomic weight of cesium was undertaken on account of the difference in this value as found by chemical and physical methods. The modern value of 132.81 is based primarily upon the work of Richards and Archibald.[2] Earlier atomic weight determinations are adequately treated by Clarke.[3]

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[4] Quam and Wilkinson, THIS JOURNAL, 47,989 (1925).

[1] The research here reported was completed under the direction of Professor Richards but the manuscript was written after his death. The junior author is responsible for the conclusions drawn and any opinions expressed.

[2] Richards and Archibald, *Proc. Am. Acad.*, **38, 443** (1903).

[3] F. W. Clarke, "The Constants of Nature," Part V, "A Recalculation of the Atomic Weights," 4th ed., 1920, Nat. Acad. of Sciences, Washington, D. C.

By the mass spectrograph Aston[4] in 1921 found cesium to be a simple element with a mass of **133** ± 0.2. Although the possible error in his early work happens to be as great as the difference, 0.2 unit, there are very few cases of simple elements for which there is such a discrepancy between the atomic weight and the mass number; but, particularly when a negative packing exists, the differences between the true weight of the atoms of an element and an integer are usually smaller than is the case for cesium.[5]

Further interest in a chemical study of the atomic weight of cesium was stimulated by recent efforts to find "element 87,"[6] and also from certain theoretical considerations arising from Aston's discussion of the "packing effect."[7] He has defined the "packing fraction" as the divergence of the mass of an atom from an integral value, divided by its mass number. To this fraction may be related the stability of the atoms and the forces binding the protons and electrons together. A great loss of weight may correspond to a great loss of energy, which is the result of tightly bound electrons, while a small loss of weight might correspond to a loose packing of electrons. Tight packing would then indicate stability and loose packing the reverse. Cesium occurs in the region of tight packing, being only slightly removed from the minimum of Aston's curve. At one end of this curve the light elements may be supposed to build up with a loss of mass corresponding to a loss of energy[8] and at the other end the heavy elements disintegrate into lighter elements.[9] The elements of greatest stability as indicated by their abundance[10] are found to the left of cesium in the curve of packing effect and mass number. An accurate determination of discrepancies from the whole number rule should, according to this interpretation, be of fundamental importance in providing information as to the structure of atoms.

It was with due consideration of these ideas that this determination of the atomic weight of cesium was undertaken.

Procedure

Purification of Materials.—All materials were purified according to the usual methods and the usual standards of purity of reagents were

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[4] Aston, *Phil.* Mag., [6] 42, 436 (1921).

[5] Examples of cases in which discrepancies have been accounted for recently are boron and strontium. Aston predicted an atomic weight of about 10.85 for boron, and in a redetermination of this value Baxter and Scott, *Proc Am. Acad.*, 59, 21 (1923), found 10.82. On the other hand, strontium, atomic weight 87.63, at first appeared to have only one mass line at 88, but lately Aston, *Phil.* Mag., [6] 49, 1191 (1925), found another faint line at 86.

[6] Herszfinkiel, *Compt. vend.*, 184, 968 (1927).

[7] Aston, *Pvoc. Royal Soc. London*, **115A,** *487* (1927).

[8] Millikan and Cameron, *Science*, N. *S.*, 67, 401 (1928); *Phys.* ***Rev.***, 31, 921 (1928).

[9] Cabrera, *Compt. rend.*, 186, 228 (1928); 186, 501 (1928).

[10] See F. W. Clarke, "The Data of Geochemistry," U. S. G. S. Bulletin 770, Washington, 1924, p. 36.

maintained. The silver used in this work was identical with that used in other researches in this Laboratory.[11]

Cesium chloride was made from pollucite from Maine. After the mineral had been finely ground, it was attacked with hydrochloric acid which had been diluted with an equal volume of water. A small amount of nitric acid was added to oxidize the iron. The solution was filtered, evaporated to dryness, treated with hydrochloric acid and water, and then these steps were repeated twice to separate out silica.

The chlorides were then converted to sulfates by the addition of sulfuric acid and cesium alums were obtained, separated and centrifuged. From this point on quartz dishes were used. The alums were crystallized three more times with centrifuging. It should be noted that to obtain alums it is not necessary to add anything other than sulfuric acid to the material extracted from pollucite, the composition of which as determined by Wells[12] and Kastler[13] indicates enough iron and aluminum for this purpose. The solubility relationships of the alums[14] are very favorable for the separation of other alkali metals. Murman[15] has recommended cesium alums for separation from potassium and rubidium. Godeffroy[16] made use of the alums in preparing pure cesium chloride. Our experience indicates that sodium, which forms stable alums only with the lighter of the tervalent metals, is best removed by crystallization of the alums.

To a hot, dilute solution of the cesium alums was added a hot solution of barium chloride, which had been twice recrystallized from the best obtainable material. After digestion of the precipitated barium sulfate, the solution was filtered through a Gooch-Monroe crucible. This cesium chloride solution was then treated with perchloric acid, carefully purified by Willard.[17] 'The cesium perchlorate crystals thus obtained were centrifuged and recrystallized three times.

The transformation into chloride was accomplished by thermally decomposing the perchlorate in a large platinum boat, placed within a quartz tube, which was heated electrically. It was necessary to carry the temperature to about 800° to decompose the trace of chloroplatinates which resulted on decomposition of the chlorate in platinum. The fused cesium chloride was dissolved in doubly distilled water and filtered through a Gooch-Monroe crucible, to separate a few particles of platinum. This cesium chloride was purified by two crystallizations.

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[11] (a) Richards and Hall, THIS JOURNAL, 48, 704 (1926); (b) Richards, King and Hall, *ibid.*, 48, 1530 (1926).

[12] Wells, *Am. J. Sci.*, 41, 216 *(1891).*

[13] Kastler, Bull. *soc. chim., 41, 428 (1927).*

[14] Locke, *Am. Chem. J., 26,* 166 (1901).

[15] Murman, *Oesterr. Chem.-Ztg., 27,* 129 (1924).

[16] Godeffroy, ***Ann.,*** 181, 176 (1876).

[17] Richards and Willard, THIS **JOURNAL, 32,** 4 (1910).

It was then fused in a platinum boat in the well-known bottling apparatus of quartz, described in recent publications.[18] The fusion was made in an atmosphere consisting for the greater part of dry nitrogen with a small amount of hydrogen chloride. The cesium chloride was cooled in a current of dry nitrogen, which was displaced when entirely cold by dry air before transference to a weighing bottle.

Cesium chloride thus prepared reacted neutral to indicators, whereas a solution of cesium chloride which had been fused in an atmosphere of hydrogen chloride alone was acid to methyl red.

The final product was examined in a Féry quartz spectrometer. By comparison with other spectra the cesium chloride did not contain any aluminum, barium, potassium or thallium. The presence of sodium was doubtful, although if it was present, there was only a very faint trace of it. Cesium chloride from the mother liquor seemed almost equally pure spectroscopically and did not react to any chemical tests for impurities.

Weighings were made with the usual care and the cesium chloride was compared nephelometrically with pure silver. The following factors were used in the calculations.

Atomic weights		Vacuum corrections		Densities	
Silver........	107.880	Silver.....	−0.000031	Weights.........	8.3
Chlorine......	35.457	Cesium chloride..	+0.00016	Silver...........	10.49
				Cesium chloride...	3.97

TABLE I

ATOMIC WEIGHT OF CESIUM

Wt. of CsCl in vac., g.	Wt. of Ag in vac., g.	Wt. of Ag added or subtracted	Corrected wt. of Ag, g.	Atomic wt. of cesium
4.42344	2.83611	−0.00001	2.83610	132.802
5.01421	3.21436	− .00020	3.21416	132.832
4.14983	2.66076	+ .00023	2.66099	132.783
4.48842	2.87830	− .00083	2.87747	132.820
			Av.	132.809

The error of the average of these determinations can be evaluated in several ways. The "probable error," calculated from 0.6745 times the mean error, is 0.012. This is within the "experimental error" of 0.015 which is based upon the accuracy of weighing and the accuracy of determining the end-point.

The average of the analyses confirms the present accepted value of 132.81, which Richards and Archibald found by analysis of the chloride, bromide and nitrate. However, since all of these salts were prepared from recrystallized dichloro-iodide, confirmation by analysis of a salt prepared by a different method is of importance.

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[18] Richards, King and Hall, THIS JOURNAL, 48, 1537 (1926); see also Baxter and Grover, *ibid.*, 37, 1027 (1915).

The deviation from an integral value found corresponds to a packing fraction of -14 ($\times 10^{-4}$), which is much greater than would be indicated by Aston's curve, provided that cesium is a simple element. Another unexpectedly large packing fraction was recently found by Baxter and Butler[19] for titanium, although in this case doubtful indications of another mass line have been reported and the element may not be simple. It may well be that further investigation will prove that cesium is also complex.

Acknowledgment for financial assistance is made to an anonymous benefactor of this Laboratory, and to the Carnegie Institution of Washington.

Summary

An analysis of cesium chloride, prepared by the recrystallization of alums of cesium, by comparison with silver confirmed the atomic weight of cesium to be 132.81.

CAMBRIDGE, MASSACHUSETTS

THE VAPOR DENSITY AND SOME OTHER PROPERTIES OF FORMIC ACID

BY ALBERT SPRAGUE COOLIDGE

RECEIVED MAY 31, 1928 PUBLISHED AUGUST 4, 1928

Introduction

In connection with some work on the adsorption of formic acid vapor, it became necessary to know the density of the vapor at ordinary temperatures and at pressures below the vapor pressure of the liquid. The only measurements seem to be those of Bineau;[1] Peterson and Ekstrand[2] give fragmentary data at higher temperatures and pressures. It seemed necessary to undertake direct determination of the vapor density. The acid prepared for this purpose appeared to be of exceptional purity, and certain other properties were determined for purposes of comparison.

Purification and Preservation of Formic Acid

Even at room temperature, formic acid slowly decomposes into water and carbon monoxide. Bulbs of Kahlbaum's best acid, which had presumably been stored for some time, were found to contain high pressures of the latter, while freshly imported bulbs did not. After fruitless attempts to remove the water by distillation over phosphorus pentoxide, acid sodium sulfate and magnesium perchlorate trihydrate (the first two decomposed the vapor, while the third absorbed it copiously), it was

[19] Baxter and Butler, THIS JOURNAL, 50, **408 (1928)**.

[1] Bineau, *Ann. chim. phys.*, [3] **18, 228 (1846)**.

[2] Peterson and Ekstrand, Ber., **13, 1194 (1880)**.

decided to fall back on vacuum distillation, crystallization and sublimation. (That is, these processes were carried out in a vacuum apparatus, constantly pumped free of all gases other than the vapor of the acid.) As a test of the purity of the acid, the vapor pressure at 0° was observed. This is more than 8 degrees below the freezing point, but no difficulty was encountered in preventing crystallization, provided that the liquid (if formed by recent melting of the solid) was previously heated to about 20° for a minute or two. If this precaution was neglected, the liquid invariably froze upon applying the ice-bath, even though the solid previously present had first been entirely melted.

Distillation was carried out at room temperature, the distillate being condensed in a bulb packed in ice. Heating was avoided, both in order to prevent decomposition, and because the effectiveness of the separation is greater at low temperatures.[3] Five fractional distillations yielded a volatile fraction having a vapor pressure of 11.15 mm. Crystallization was carried out in an apparatus similar to a small ice calorimeter, connected to the source of acid by a mercury trap at the bottom. The inner tube was first filled with solid carbon dioxide, and allowed to collect a sheath of solid formic acid. The mercury trap being closed, the acid was melted and the major portion again frozen out on the inner tube. The mercury was then lowered to allow the mother liquor to be blown out into the evacuated system beyond. The vapor pressure of samples prepared in this way approached the same value, but the method was cumbersome and slow. The most effective procedure was found to be to freeze the whole sample with an ice-bath, and then to pump off about a tenth of it without allowing the rest to melt. The water came off with the volatile fraction, the residue being nearly pure. The vapor pressure of the residue (after fusion, of course) rose rapidly on successive sublimations to the value 11.16 mm., which was repeatedly attained, but never exceeded, in purifying different portions. This may therefore be taken as the value for pure formic acid.

In order to estimate the degree of purity attained, an isolated portion of the acid was successively diluted with known amounts of water, and the vapor pressures observed. The water was weighed into thin glass sealed bulbs, which it nearly filled, and which were placed in fingers depending from the apparatus near the manometer. The bulbs were broken one at a time, by causing their contents to freeze, and the water completely transferred to the sample of acid by immersing the bulb containing the latter in carbon dioxide. At the same time, any air which might have been introduced in sealing the water into the bulbs was pumped off, the volatility of both water and formic acid being negligible at −79°. The acid was then melted, the bulb well shaken to ensure thorough mixing,

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[3] Jones, *J. Soc. Chem. Ind.*, **38,** 362T (1919).

and the pressure determined. At the conclusion of the series, the diluted acid was sealed off and weighed. No correction was required for the amount of acid existing as vapor in the free space, which was of the same order of magnitude as that occupied by the liquid.

The vapor pressures of the pure acid, as solid and liquid, and of the diluted acids as liquids, are given in Table I. The temperatures other than 0° were read on a tenth-degree thermometer with Bureau of Standards certificate. The values given in International Critical Tables[4] are included for comparison. My values are consistently higher, which is presumably an indication of greater purity. It will be observed that at 0° the vapor pressure is depressed 0.01 mm. by about 0.02% of water. Since the purifying process was repeated twice, even after the vapor pressure had reached a value constant within this limit, it seems probable that the final product was of the order of 99.99% pure.

TABLE I

VAPOR PRESSURES OF PURE AND AQUEOUS FORMIC ACID IN MM. OF HG

Water. %		Pressures			Pressure lowering per 1% of H_2O	
		0°	10°	20°	0°	20°
0.00	(solid)	8.67				
.00	I. C. T.	8.0				
.00	(liquid)	11.16	19.88	33.54		
.00	I. C. T.		18.9	33.1		
.29		11.08		33.19	0.28	1.20
.59		10.92		32.85	.41	1.17
1.30		10.62		31.99	.42	1.19
4.09		9.47		28.83	.41	1.15
7.96		8.00		25.01	.40	1.09
10.47	I. C. T.		12.4	22.1		1.05

It is of interest to compare the lowering of the vapor pressure produced by water with the theoretical value for an involatile solute of molecular weight 18. Assuming that sufficiently dilute solutions obey van't Hoff's law, the osmotic pressure of such a solute would be $RT\delta m/18$, where 6 is the density of the liquid solvent and m the weight fraction of the solute. The lowering of the vapor pressure bears to the osmotic pressure the ratio which the density of the vapor of the solvent bears to that of the liquid. Now, at 20° and 33 mm. pressure, as will appear later, the density of formic acid vapor can be calculated from the gas law on the basis of an apparent molecular weight of 83. We have, then, for the lowering of the vapor pressure

$$\mathrm{Ap} = \frac{83p}{RT\delta} \times \frac{RT\delta m}{18} = 4.6\,pm = 155\,m$$

The limiting value of the observed ratio is about 120. The discrepancy is doubtless due primarily to the volatility of the dissolved water, 'If

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[4] Volume III, p. 209 (solid, extrapolated), 215 (liquid), 364 (aqueous).

the water polymerized, an effect in the same direction would be produced; but the degree of polymerization should change with dilution, whereas the observed lowering bears a nearly constant ratio to the concentration over the four lowest values, (The observation on the most dilute solution at 0° is plainly in error.)

It was noticed that the pressure in a bulb half full of pure acid rose at the rate of about a millimeter per day. The actual fraction decomposed. must have been very small, but the carbon monoxide evolved greatly hindered the manipulation of the apparatus. It was found that decomposition could be entirely prevented by keeping the acid frozen. The main supply of purified acid was accordingly kept constantly frozen, the ice-pack never being removed except during the process of drawing off a sample for use, during which the high latent heat of evaporation prevented fusion.

The freezing point of the pure acid was determined in a double-walled tube. The inside tube contained the bulb and stem of the thermometer, while the space between the walls was occupied by partly frozen acid under its own vapor pressure. The whole was surrounded by air at about 8°. The thermometer was constant at 8.26°, even when the proportions of solid and liquid were varied.

The density of the acid was found to be 1.2456 at 0° and 1.2206 at 20°, both at atmospheric pressure.

The Vapor Density Measurements

In order to determine the vapor density, the method adopted was to transfer known quantities of acid (measured volumetrically in the liquid state) to containers of known volume, and observe the pressure developed at a series of temperatures. The apparatus is outlined in Fig. 1. It was necessary to make allowance for possible adsorption on the glass, which would cause the results to be too high. This was accomplished by comparison of the results obtained with two different containers having very different ratios of surface to volume. The first, called the globe (G, Fig. 1), was a 5-liter spherical Pyrex flask, and had, together with its connecting tubing, a volume of 5218 cc. and a wall surface estimated at 1500 cm.^{2}, giving a surface-volume ratio of 0.287 cm.$^{-1}$. The second container took the form of 13 meters of tubing arranged in a coil (C, Fig. 1) containing 324 cc., and having a wall surface of 2284 cm.^{2}, bearing to the volume the ratio 7.05 cm.$^{-1}$. Each container was connected to one arm of its own manometer (M, M, Fig. 1), which was of 2cm. diameter, and could be read to 0.02 mm. by means of a micrometer microscope sliding on parallel ways. The mercury level was adjustable by tube and leveling bulb (not shown in the figure), care being taken always to bring the mercury to the calibration mark for each reading.

By lowering the mercury, the manometers could be made to serve as valves, giving communication to the rest of the apparatus. The containers and manometers were mounted in a large iron tank, fitted with a powerful stirrer, and filled with water (or brine) which could be heated rapidly by running in live steam, or held at any desired temperature during a reading, within 0.05°, by adjustable gas burners. A plate glass window permitted reading of the manometers and also of a tenth-degree thermometer which had been compared with one standardized by the Bureau of Standards.

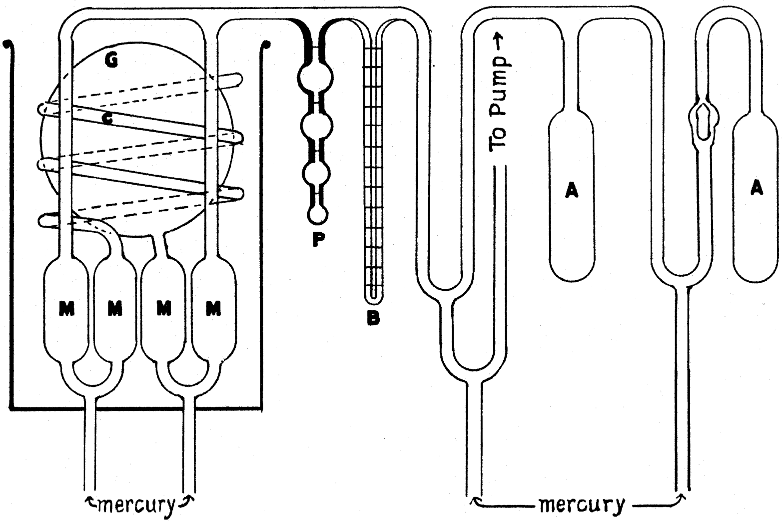

Fig. 1

Outside the tank were located a series of little bulbs (P, Fig. 1), accurately calibrated, and a capillary buret (B) which could be read to 0.1 mg. of liquid. Other mercury valves, operated by leveling bulbs not shown in Fig. 1, gave communication to a mercury diffusion pump, and to several appendixes (two, **A, A,** are shown in Fig. 1) which were useful in subliming the acid during purification, in storing the final product, and in testing the vapor pressure. (For this purpose, the globe was first exhausted and its manometer closed. The sample was then placed in one of the appendixes A, an ice-pack applied, and communication established with the outside arm of the manometer M, upon which the pressure was read. In order to eliminate the possibility of traces of air or carbon monoxide being present, a series of readings was made on each sample, separated by intervals of pumping. When the acid was pure no diminution in pressure could be detected.) The appendix used for storage was fitted with a glass valve, which prevented mercury from being forced over when the pressure in the rest of the apparatus rose, either accidentally or by design.

The diffusion pump was backed by a Hyvac oil pump. In spite of the intermediate presence of a soda-lime tube, a great deal of trouble was caused by corrosion of this pump. It was finally replaced by a 3-stage rotary pump, which was not affected by the acid, even when the protecting tube was removed.

In use, the globe and coil were first evacuated for an hour at about 70° or higher. At the conclusion of the evacuation, the manometers were tested and any required corrections determined. It was anticipated that at temperatures above 70° there might be a correction due to the fact that the inside arms were exposed to the full pressure of saturated mercury vapor, while from the outside arms mercury vapor must have been constantly escaping into the cold connecting tubing. Evidently the rate of escape was small in comparison to the rate of evaporation from the relatively large mercury surface, for no significant difference in levels was observed. The apparatus was then allowed to cool, the manometer valves were closed and a suitable quantity of acid was condensed into one of the measuring devices. The buret was read, or the liquid meniscus adjusted to the mark, keeping the liquid at 0°, and the pressure in the connecting tubing at 11.2 mm. As much as possible of the measured sample was then distilled into the globe or coil, with the aid of a freezing mixture if necessary. The remainder was condensed in the capillary buret and measured, great care being taken that the volume, temperature and pressure of the vapor remaining in the connecting tubing (a small fraction of the whole charge) were exactly as before.

The manometers and connection's were then exhausted, and the pressures in globe or coil determined at 10° intervals. The stirring was momentarily interrupted during the final adjustment of the micrometer. An idea of the reproducibility obtained will be given by comparison of the following figures, obtained entirely independently (except, of course, for the fundamental calibrations).

Volume of liquid used, cc.	0.1962	0.1960
Weight, mg.	0.2432	0.2429
Pressure at 10°, mm.	10.10	10.08
Pressure at 20°, mm.	11.02	11.02
Pressure at 30°, mm.	12.14	12.13
Pressure at 40°, mm.	13.44	13.42
Pressure at 50°, mm.	14.92	14.90
Pressure at 60°, mm.	16.52	16.50
Pressure at 70°, mm.	18.10	18.10

While the data obtained in this manner were sufficient for the original purpose for which the work was undertaken, it seemed worth while to extend the range to somewhat higher temperatures, in order to make possible a comparison with the data of Peterson and Ekstrand. In order to secure a favorable degree of dissociation, it was necessary to work at higher pressures. Therefore, in order to economize material, the apparatus was altered by the substitution of a bulb of 500cc. capacity in place of the 5-liter globe. The work already completed showed that the correction for wall adsorption is negligible above 40°, so that no control with the coil would be required. The bulb contained a pocket in which a standardized Anschutz thermometer was entirely contained. The bulb and manometer valve were heated by a large vapor-jacket, in which was boiled water, toluene, chlorobenzene or bromobenzene. The exact temperature of each determination was noted and the observations corrected to the nearest whole degree (100°, 111°, 132°, 156°) by means of a small correction readily determined from the observed temperature coefficients. In order to reduce the length of the manometer inside the vapor jacket, and to compensate the vapor pressure of mercury, both arms of this manometer were kept at the same pressure by admitting air to the outside arm when the bulb was being heated and the inside pressure was increasing, until a steady state was reached. The pressures were adjusted to equality within 0.1 mm. by small variations in the volume of the system outside the vapor jacket, accomplished by slightly changing the position of the mercury in one of the valves. The reading was finally taken on an outside manometer by the aid of a cathetometer.

In order to determine whether significant decomposition occurred, during the determination at the highest temperature (156°), in one experiment the acid was cooled to 100° at the completion of the series and its pressure compared with that initially determined at the same temperature. No significant difference was detected..

Reduction of Experimental Data

It is convenient to express gas densities in terms of apparent molecular weight; that is, the weight which 22.41 liters of the gas would possess if, in passing from the observed conditions of temperature and pressure to standard conditions, it expanded and contracted as a perfect gas. Changes in M, the apparent molecular weight, are a measure of the departure from the gas laws.

The results are set forth in Table II. The first column gives the pressures at which determinations were made with the globe or bulb and the second gives the calculated values of M. These data are represented by circles on Fig 2, in which the logarithm of the pressure serves as abscissa. The data obtained with the coil are not tabulated, but are entered as crosses on Fig. 2. As was anticipated, they are somewhat higher than those yielded by the globe at the same temperatures and pressures; the difference, however, is negligible except below 50°. Since the pressures in the two series were not identical, it was necessary to interpolate the coil values to the same pressures as the globe values. This was done with the aid of smooth curves, drawn dashed in Fig. 2. The results so obtained are entered in the third column for the five lowest temperatures in Table II. Now, the differences between corresponding globe and coil values are due to surface condensation, the error in each value due to this cause being proportional to the surface-volume ratio of the container in question. The error in the coil values must therefore be about 25 times that in the globe values. The values in the fourth column, marked "corrected," were computed by subtracting from each globe value one-twenty-fourth of the difference between it and the corresponding coil value. It will be seen that in order to determine this correction with an absolute accuracy equal to that of the globe values, comparatively rough coil values will suffice.

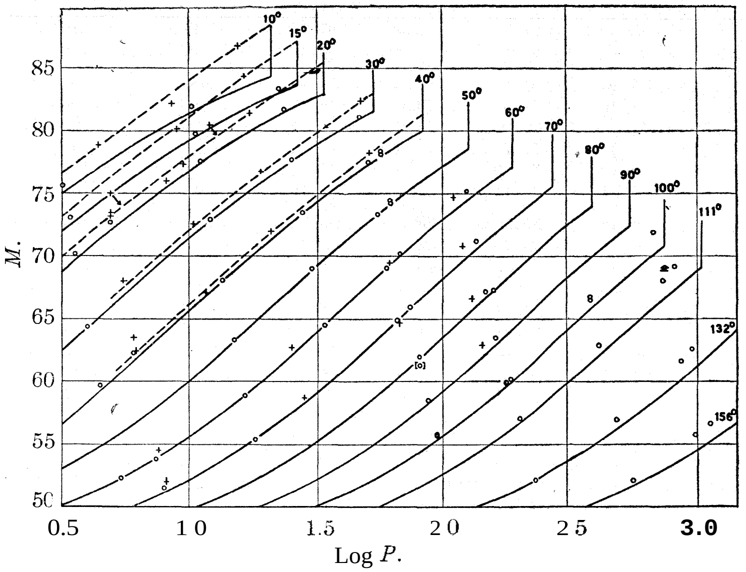

Fig. 2.—Circles represent experiments with globe or bulb. Crosses represent experiments with coil. Triangles represent experiments of Peterson and Ekstrand. Solid lines are solutions of Equations (2) and (3). The vertical portions at the upper ends show the pressures at which condensation occurs. Dashed lines are smooth curves drawn through the crosses.

Table II

Reduction of Experimental Data

	Press., mm. of Hg	Apparent molecular weight				
		Globe	Coil	Corr.	Calcd.	Difference
	3.19	75.7	76.5	75.7	75.1	+0.6
10°	10.08	81.92	83.5	81.85	81.55	+ .30
	10.10	81.92	83.5	81.85	81.55	+ .30

TABLE II (Concluded)

	Press., mm. of Hg	Apparent molecular weight Globe	Coil	Corr.	Calcd.	Difference
	3 36	73.1	74.0	73.1	72.5	+ .6
15°	10 53	79.76	81.0	79.72	79.63	+ .09
	10.54	79.84	81.0	79.80	79.63	+ .17
	22 56	83.38	86.0	83.25	83.16	+ .09
	3.56	70.2	71.0	70.2	69.7	+ .5
	4 87	72.7	73.5	72.7	72.1	+ .6
20°	11.02	77.65	78.8	77.60	77.52	+ .08
	11.02	77.71	78.8	77.66	77.52	+ .14
	23 41	81.75	83.2	81.69	81.57	+ .12
	23 48	81.50	83.2	81.43	81.57	− .14
	4.01	64.4	65.3	64.4	64.4	.0
	12.13	72.92	74.0	72.87	72.93	− .06
30°	12.14	72.92	74.0	72.87	72.93	− .06
	25 44 ,	77.79	79.0	77.74	77.79	− .05
	25.46	77.73	79.0	77.68	77.79	− .11
	46.24	81.14	82.3	81.09	81.10	− .01
	4 47	59.7	60.0	59.7	59.5	+ .a
	6.07	62.3	62.4	62.3	61.8	4 .5
	13.42	68.07	68.5	68.05	68.07	− .02
	13.44	68.05	68.5	68.03	68.07	− .04
40°	27.78	73.59	74.0	73.57	73.56	+ .01
	27.85	73.41	74.0	73.39	73.56	− .17
	50.06	77.43	78.0	77.41	77.48	− .07
	56.81	78.37	78.7	78.36	78.27	+ .09
	56.88	78.27	78.7	78.25	78.27	− .0a

	Press., mm. of Hg	Molecular weight Obs.	Calcd.	Difference
	14.90	63.28	63.36	− .08
	14.92	63.27	63.36	− .09
	30.55	69.06	69.02	− .04
50°	30.61	68.92	69.02	− .10
	54.52	73.36	73.41	− .05
	61.76	74.39	74.33	+ .06
	61.85	74.28	74.33	− .05
	5.43	52.3	52.2	+ .1
	7.48	53.8	53.9	− .1
	16.50	58.90	59.09	− .19
	16.52	58.89	59.09	− .20
60°	33.68	64.58	64.60	− .02
	59.70	69.07	69.21	− .14
	67.51	70.16	70.16	.00
	67.56	70.11	70.16	− .05
	126.1	75.11	74.88	+ .23
	5.83	50.2	50.0	+ .2
	8.05	51.5	51.3	+ .2
	18.10	55.32	55.50	− .18
70°	18.10	55.36	55.50	− .14
	65.50	64.84	65.08	− .24
	74.04	65.86	66.09	− .23
	74.11	65.80	66.10	− .30
	137.0	71.21	71.16	+ .05
	81.04	61.99	62.14	− .05
80°	81.87	(61.33)	62.20	(− .87)
	149.4	67.20	67.14	+ .06
	160.6	67.32	67.73	− .41

	Press., mm. of Hg	Molecular weight Obs.	Calcd.	Difference
	88.28	58.49	58.57	−0.08
90°	88.30	58.47	58.57	− .10
	162.6	63.51	63.34	+ .17
	95.22	55.71	55.55	+ .16
	95.41	55.60	55.55	+ .05
	177.1	59.91	59.98	− .07
100°	189.3	60.21	60.48	− .27
	389.5	66.80	66.57	+ .23
	391.6	66.54	66.62	− .08
	688.2	71.87	71.80	+ .07
	205.2	57.05	57.11	− .06
	424.4	62.90	62.91	− .01
111°	424.4	62.90	62.91	− .01
	745.5	68.10	68.06	+ .04
	824.2	69.20	69.01	+ .19
	236.9	52.15	52.40	− .25
132°	495.3	56.92	56.92	.00
	869.0	61.65	61.48	+ .17
	961.0	62.66	62.41	+ .25
	573.1	52.21	52.24	− .03
156°	574.0	52.10	52.24	− .14
	1018	55.81	55.70	+ .11
	1127	56.64	56.48	+ .16

Adsorption

The amount of adsorption on the glass walls, in mg. per square meter, was calculated by interpolation from the curves in Fig. 2 and is shown in Table III. Being obtained as the differences between much larger numbers, these values have no claim to accuracy, but indicate the order of magnitude of the effect.

TABLE III

ADSORPTION OF FORMIC ACID ON GLASS, MG. PER SQUARE METER, AT DIFFERENT TEMPERATURES AND PRESSURES

Press., mm.	10°	15°	20°	30°	40°
50	0.74	0.57	0.44	0.31	0.18
100	2.00	1.46	.96	.66	.35
200		4.1	2.5	1.2	.75
500				5.0	2.9

Theory of the Vapor Density

The simplest assumption concerning the density of the vapor of formic acid is that it is the weighted mean of the densities of two perfect gases having molecular weights 46.02 and 92.03, and present in proportions given by the mass law, the equilibrium constant being an exponential function of the temperature. Thus, if δ be the density of the vapor in grams per liter, we have for the apparent molecular weight

$$M = \frac{\delta \times 22.41 \times 760 \times T}{273 \times P} \qquad (1)$$

and for the dissociation constant (in terms of partial pressures, and having the physical dimensions of pressure, in millimeters of mercury)

$$K = \frac{P \times (92.03 - M)^2}{46.02(M - 46.02)} \qquad (2)$$

In Fig. 2 the curves represent the values of M which satisfy this equation, when K is calculated from the equation

$$\text{Log } K = 10.755 - 3090/T \qquad (3)$$

Inspection shows that this formula satisfactorily reproduces the observed densities at low temperatures and pressures, but that at higher temperatures and pressures the observed densities are systematically greater. There appear to be three directions in which the explanation of this discrepancy may be sought. In the first place, the individual gases supposed to constitute the mixture may not be perfect gases, but may have densities greater than that calculated from their molecular weights. In the second place, the mixture of the two gases may not obey the laws of ideal solutions. Finally, it is possible that the dissociation constant does not increase with rising temperature strictly according to Equation (3), but that at higher temperatures its temperature coefficient is somewhat smaller. Since the whole discrepancy is small, it will obviously be impossible to determine with certainty the degree in which the three factors contribute; the best that can be done is to show that reasonable assumptions can be made, by the aid of which the observed densities can be reproduced.

It is certain that some allowance must be made for the departure of the individual gases from the gas law. We can advantageously follow the treatment of Lewis and Randall.[5] We suppose that, for each single gas, were it capable of independent existence, the equation of state would be reducible, within the range of temperature and pressure here considered, to the form

$$PV = RT(1 - \alpha P) \tag{4}$$

where a is a function of temperature only, and is small, so that $1 - \alpha P$ may be considered equal to $1/(1 + \alpha P)$. We shall assume provisionally that the mixture of gases is an ideal solution. This means that the single molecules behave, not as if the double molecules were absent, but as if their places were taken by equal numbers of single molecules, and ***vice versa,*** since only in this way can the necessary condition he fulfilled that when the two pure gases at the same pressure are allowed to interdiffuse, there will be no expansion or cooling. Now, the apparent molecular weights of the pure gases would be $M_1 = 46.02(1 + \alpha_1 P)$ and $M_2 = 02.03$ $(1 + \alpha_2 P)$, respectively, and that of the mixture $M = n_1M_1 + n_2M_2 = 46.02\,[n_1(1 + \alpha_1 P) + 2n_2(1 + \alpha_2 P)]$, where n_1 and n_2 are the mole fractions of single and double molecules, respectively. Solving for n_1 and n_2, we obtain

$$n_1 = \frac{92.03(1 + \alpha_2 P) - M}{46.02[1 + (2\alpha_2 - \alpha_1)P]} \text{ and } n_2 = \frac{M - 46.02(1 + \alpha_1 P)}{46.02[1 + (2\alpha_2 - \alpha_1)P]} \tag{5}$$

The degree of dissociation is

$$x = \frac{92.03(1 + \alpha_2 P) - M}{M + 92.03(\alpha_2 - \alpha_1)P} \tag{6}$$

To calculate the equilibrium, we use the relations advocated by Lewis and Randall, namely, that the fugacity of a pure gas whose pressure is only slightly less than the ideal pressure is itself less than the actual pressure by the same ratio, and that in a mixture of gases the fugacity of each component is to be found by multiplying its fugacity in the pure state at the same total pressure by its mole fraction. We therefore write, for the fugacities in the mixture, $f_1 = n_1P(1 - \alpha_1 P)$ and $f_2 = n_2P(1 - \alpha_2 P)$.

The condition for equilibrium is

$$K = \frac{f_1^2}{f_2} = \frac{n_1^2}{n_2}P[1 + (\alpha_2 - 2\alpha_1)P] = \frac{P[92.03(1 + \alpha_2 P) - M]^2}{46.02[M - 46.02(1 + \alpha_1 P)]}[1 - (\alpha_1 + \alpha_2)P] \tag{7}$$

It will be seen that the departure from the gas law affects the observed apparent molecular weight not only directly, by increasing the densities

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[5] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, 1923, pp. 198,226.

of the components, but indirectly, by displacing the equilibrium; the latter effect is represented by the factor $1 + (\alpha_2 - 2\alpha_1)P$. As would be expected, this vanishes in case the mutual attractive energy of two single molecules is equal to that of one double molecule.

In order to see how far the observations can be accounted for by thus modifying the original simple Equation (2), it is necessary to assume values for α_1 and α_2, reasoning by analogy from observations on vapors of molecular weight of the same order of magnitude, which are known to be monomolecular. Such observations seem to be lacking, except in the cases of saturated vapors .or superheated vapors under several atmospheres' pressure. Inspection of the orthobaric densities of several organic vapors, as given in Volume **3** of International Critical Tables, indicates that at 100° these densities exceed those calculated from the gas law by 2 or 3% per atmosphere, as a rule. The deviation is greater than that calculated by van der Waals' equation with the usual values of the constants computed from critical data. It should decrease with rising temperature, and, in general, would be expected to be greater for heavy than for light molecules. For a first trial, the following values for α_1 and α_2 in % per **atm.** were arbitrarily assumed:

T	10°	15°	20°	30°	40°	50°	60°	70°	80°	90°	100°	111°	132°	156°
α_1	4.5	4.2	4.0	3.6	3.3	3.0	2.8	2.6	2.4	2.2	2.0	1.8	1.5	1.3
α_2	6.7	6.3	6.0	5.5	5.0	4.5	4.2	3.9	3.6	3.3	3.0	2.7	2.3	2.0
K	0.684	1.060	1.618	3.605	7.64	15.41	29.90	56.60	100.2	175.0	296.0	511.0	1336	3573

The values of K, given by Equation (3), are also included.

The apparent molecular weights which satisfy Equation (7) for the experimental temperatures and pressures, and with the numerical constants just given, are tabulated in Table II under the heading "Calcd." It will be seen that the discrepancies remaining are very small, except in the case of experiments at pressures below 10 mm., where an error of 0.01 mm. would suffice to cause a discrepancy of 0.2 unit in M. The agreement is so satisfactory that it seems needless to seek to improve upon the original, supposedly preliminary, assumptions.

Equation **(3)** indicates that the heat of dissociation at constant pressure is 14,125 calories per mole, and does not vary within the temperature range covered by the experiments. This range, however, is too small to permit drawing reliable conclusions about the temperature coefficient of the dissociation heat, which depends on the difference in the specific heats of the two forms. The customary assumption[6] is that a reaction which produces one new gas molecule involves an increase of 3.5 in the molecular heat. The equation

$$\text{Log } K = 5.542 + 1.75 \log T - 2827/T \qquad (8)$$

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[6] See A. Eucken, "Fundamentals of Physical Chemistry," First English Edition, McGraw-Hill Book Co., New York, 1925, p. *417.*

has been adjusted to take this increase into account, and to reproduce as well as possible the results of experiment. It leads to values for M which exceed those calculated from Equation (3) by about 0.1 unit at 10° and 156°, fall below them by the same amount at 70°, and are indistinguishable at 40° and 111°.

It seems to be by no means certain that an increase in specific heat is theoretically necessary. True, it is always found to accompany the dissociation of gas molecules which are held together by primary valence, presumably because in such molecules certain possible modes of vibration are not developed at the temperatures in question, But when liquids evaporate without breaking primary valence bonds, a decrease of specific heat ensues, in spite of the increase in the number of gas molecules. It is conceivable that the dissociation of a double molecule of formic acid is a process of intermediate character and really involves very little change in specific heat. Unfortunately, the chemical instability of the single molecules prevents the extension of the temperature range which would be necessary to decide the question.

Summary

Formic acid probably 99.99% pure has been prepared by vacuum sublimation and some of its physical properties have been determined.

The density of the vapor has been determined at temperatures between 10 and 156°, and at pressures favorable to partial dissociation. A correction for wall adsorption has been determined and applied.

The results can be satisfactorily interpreted by assuming that the vapor is an ideal mixture of two gases, having single and double molecules, respectively, each of which deviates from the perfect gas laws in the same way as would a monomolecular vapor of similar molecular weight.

CAMBRIDGE, MASSACHUSETTS

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

A FURTHER STUDY OF THE REACTION BETWEEN NITROGEN DIOXIDE AND LIQUID MERCURY

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

RECEIVED JUNE 6, 1928 PUBLISHED AUGUST 4, 1928

In an earlier article[1] a report was made of some experiments on the reaction, both thermal and photochemical, between nitrogen dioxide and liquid mercury. In that article it was reported that radiation of frequency greater than the threshold frequency of mercury caused the reaction to proceed more rapidly than in the dark. This effect was ascribed, at that time, to an activation of the mercury surface which was in some way associated with the photoelectric emission. In a somewhat later article[2] a revised explanation of the phenomenon was given in which the formation of negative ions due to the electron affinity of the nitrogen dioxide was suggested as the crucial factor in the acceleration of the reaction by short wave length radiation. Moore[3] has attempted to activate a mercury surface by electron bombardment. He offered a tentative explanation based on the formation of a monomolecular layer of mercuric oxide by the action of the filaments used. This film might hold mechanically any electrons emitted from the filament.

The experiments to be reported in this article were undertaken with the object of elucidating some of the factors involved in the reaction between mercury and nitrogen dioxide. The phenomena to be reported agree, in so far as they overlap, with results previously reported. It is, however, demonstrated that there are many variable factors, some of which are difficult, if not impossible, to control. A heterogeneous reaction of the type under consideration may be affected by many things such as the state of the surface, impurities in the gas and the possibility of the development of surface charges which lead to spurious effects. The present results may be deemed to be somewhat inconclusive, but they are reported at this time as it seems doubtful whether further experimentation along the lines indicated will lead to important results.

I. Preliminary Discussion

The reaction between liquid mercury and nitrogen dioxide presumably leads to the formation of mercuric oxide and nitrogen.[4] These final products are doubtless not formed quantitatively. The initial step in the process would seem to be, logically, the formation of a salt of the type of a

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[1] Moore and Noyes, THIS JOURNAL, 46, 1367 (1924).

[2] Noyes, *Trans. Faraday Soc.*, 21, 569 (1926).

[3] Moore, THIS JOURNAL, 47, 2932 (1925).

[4] Watts' "Dictionary of Chemistry," Longmans, Green and Co., London, 1894, Vol. III, p. 566.

nitrite. Nitrogen dioxide has many of the characteristics of a free radical and possesses, as far as can be ascertained, an appreciable electron affinity.[5] One might expect the formation of a polar compound of the type of a mercurous (or mercuric) nitrite to be brought about by the transfer of an electron from the mercury to the nitrogen dioxide molecule. The reaction might be initiated, or accelerated, by the presence of negative ions in the nitrogen dioxide or by a positive charge on the mercury surface. In the experiments previously reported a large number (at least 10^8) molecules reacted per electron, assuming that the reaction with light is the sum of the normal dark plus the photochemical reaction. It is necessary, therefore, to postulate a chain mechanism to account for the results or to ascribe the action to the formation of nuclei on the surface.

The reaction between mercury and nitrogen dioxide is exothermic. If the activated state consists in the removal of the electron from the mercury, one should expect a relatively high energy of activation and consequently a high temperature coefficient for the reaction rate. The results to be reported indicate a low temperature coefficient. Since the reaction does not seem to be termolecular (or of higher order with respect to the pressure of nitrogen dioxide), the activated state for the dark reaction does not seem to be greatly different from the normal state. This means that the same proportion of the collisions between nitrogen dioxide molecules and the mercury surface will be effective regardless of temperature. The manner of the growth of the film indicates that nuclei on the surface act as centers of film formation. Since the number of molecules of gas hitting the surface will vary as the square root of the absolute temperature, the temperature coefficient of the reaction rate might be low if the reaction took place only around nuclei already present. However, the dependence of reaction rate on pressure of nitrogen dioxide does not indicate that the reaction is first order with respect to nitrogen dioxide. In fact under certain conditions lowering the pressure of nitrogen dioxide will cause an increase in reaction rate. This, upon consideration, would seem to indicate that the process of diffusion of some molecules through the gas phase plays an important part. The nuclei on the surface may well be, therefore, minute amounts of oxide formed by the reaction of mercury vapor with nitrogen dioxide or removed from the walls by the rush of incoming gas. That the latter effect is important is indicated by the gradual acceleration of the reaction with use of the reaction vessel.

II. Experimental

A. A Study of the Thermal Reaction

1. Effect of Length of Use of the Reaction Vessel on the Rate of Reaction.—After a lengthy consideration of the possible ways of measur-

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[5] Gibson and Noyes, THIS JOURNAL, 43, **1255** (1921).

ing the rate of reaction between mercury and nitrogen dioxide, it was decided to adopt the technique used in the previous investigation.[1] This consists in admitting the nitrogen dioxide and in observing the time of formation of a solid film on the surface. This method leaves something to he desired in a quantitative sense, but the rate of reaction may be considered to vary inversely with the time of formation of the film.

In the earlier experiments* only one reaction vessel was used. The times of formation of the film were found to be very reproducible over short intervals of time, providing the nitrogen dioxide was carefully dried. A reduction in the pressure of the nitrogen dioxide caused a slight increase in the time of formation of the film.

In the present experiments, certain reaction vessels gave values of the time of formation of the film (t_0) which were in good agreement with previous values. However, many reaction vessels gave times of formation which differed by more than the experimental error from the values previously reported. In general, the values of t_0 decreased with use of a given reaction vessel. Table I shows values of t_0 for a certain reaction vessel.

TABLE I

EFFECT OF LENGTH OF USE ON THE TIME OF FORMATION OF A SOLID FILM

Run numbers	1–18	19 36	3746	47–53"
t_0 (av.) secs.	48	38	24	37

[a] Cell cleaned before making these runs.

2. Effect of the Shape of the Reaction Vessel on the Rate of Reaction.—It became clear early in this work that some factors were present and caused variation in the values of t_0 and which were not of obvious importance. Factors which, at first glance, would seem to be of importance are: radiation, temperature, purity of the mercury and purity of the nitrogen dioxide. There seemed, however, to be a great variation between various reaction vessels. Table II illustrates the point in question. The two reaction vessels were sealed together so that the same pressure of nitrogen dioxide was introduced into the two vessels at the same time. The mercury used was from the same source.

TABLE II

VARIATION OF t_0 WITH REACTION VESSEL

Run numbers	3–8	1418
t_0 (av.) secs. I	34	23
t_0 (av.) secs. II	55	33

Many different reaction vessels were used in these experiments and many changes in design were made. As a result of all of the observations made, the following statements seem justified: the values of t_0 do not depend in any obvious manner on the ratio of surface to volume in the reaction vessel. While less accuracy was possible with small surfaces of mercury than with large, the value of t_0 does not depend primarily on the surface. The only factor of importance in this connection we were able to discover was in the relation of the entrance of the gas to the mercury surface. If the inlet was so placed that any dust particles or impurities from the wall would be carried to the surface of the mercury, the rate of reaction seemed to be rapid. Reaction vessels with the well containing the mercury large compared to the diameter of the vessel seemed to exhibit abnormally fast reactions. In cells of this type any impurity removed from the walls by the rush of incoming gas would be sure to impinge upon the surface.

3. Effect of Moisture on the Values of t_0.—A vessel which had shown an average value of t_0 with dry nitrogen dioxide of forty-three seconds, was filled with water vapor at a pressure of 5 mm. prior to admitting the nitrogen dioxide. The value of t_0 then became twenty seconds and remained short for several runs.

4. Effect of Temperature on the Values of t_0.—Most of the experiments reported in this article were carried out at room temperature. Minor variations in temperature did not seem to produce a marked change in the values of t_0. One vessel which showed an average value of t_0 of forty-five seconds at a temperature of 23° showed a value of sixty seconds at a temperature of 2°.

5. Effect of Pressure on the Values of 20.—In the previous work[1] it was found that the time of formation of the film increased with reduction in pressure of the nitrogen dioxide. The change was not very great, an increase in time from seventy to one hundred seconds being noted as the pressure fell from 400 mm. to 40 mm. Phenomena similar to those previously reported could be obtained when the reaction vessel had been freshly cleaned and the values of t_0 were of the same order as those previously reported. However, after the reaction vessel had been used for some time and the time had become appreciably shorter than those previously reported, a reduction in pressure led to a reduction in time of formation of the film until very low pressures had been reached. Very low pressures invariably led to an increase in the values of t_0. However, it was observed that the thickness of the film was considerably greater for high pressures than for low pressures. Table III shows data illustrating this point.

TABLE III

EFFECT OF PRESSURE ON THE VALUES OF t_0

(T = 25°)

Run no.	1	2	3	4	5	6	7
Press. of NO_2, cm.	46	30	26	17	10	5	2
t_0, seconds	43	47	48	42	46	28	34

At lower pressures t_0 became as long as three minutes or more. Runs 1 to 5 agree within experimental error.

6. Effect of Foreign Gases on the Values of t_0.—After each run the reaction vessel was flushed out with either nitrogen or hydrogen which had been dried by passage through phosphorus pentoxide. The system was then evacuated to a pressure below a tenth of a millimeter before admitting the nitrogen dioxide. No difference in behavior was noticed between cells flushed with hydrogen and those flushed with nitrogen. In order to determine the effect of foreign gases, nitrogen and oxygen were mixed at different times with the nitrogen dioxide before admitting it to the reaction vessel. The time of formation of the film seemed to be independent of the pressure of foreign gas at constant pressure of nitrogen dioxide. This point is shown in Table IV.

TABLE IV

EFFECT OF FOREIGN GASES ON THE VALUE OF t_0 ($T = 25°$)

Number of runs	Press. of NO_2, cm.	Foreign gas	Press. of foreign gas, cm.	t_0 secs.
4	24	..	..	42
4	24	O_2	24	42
4	24	N_2	24	44

B. Attempts to Accelerate the Reaction by Various Means.

1. The Effect of Radiation.—An attempt was not made to repeat all of the previous work on the acceleration of the reaction by radiation. The effect of radiation shown in the previous work[1] could be duplicated if the reaction vessel was clean, that is, before the value of t_0 had become very short. Accelerating and retarding potentials produced about the same effect as those found previously. For example, a vessel which showed a value of t_0 of eighty-eight seconds (average of twelve determinations) showed a time of formation of the film under the influence of radiation from a quartz mercury arc lamp of sixty-five seconds (average of sixteen determinations) when small accelerating potentials were used. However, the behavior of the reaction was much more erratic than was found previously. Great care in drying the nitrogen dioxide, changing the type of stopcock grease and even rebuilding the entire apparatus to eliminate possible impurities did not produce any distinct improvement in the reproducibility of the results. Some factor which we were unable to discover caused variations in the results. However, there is no reason to doubt the previous work and the effect of radiation can be duplicated under proper conditions.

As shown in the preliminary discussion, the effect of radiation may be open to a variety of interpretations, so that it was thought desirable to carry out a series of experiments which would permit a decision as to the relative merits of the various hypotheses.

2. Effect of a High Potential Discharge.—The reaction vessel was thoroughly swept out with either dry nitrogen or dry hydrogen and then pumped out to a pressure of about a tenth of a millimeter. A discharge was started, either with a spark coil or with a 1/4 kw. transformer. Small amounts of residual gas would frequently cause a film of oxide to form on the surface. The surface was always renewed before admission of the nitrogen dioxide. The admission of the nitrogen dioxide stopped the discharge due to its relatively high pressure. However, the gas is admitted into a space plentifully supplied with ions (and radiation), certainly a far higher concentration than was ever obtained by the photoelectric effect. Several possibilities may now be discussed. 1. In some experiments the discharge was passed between the mercury and an electrode placed above the surface. 2. In other experiments the discharge was passed between two electrodes placed in the tube through which the nitrogen dioxide passed in entering the reaction vessel. Varying low potentials were imposed between the mercury and an electrode placed above the surface of the mercury at a distance of about one and a half centimeters. Table V presents a summary of data obtained with one reaction vessel.

TABLE V

EFFECT OF DISCHARGE ON THE VALUES OF t_0

Number of runs	Pressure of NO_2, cm.	t_0, secs., av.	Remarks
..	17–20	180–300	Hg one electrode. Light, uniform film formed instantly. Heavy film very slow in forming
10	17–20	54	No discharge
6	17–20	43	Discharge in entrance tube. Potentials on Hg with ref. to electrode above surface of –35 to +35 volts produced no regular effect
8	17–20	61	No discharge
27	17–20	39	Discharge in entrance tube

3. Effect of Electrons Emitted by Radiation from a Platinum Electrode Placed Above the Mercury Surface.—A few experiments were tried in which the nitrogen dioxide entered the reaction vessel in such a manner that it passed in front of a platinum plate on which radiation from a quartz mercury arc lamp was incident. No acceleration of the reaction was observed although the photoelectric current was so small that no decided effect would have been expected.

4. Effect of a Beam of Cathode Rays.—One reaction vessel was arranged in such a way that an electron beam formed in a low pressure discharge in hydrogen (with heated cathode) was directed into the space directly above the mercury surface. The beam could be deflected toward or away from the mercury surface by varying the potential between the mercury surface and an electrode placed above the surface. No definite acceleration was noted.

5. Effect of Strong Radiation (not Incident on the Mercury Surface).—

It has been shown by Norrish[6] that nitrogen dioxide decomposes under the influence of radiation. It is possible that the nitrogen dioxide might be activated by the radiation which it absorbs and react more rapidly than normally with mercury. However, radiation in the visible and near ultraviolet regions was found to be without effect. This agrees with previous observations.[1]

An attempt was also made to accelerate the reaction between nitrogen dioxide and hydrogen by radiation. Norrish[6] had found that hydrogen produced little effect on the pressure increase when nitrogen dioxide was illuminated by radiation from a quartz mercury arc lamp. This observation has been confirmed for the three regions of the spectrum, *(a)* visible, (b) to the limit of transmission of quartz and (c) through fluorite, using a condensed discharge through hydrogen.? A discharge through the hydrogen–nitrogen dioxide mixture caused an explosion. This indicates, presumably, that activation of nitrogen dioxide is in itself not sufficient to cause reaction with hydrogen. This evidence, coupled with the lack of effect of visible radiation on the rate of reaction of nitrogen dioxide with mercury, indicates that activated nitrogen dioxide molecules are not appreciably more reactive chemically than normal molecules toward mercury and hydrogen.

6. Effect of Electrons Emitted by Thermal Means from a **Filament** Placed Above the **Surface.**—A few experiments were made in which a heated filament was placed in the reaction vessel above the mercury surface. A high vacuum was attained before the admission of the nitrogen dioxide. Table VI shows results obtained in this manner with one reaction vessel.

TABLE VI

EFFECT OF ELECTRON EMISSION FROM FILAMENT

Pressure of nitrogen dioxide, 7–10 cm.; $T = 25°$

Number of runs	to, av.	Remarks
12	45	No filament
30	46	Filament on. Potential between filament and Hg surface varied from +6 to −6 volts

The thermoelectric currents observed in these experiments were far greater than the photoelectric currents observed in paragraph 1.

III. Discussion of Results and Conclusions

From the results on the thermal reaction, it is obvious that the time of formation of the film is not solely a function of the pressure of the nitrogen dioxide, the temperature and the purity of the mercury. Indeed, it

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[6] Norrish, J. *Chem. Soc.,* 1927,761. See also Dickinson and Baxter, THIS JOURNAL, 50, 774 (1928).

[7] Kassel and Noyes, THIS JOURNAL, 49,2495 (1927).

seems that some factor which depends on the geometry of the reaction vessel must be taken into account. The authors are inclined to the conclusion that impurities may be removed from the walls by the incoming gas and that these impurities, if carried to the mercury surface, may catalyze the reaction. The impurities would seem to be mainly mercuric oxide. This hypothesis satisfactorily explains the decrease in the values of t_0 with increased use of the cell. Also, we may have here an explanation of the peculiar effect of pressure. Indeed one may derive an equation which fits the data reasonably well by assuming that two effects are to be considered, one dependent on the pressure of the nitrogen dioxide directly and the other a diffusion process involving some impurity which must diffuse through the gas. The diffusion would be more rapid at low pressures and only at exceedingly low pressures would the values of t_0 increase markedly. The phenomena are doubtless very complex and it is entirely possible that other effects due to stopcock grease and to spurious charges induced by the rush of gas must be considered. However, the authors are inclined to the belief that the above explanation will account for many of the facts observed.

When attention is turned to an explanation of the various attempts to accelerate the reaction, the following facts seem to be proved. The presence of ions in the gas (nitrogen or hydrogen) in the reaction vessel at the time the nitrogen dioxide is admitted will cause an increase in the rate of reaction between nitrogen dioxide and mercury. In the case of some of the extremely long times observed when the discharge method was used, it is obvious that there is a very rapid reaction which caused a uniform film, exceedingly thin, to be formed on the surface and that this film acts as a protective coating. With the discharge in the entrance tube so that the mercury did not serve as one electrode, the film seemed to be normal in character but formed more rapidly than in the absence of discharge. These facts indicate that the presence of ions will cause an increase in the rate of reaction between mercury and nitrogen dioxide. However, the presence of small numbers of ions (comparable to the number given off due to the photoelectric effect or somewhat larger) is without effect that can be detected. Activation of the nitrogen dioxide by radiation is also without effect. There is no evidence to indicate that negative ions produce more effect than positive ions.

The effect of the light announced in the previous article[1] and confirmed in the present investigation must, therefore, be associated with the activation of a surface layer of gas (or perhaps of mercury). This activation seems to be associated in some way with the photoelectric effect.

As a general conclusion we may state that the thermal reaction between mercury and nitrogen dioxide depends on conditions which vary with the geometry and cleanliness of the reaction vessel. The rate (as determined by the formation of a surface film) is accelerated by the presence of relatively large numbers of ions in the gas at the time it is admitted. There may, however, be a rapid reaction uniform over the surface which will hinder the formation of a heavy film. Evidence indicates that positive and negative ions are equally effective in producing acceleration of the reaction. The action of light is best ascribed to the activation of a surface film on the mercury, perhaps adsorbed gas or a small amount of oxide, which is associated with the photoelectric emission. Numbers of ions in the gas comparable to the number produced by the photoelectric effect do not produce noticeable changes in the time of formation of heavy films. This view is more in accord with the views first expressed,[1] but the phenomena are shown to be more complicated than had been supposed. Acceleration due to radiation is not observed when the reaction vessel has become dirty and the dark reaction has become very fast.

Summary

1. The rate of reaction between mercury and nitrogen dioxide as measured by the time of formation of a uniform visible film is dependent, among other things, on the shape of the reaction vessel. The times tend to become short as the reaction vessel is used. There are variable factors which have not been entirely determined.

2. The reaction is accelerated by the presence of large numbers of ions. Positive and negative ions, as far as can be determined, have equal effects.

3. The action of light in accelerating the reaction is most probably to be ascribed to the activation of a surface film. This seems in some way to be associated with the photoelectric effect.

4. Acceleration of the dark reaction with continued use of the vessel may be due to the contamination of the surface by minute crystals swept in by the nitrogen dioxide. This acceleration may obscure the action of the light.

CHICAGO, ILLINOIS

[Contribution from the Department of Chemistry, Columbia University,
No. 575]

WATER CONCENTRATION AND THE RATE OF HYDROLYSIS OF SUCROSE BY INVERTASE

By J. M. Nelson and Maxwell P. Schubert

Received June 7, 1928 Published August 4, 1928

Many investigators[1] have studied the relation between the rate of hydrolysis of sucrose by invertase from yeast and the concentration of the sugar. This relationship, as observed by Ingersoll, is shown graphically by the heavy lined Curve 1, in Fig. 1. It will be seen that the velocity rises gradually as the sucrose concentration is increased until the latter reaches about 5%, after which there is a dropping off, and at 70% of sucrose the velocity is only about one-fourth of the maximum value reached at 5%. So far no very satisfactory explanation has been found

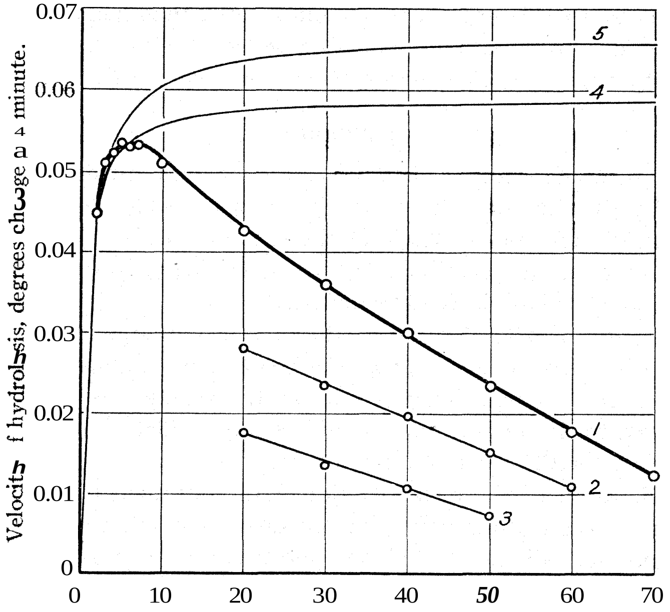

Fig. 1.—Curve 1, sucrose and no alcohol; 2, sucrose and 10% alcohol; 3, sucrose and 20% alcohol; 4, theoretical curve, K = 0.017; 5, theoretical curve, K = 0.030.

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[1] (a) O'Sullivan and Tompson, J. *Chem. Soc.*, 57, 834 (1890); (b) Brown, *ibid.*, 81,373 (1902); (c) Henri, *Z. physik. Chem.*, 39,215 (1902); (d) Michaelis and Menten, *Biochem.* Z., 49,333 (1913); (e) Euler and Myrbeck, Z. *physiol. Chem.*, 124, 159 (1922); (f) Achalme and Bresson, *Compt. rend.*, 152, 1328, 1420, 1621 (1911); (g) Colin and Chaudun, J. *chim. physik.*, 20, 4719 (1925); (h) Ingersoll, *Dissertation*, Columbia University, 1925; (i) Bull. *soc. chim. biol.*, 8,264, 276 (1926).

for this peculiar relationship. It is apparent from the shape of Curve 1 in Fig. 1 that in the more concentrated region, 10 to 70% sucrose, it approaches very closely to a straight line and at a first glance it might seem that the velocity is some simple function of the sucrose concentration. But, as Ingersoll has pointed out, the water concentration also drops off linearly with the increase in sucrose concentration and if the velocity is plotted against the concentration of water instead of the concentration of sucrose, then a curve, heavy lined in Fig. 2, is obtained which it will be noticed is very similar in shape to the velocity–sucrose concentration

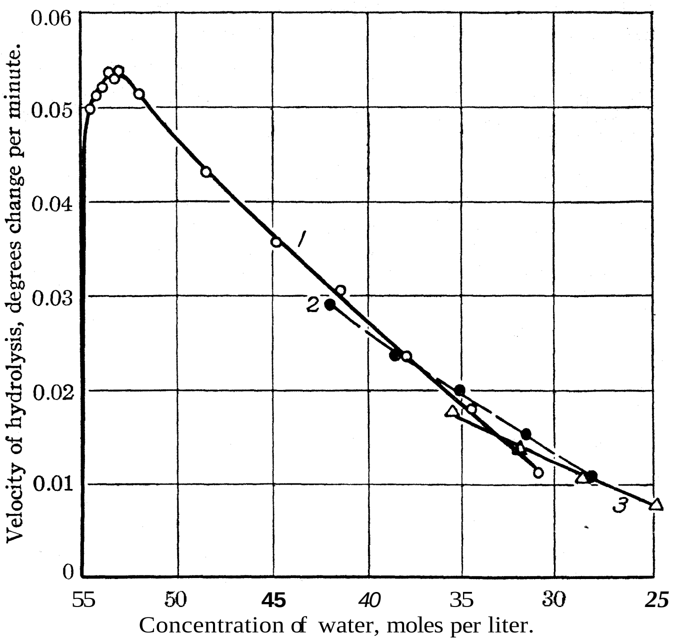

Fig. 2.—Curve 1, sucrose and no alcohol; 2, sucrose and 10% alcohol; 3, sucrose and 20% alcohol.

Curve 1, in Fig. 1. In other words, the velocity in the case of sucrose solutions ranging in concentration from 10 to 70%, drops off as the sucrose concentration increases and as the water concentration decreases, and for this reason Ingersoll was unable to decide whether it is the concentration of sucrose or the concentration of water or both together which determines the magnitude of the velocity of hydrolysis when the concentration of sucrose is greater than 5%.

In the present study, the authors have tried to avoid the difficulty encountered by Ingersoll, that is, not being able to vary the sucrose concentration without simultaneously varying that of the water, by adding to the sucrose solutions alcohol, which has only a small retarding effect, thereby making it possible to vary the sucrose and water concentrations independently of each other. For this purpose several series of solutions, varying in sucrose content from 20 to 70%, were made up. Each solution of these series contained a constant quantity of alcohol, and the composition of the solutions and their respective rates of hydrolysis are given in Table I. These values have been plotted in two different ways; that is, in Fig. 1 the velocities have been plotted against the corresponding sucrose concentrations, while in Fig. 2 the velocities are plotted against the corresponding concentrations of water. Upon comparing the curves in the two figures, it will be seen that when the velocities are plotted against water concentration, then Curves 2 and 3, Fig. 2, lie very close to the curve (1) for sucrose alone. On the other hand, when the velocities are plotted against sucrose concentration, Curves 2 and 3, Fig. 1, then they are spread much farther apart.

TABLE I

HYDROLYSES AT VARIOUS CONCENTRATIONS OF SUCROSE AND ALCOHOL

Constant amount of a yeast invertase preparation, "Convertit," diluted 200 times used in all hydrolyses. Buffer, 0.01 molar sodium citrate, $P_H = 4.5 \pm 0.1$. Velocity given in degrees change in rotation per minute. Hydrolyses run at 25.00'. All rotations determined at 25.0°; light source, 5461 Å. Water concentrations given in moles per liter of solution

Sucrose, g /100 cc. of soln.	No alcohol		10% alcohol		20% alcohol	
	Vel.	Water concn.	Vel.	Water concn.	Vel.	Water concn.
2	0.0448	54.6	...	..	...	..
3	.0511	54.2	...	..	...	
4	.0522	53.9	...	..	. .	..
5	.0534	53.5	...		...	..
6	.0530	53.2	...	..	...	
7	.0532	52.8	...		...	
10	.0512	51.8	...		. .	..
20	.0428	483	0.0280	41.9	0.0177	36.5
30	.0360	44.9	.0236	38.4	.0137	32.0
40	.0301	41.4	.0197	35.0	.0106	28.5
50	.0235	38.0	.0153	31.5	.00716	24.9
60	.0178	34.4	.0109	28.0	...	..
70	.0124	30.9	...	..	...	..

The fact that the alcohol curves in Fig. 2 fall so close to the sucrose only curve indicates that the velocities of hydrolysis are nearly the same, irrespective of the amounts of alcohol and sucrose which the solutions contain (provided the water concentration is the same). Thus it does not make so very much difference in the magnitude of the velocity whether, for example, the following three solutions contain: 20% of alcohol and 20% of sucrose; 10% of alcohol and 45% of sucrose; or no alcohol and 60% of sucrose, the velocities for these three solutions being 0.0177, 0.0175 and 0.0178, respectively. In other words, the above results indicate that the concentration of water is the primary factor, while the concentrations of alcohol and sucrose and possibly some other influences are of minor significance in determining the magnitude of the velocity of hydrolysis when the concentration of sucrose is beyond 20%.

Significance of Results for Current Theories.—The theory of the mechanism of the invertase inversion of sucrose most widely accepted is that of Michaelis. The two fundamental assumptions of this theory are (1) that sucrose combines with invertase according to the mass law and (2) that the velocity of inversion is proportional to the amount of invertase combined with sucrose. With these assumptions, the mass law is used to calculate from measurements of velocities of hydrolysis the affinity constants of various invertases for sucrose. The relation between velocity of inversion and sucrose concentration derived on these assumptions is represented in Curve 4, Fig. 1. According to this theory, as the sucrose concentration is increased, more and more of the invertase combines with sucrose to form a complex and the velocity of hydrolysis increases until a sufficiently high sucrose concentration is reached so that practically all of the invertase exists in the combined form. Then the velocity has reached a maximum value and further increase of sucrose should have no effect on the velocity.

One of the methods for determining the affinity constant of invertase for sucrose requires the determination of the maximum velocity of hydrolysis with a given amount of invertase, the assumption being that then all the invertase is in combination with sucrose. But the experimentally determined relation (Curve 1, Fig. 1) shows that the velocity maximum is attained at 5% or 0.176 M sucrose. Since the velocity drops off beyond this sucrose concentration, it has been customary with workers determining affinity constants to neglect the portion of the curve corresponding to sucrose concentrations above 5 to 6% and to assume that, at the experimental maximum, all of the enzyme is combined with sucrose. Yet examination of the curves in Fig. 1 shows that at 5% of sucrose the theoretically derived curve (4) is still 10% short of the true maximum velocity attainable. Curve 4 is plotted,[2] using Michaelis and Menten's original value of 0.017 as the dissociation constant of the sucrose–invertase complex. More recent work, like that of Kuhn and Münch[3] and also the results obtained by Nelson and Larson, give an average value for the above dissociation constant of about 0.030. Using this value in the Michaelis and Menten equation, Curve 5, in Fig. 1 is obtained, where at 5% of sucrose the velocity is still 17% short of its maximum. This means that the affinity constant

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[2] The data for Curves 4 and 5 in Fig. 1 were obtained by substituting for S, in the equation $V = S/(S + K)$, the sucrose concentrations above, and multiplying the values obtained by the factors 0.590 and 0.6688, respectively, to make the curves coincide roughly with the first portion of Curve 1.

[3] Kuhn and Münch, *Z. physiol. Chem.*, **163**, 1 (1927); Nelson and Larson, *J. Biol. Chem.*, **73**, 223 (1927).

of invertase for sucrose determined by the method of Michaelis and Menten, if it exists at all, is probably wide of its true value.

The results obtained in the present work with alcohol and more concentrated sucrose solutions make it look as if the decrease in water concentration might be the disturbing factor. As the sucrose concentration increases, the influence of the decreasing water concentration becomes relatively more significant and therefore will tend to mask the increase in velocity brought about by the increasing sucrose concentration forming a higher concentration of the enzyme–sucrose complex. From this point of view, the peculiar shape of the curve relating velocity of hydrolysis to sucrose concentration (Fig. 1, Curve 1) must be considered to be the resultant of at least two effects, both due to the increase in sucrose: (1) the increasing formation of sucrose–invertase complex and (2) the decrease in water concentration. Furthermore, the influence of the decreasing water concentration, which predominates at sucrose concentrations above 7% has very probably begun to operate at lower sucrose concentrations. Thus it seems that even in the first segment of the velocity–sucrose concentration curve (Curve 1, Fig. 1) up to 6% of sucrose, the water concentration factor of which the Michaelis theory takes no account will have to be considered. In view of the extensive application of the affinity constant of an enzyme as an essential characteristic in its description, and also in accounting for its specificity,[4] this influence of the water concentration becomes a matter of considerable importance.

Experimental Procedure.—The hydrolyses were run by making up 250 cc. of solution containing sucrose, alcohol for some and buffer of such concentrations that when 200 cc. was placed in a bottle and 25 cc. of invertase solution added, the resulting solution was of a certain desired sucrose and alcohol concentration as well as 0.01 M with respect to buffer (sodium citrate was used) and at a PH of 4.5 ± 0.1. Solutions of 30%, that is, 30 g. per 100 cc. of solution, total (sucrose and alcohol) concentration or less were measured out by pipetting, using calibrated pipets; those of higher total concentration were weighed, using the specific gravities to calculate the weight of 200 cc. Hydrolyses were started by allowing the 200 cc. of sucrose and alcohol solution at least forty minutes to come to the bath temperature (25.00 ± 0.02°), then delivering into it 25 cc. of invertase solution, which had also come to that temperature, and shaking vigorously. The invertase delivery was made by a pipet calibrated to deliver 25.00 ± 0.02 cc. of invertase solution in seven seconds. For solutions below 30% total concentration, 25cc. samples were withdrawn at various intervals of time after the start and added to 5 cc. of 0.2 *M* sodium carbonate solution to stop the reaction and complete mutarotation. In the case of solutions of total concentration above 30%, sample were withdrawn and 25 cc. weighed out as recommended by Ingersoll[1h,i] and then 5 cc. of the carbonate solution added. Hydrolyses were run at 30% total concentration, using both methods to make sure they checked. Individual hydrolyses were run as

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[4] Kuhn, *Z. physiol. Chem.*, **125**, **1** (1923); Euler, "Chemie der Enzyme," Bergmann, Munich, **1925**, p. 350; Waldschmidt-Leitz, "Die Enzyme," Vieweg and Son, Braunschweig, **1926**, p. 67; Oppenheimer, "Die Fermente," Georg Thieme, Leipzig, **1925**, p. 193.

far as they could be without showing deviations of more than the experimental error from a linear course.

The method of calculating the initial velocity of hydrolysis consists in dividing the change in rotation for each sample of the hydrolyzing sucrose solution taken by the time in minutes after the start at which that sample was taken. The change in rotation for a given sample is the difference between the initial rotation of the hydrolyzing solution and the rotation of that sample after the addition of 5 cc. of sodium carbonate solution. This ratio was calculated for each sample and the mean taken as the velocity for that particular sucrose solution. This procedure made it quite essential to determine the initial rotation very accurately and this was found to be rather difficult in the more concentrated solutions where slight errors in weighing out samples (weighed to the nearest drop) were liable to make a considerable error in the observed rotation. So in addition to synthetic initials, made by mixing 3.125 cc. of invertase solution with 5.625 cc. of the carbonate solution and then adding 25.00 cc. of the original 250 cc. of sucrose solution made up for the hydrolysis, a sample was taken within three to six minutes after the start of the reaction and its rotation used as a basis for extrapolating back to find the rotation at zero time. The mean of these two, the synthetic and the extrapolated initials, was used as the true initial rotation.

Summary

The above study shows that the concentration of water is a factor in determining the magnitude of the velocity of hydrolysis of sucrose by invertase.

NEW YORK CITY

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

THE HEAT CAPACITY OF HYDROGEN BROMIDE FROM 15°K. TO ITS BOILING POINT AND ITS HEAT OF VAPORIZATION. THE ENTROPY FROM SPECTROSCOPIC DATA

BY W. F. GIAUQUE AND R. WIEBE

RECEIVED JUNE 18, 1928 PUBLISHED AUGUST 4, 1928

In a recent paper[1] we have shown that the entropy of hydrogen chloride as calculated with the assistance of spectroscopic data is in agreement with the value as obtained from measurements of heat capacity and the third law of thermodynamics. Here we shall present similar calorimetric data on hydrogen bromide and show, in this case, also, agreement between the two methods of obtaining the entropy.

Preparation of Hydrogen Bromide.—Hydrogen bromide was prepared directly from the elements. The hydrogen was prepared by electrolysis and the oxygen present

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[1] Giauque and Wiebe, THIS JOURNAL, 50, 101 (1928).

by diffusion was reduced to 0.01% by means of a nickel catalyst. Analysis of the bromine used showed no trace of chlorine or of iodine.

Dry hydrogen was bubbled through liquid bromine and the resulting mixture passed over a platinum spiral supported on a quartz rod and electrically heated to about 600–700°. The reaction tube was immersed in water which boiled during the procedure. To prevent excessive lowering of the vapor pressure of the liquid bromine due to cooling by evaporation, it was found desirable to immerse the mixing flask in warm water. The hydrogen bromide and unreacted bromine were condensed in a trap by means of liquid air. When enough material, approximately ten moles, had been prepared, the collection line was evacuated and most of the bromine separated by a rough distillation. The remaining bromine was easily removed by means of mercury, which had previously been condensed on the walls of a bulb. A small amount of mercury in the bottom of a bulb had previously proved to be rather slow in its action. The hydrogen bromide was then distilled into a bulb containing an amount of phosphorus pentoxide sufficiently large to bring it into intimate contact with all of the liquid. The material was dried for about one week, the liquid state being retained by means of a bath made from solid carbon dioxide and ether. Following this the material was distilled several times, the middle fractious being retained.

Heat Capacity Measurements and the Data.—The heat capacity determinations were made in gold calorimeter II. This calorimeter has been described in our previous paper[1] which also includes a description of the experimental method; 3.05 moles of hydrogen bromide were used for the measurements. The data are given in Table I. The first column gives the run number, which is included because the chronological order of the measurements is of interest in connection with the transition phenomena.

TABLE I

HEAT CAPACITY OF HYDROGEN BROMIDE

Molecular weight, 80.924

Run no.	T, °K	AT	C_p/mole in cal./deg.	Run no.	T, °K.	AT	C_p/mole in cal /deg.
20	15.72	2 097	1.831	15	95.12	4 214	9.90
21	17 81	1.692	2.160	16	98.71	4024	10.21
22	1975	2.039	2 615	17	103.09	4.497	10.79
23	22 32	3 002	3.010	18	107 44	4.155	11.52
24	2549	3.641	3 459	45	109.30	3.239	1186
25	30.16	4 704	3 955	19	11147	3806	1258
26	34 58	3 922	4 415	53	113 31	.124	135
27	39 15	4.836	4.827	54	113 37	.021	1290
28	43.75	4.266	5.160	55	114.13	1.365	19.32
29	48.32	4.578	5.453	56	115.76	1835	13.06
30	52 93	4.595	5 832	57	116.76	,132	239
31	57.80	4.978	6.171	58	116 86	.044	860
32	62 23	3.768	6.559	59	117.09	.394	74.1
1	65 67	4.718	6.877	46	118.99	3.344	10.79
4	6896	4.367	7.291	60	120.76	4643	10.80
2	70 68	5.086	7.460	47	122 71	3.966	10 86
5	73.63	4.683	7.951	61	125.48	4 488	10 93
3	75.60	4 473	8 323	48	127.31	4.555	10.99
6	50.03	3.882	9.368	62	130.06	4.383	10.96

TABLE I (*Concluded*)

Run no.	T, °K.	ΔT	C_p/mole in cal./deg.	Run no.	T, °K.	ΔT	C_p/mole in cal./deg.
7	8349	2.807	10.86	49	132.41	5.267	10.98
9	84.62	3.319	11.50	63	135 89	4 986	11.03
8	86.15	2.359	13.10	50	139.02	7.490	11.08
10	86.79	.907	13.55	64	140 26	4 807	11.10
33	87.20	.830	14.51	65	14561	5.437	11.19
11	87.69	.814	15.20	70	153 45	4 400	11.25
34	88.00	.741	16.36	71	158 03	4 252	11 40
35	88.68	.612	20.62	72	162 72	4 770	11.61
12	88.74	1.158	21.44	73	167 67	4.660	11 69
36	89.23	.446	29.08	74	172 86	4 466	11 91
38	89.39	.122	114	75	177.52	4.396	12.07
13	89.45	.241	190	76	18209	4.259	1232
37	89.49	.060	268		186 24 Melting point		
39	89.50	.029	483	66	189 93	5.330	14 20
40	89.53	.032	437	51	19094	4.366	14.25
41	89.59	.075	187	67	195 08	4.182	14.21
42	90.01	.702	17.02	52	195 59	4.206	14.33
43	90.91	1.091	9.87	68	19967	4.073	14.26
14	91.23	3.306	14.09	69	20511	4.035	14.31
44	92.01	1.076	9.87		206 38 Boiling point		

The data are also shown graphically in Fig. 1. The heat capacity of hydrogen bromide has previously been measured by Eucken and Karwat[2] and their data have been included in Fig. 1 for comparison. The disagreement between the two pieces of work is large and is very similar to the disagreement previously observed in the case of hydrogen chloride.[1]

Excepting certain measurements in the transition ranges which will be referred to later, most of our data are accurate to two or three tenths of one per cent. Runs 70, 71 and 72 may be somewhat in error due to heat effects associated with accidental distillation effects in the connecting tube of the calorimeter. Runs 66, 67, 68 and 69 on the liquid were made under poor conditions of vacuum around the calorimeter. This resulted from the presence of a small variable pressure of water vapor which reduced the accuracy of the heat interchange corrections. Below 20°K. the measurements may be in error by one per cent. This is largely due to the rapid decrease of the dR/dT of the gold thermometer in this region.

The Transitions of Hydrogen Bromide.—The three high maxima indicate gradual transitions of the type observed by Simon[3] in the case of ammonium chloride. The measurements of heat capacity within the transition range were of two types. Some were designed to have as high an accuracy as possible for use in obtaining the entropy of the substance. Others, made in order to obtain information about the character of the transitions, had a small temperature rise and were thus necessarily less

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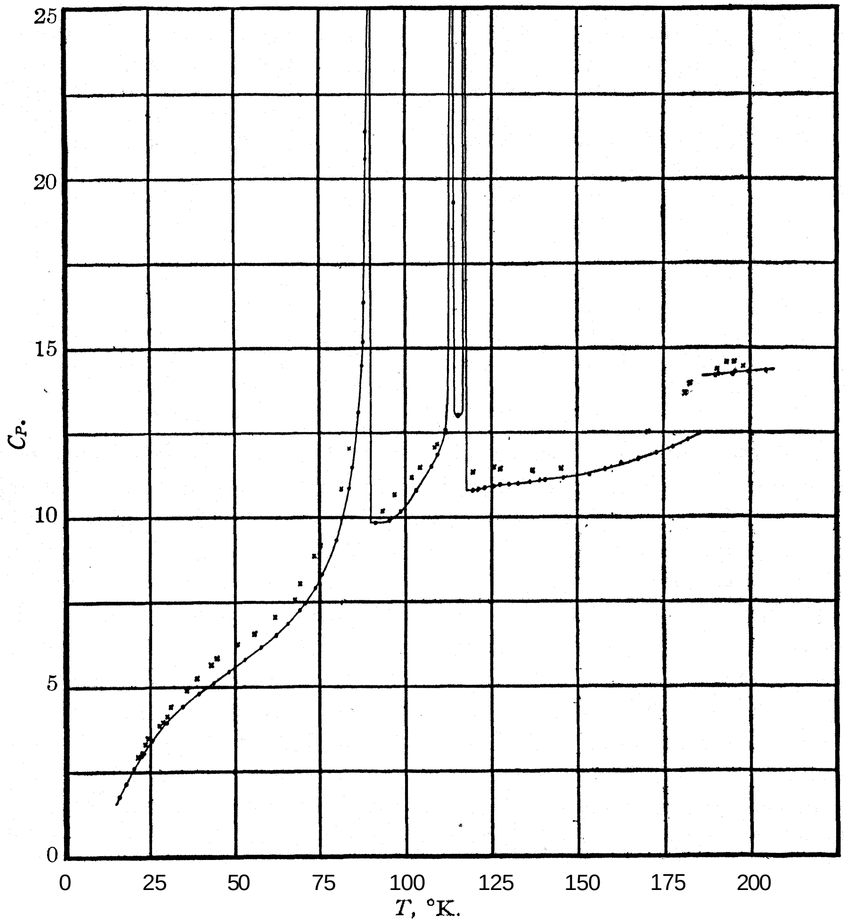
[2] Eucken and Karwat, *Z. physik. Chem.*, 112,467 (1924).

[3] Simon, *Ann. Physik.*, 68, 241 (1922).

accurate. The question of thermal equilibrium during measurement of such a transition naturally arises and we may say that while the process is one in which the measurements indicate that equilibrium is attained with difficulty, the evidence is against lack of equilibrium as a primary factor in preventing sharpness. For example, suppose that the transition is one that would occur sharply only if sufficient time were allowed. On cooling, a portion of the form stable at the higher temperature might fail to undergo the transition. When a sufficiently low temperature had been reached, the rate of approach to true equilibrium might easily become negligible. However, on heating to temperatures near to but below that of the true transition, it would be expected that a change



× Eucken and Karwat. ● **Giauque** and Wiebe.

Fig. 1.—Heat capacity in calories per mole of hydrogen bromide.

toward equilibrium would proceed with the evolution of heat, but this was not observed. It would be rather surprising if equilibrium could not be attained with sufficient rapidity to show a heat effect at temperatures within a degree or two of what might be called the transition temperature.

The two maxima near 115°K. were first noted by observing the rate of change of current with time while energy was being introduced. This was possible since the gold thermometer-heater used for introducing the energy increased in resistance as the temperature rose. The rate of change dropped to a small value at the first maximum, then increased and having maintained the increased rate for some time, it again decreased at the second maximum. These effects might result from unusual changes in thermal conductivity but the heat capacity measurements in this region eliminate that possibility. Measurements 55 and 56 between the two maxima cover a range of over three degrees of low heat capacity. It is probable that the molal heat capacity is lower than 13 cal. per degree, since the temperature rise in these two measurements was too large to give true differential values in this region.

It is difficult to decide whether the curve should be discontinuous on the high temperature side of the transitions. Measurements 55 and 59 supply little evidence on this question in the case of the two close maxima. However, measurements 41, 42 and 14 indicate a continuous drop in the case of the lower transition.

It may be noted from the run order during the transitions, particularly the lower transition, that the values fall on a smooth curve even when the measurements are taken in somewhat erratic order.

It seems plausible that such transitions may be due to internal changes in the molecular structure, as has been suggested by Simon and Simson,[4] who found, by x-ray analysis, that the similar behavior of ammonium chloride was not accompanied by a change in crystal form. Simon, Simson and Ruhemann[5] have found similar maxima in the heat capacities of the other ammonium halides.

Heats of Fusion and Transition.—The heat of fusion was found to be 575.1 cal. per mole. Eucken and Karwat[2] obtained 616 and 623. The discrepancy is about the same as was found in the case of hydrogen chloride.

It is not possible to obtain heats of transition in the ordinary sense. The amounts of energy added over the various regions of principal heat absorption are tabulated in Table II.

Purity **of** the Hydrogen Bromide.—The previously described method of preparation of the hydrogen bromide left very little possibility of appreciable impurity. It is, however, worth noting that the absence of pre-melting effect in the heat capacity measurements below the melting

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[4] Simon and Simson, *Naturwissenschaften,* 38,880 (1926).

[5] Simon, Simson and Ruhemann, Z. *physik. Chem.,* **129, 339 (1927).**

TABLE II

HEAT ABSORBED IN TRANSITION REGIONS OF HYDROGEN BROMIDE

Temp. intervals, °A.	**Heat** absorbed, cal /mole
87.37–92.19	124.7
87.39–93.21	133.5
110.97-120.38	256.3
112.35–117.25	204.3
112.39–114.86	93.3
115.04–118.31	122.1

point is the best evidence for the absence of an impurity which could affect the various measurements. This observation is especially important in that it eliminates the effect of impurity as an appreciable factor in the gradual transitions.

Melting and Boiling Point Temperatures.—The melting point was determined by introducing energy at intervals and waiting for equilibrium. Sufficient energy to melt about one-fourth of the substance at a time was added until fusion was complete. The material was then resolidified and the procedure repeated a week later. The first series covered a period of thirty hours, the second series twenty-four hours. The deviation between extremes was 0.06° on both the thermocouple and on the resistance thermometer. The average deviation from the mean was 0.02° on each. The melting point temperature was found to be 186.24 ± 0.05°K.

The measurements of pressure made in connection with the determination of the heat of vaporization gave the temperature of the boiling point as 206.38 ± 0.05°K.

A summary of the melting and boiling point temperatures obtained by various observers has been collected in Table III.

TABLE III

MELTING AND BOILING POINT TEMPERATURES OF HYDROGEN BROMIDE

Melting point, °K.	Boiling point, °K.	Observer
186	......	(1845) Faraday[6]
184.6	208.2 (738.2 mm.)	(1896) Estreicher[7]
186.9	205.0 (755.4 mm.)	(1900) Ladenburg and Krügel[8]
187	204.4	(1906) McIntosh and Steele[9]
...	203.0	(1910) Estreicher and Schnerr[10]
185.1	206.0	(1923) Henglein and Roth[11]
186.24±0.05	206.38±0.05	Giauque and Wiebe

Heat of Vaporization.—The heat of vaporization was determined by both Methods I and II as described for the hydrogen chloride measure-

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[6] Faraday, *Phil. Trans.*, 135, 161 (1845).

[7] Estreicher, *Z. physik. Chem.*, *20*, 605 (1896).

[8] Ladenburg and Krügel, *Ber.*, 33,637 (1900).

[9] McIntosh and Steele, *Z. physik. Chem.*, 55, 129 (1906).

[10] Estreicher and Schnerr, Bull. *inter. acad. sci. Cracovie, (A)*,345 (1910).

[11] Henglein and Roth, *Z. Physik*, 18.64 (1923).

ments.[1] In Method I, the evolution of hydrogen bromide from the calorimeter and energy input were measured simultaneously. In Method II, the total amount of material evaporated by the introduction of a definite amount of energy was measured. Most of the measurements were made in gold calorimeter I, which has not previously been described. It was practically identical with gold calorimeter II, except for a 0.5 mm. wall thickness. It was equipped with two thermocouples, one on the bottom and one in the middle of the side. A constantan heater wound on the lower half was used instead of the gold thermometer-heater later placed on gold calorimeter II. The data are given in Table IV.

TABLE IV

HEAT OF VAPORIZATION OF HYDROGEN BROMIDE

Boiling point, 206.38°K. Molecular weight, 80.924

HBr evap., moles	Type of run	Time of energy input, min.	AH at 760 mm. of Hg, cal./mole	HBr evap., moles	Type of run	Time of energy input, min.	AH at 760 mm. of Hg, cal./mole
Gold Calorimeter II				0.2977	I	75	4208
0.3218	I	75	4214	.2902	I	75	4211
.3143	II	75	4206	.2895	I	75	4207
.3125	II	75	4216	,2697	I	75	4207
,3087	II	75	4208	,2806	I	120	4206
Mean			4211 ± 4	.2804	I	120	4206
Gold Calorimeter I				2810	I	120	4208
.2987	I	75	4212	Mean			4209 ± 3
.2983	I	75	4218	Value selected			4210 ± 4
.2980	I	75	4205				

The values of the heat of vaporization obtained by various observers are given in Table V.

TABLE V

HEAT OF VAPORIZATION OF HYDROGEN BROMIDE

Heat of vaporization, cal./mole	Method	Observer
4160	Vapor pressure	(1906) McIntosh and Steele)[9]
4130	Direct	(1908) Elliott and McIntosh[12]
3939	Direct	(1910) Estreicher and Schnerr[10]
3953	Vapor pressure	Estreichcr and Schnerr
4405	Vapor pressure	(1923) Henglein and Roth[11]
4210 ± 4	Direct	Giauque and Wiebe

The value given by McIntosh and Steele is not corrected for gas imperfection. The vapor pressure value given by Estreicher and Schnerr is calculated from the data of McIntosh and Steele and includes a correction for gas imperfection. The value given by Henglein and Roth is uncorrected and would fall near our value if a reasonable correction were applied. The corresponding difference was 180 calories in the case of hydrogen chloride.

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[12] Elliott and McIntosh, J. Phys. Chem., 12, 163 (1908).

The Entropy of Hydrogen Bromide from the Third Law.—The entropy was calculated graphically by plotting heat capacity against the logarithm of temperature. The graphical method presented some difficulty in the transition ranges so the following procedure was used. The graph included all heat capacity up to sixteen calories per degree per mole. From the total heat input over the transition range and a plot of heat capacity against temperature, the energy represented by the area under each maximum and above 16 cal. per degree was calculated. The value of 16 cal. per degree was selected only for convenience. Since this energy was added over a narrow temperature range in each case, single temperatures could be chosen as divisors in order to obtain the respective entropy changes. The temperatures were chosen as a center of gravity on a $(C_p - 16)$ against T plot.

The temperatures and heats obtained are given in Table V. They are, of course, not to be taken as temperatures or heats of transition.

The extrapolation below 14.5°K. was carried out by means of the Debye function with an $h\gamma/k = 92$. The consideration of Einstein functions in addition seemed to offer little further advantage. The low temperature heat capacity measurements show a definite tendency to approach six calories per degree per mole as was the case with hydrogen chloride. This indicates that the molecules, having lost some of their degrees of freedom, are acting with sufficient approximation in the manner of a monatomic solid. Thus no great error would be expected in the extrapolated amount of one half entropy unit per mole.

The detail of the entropy calculation is given in Table VI.

TABLE VI

CALCULATION OF MOLAL ENTROPY OF HYDROGEN BROMIDE GAS

0–14.5°K., extrapolation	0.546	14.5–186.24°K., graphical	17.27
Transition 63.4/89.2	.711	Fusion 575.1/186.24	3.097
Transition 78.8/113.4	.695	Liquid	....
Transition 85.7/116.8	.734	186.24–206.38°K., graphical	1.464
"Transitions" are $\int(C_p-16)dT$	...	Vaporization 4210/206.38	20.40
		Entropy at the boiling point	44.9±0.1 E.U.

The critical pressure of hydrogen bromide has not been measured, which makes it difficult to determine the decrease in entropy due to the imperfection of the actual gas at its boiling point. However, the amount must be nearly the same as that for hydrogen chloride, which was estimated as 0.1 cal./deg. per mole. This value is very uncertain.

The Entropy of Hydrogen Bromide from Spectroscopic Data.—The entropy of hydrogen bromide may be calculated by combining the Sackur equation with the equation.

$$S_{R+V} = R\left[\ln \Sigma_m\Sigma_n p_{m,n}\, e^{-\frac{E_{m,n}}{kT}} + \frac{1}{kT}\,\frac{\Sigma_m\Sigma_n p_{m,n}\, E_{m,n}\, e^{-\frac{E_{m,n}}{kT}}}{\Sigma_m\Sigma_n p_{m,n}\, e^{-\frac{E_{m,n}}{kT}}}\right]_0^T$$

where S_{R+V} is the contribution made to the entropy by the rotation and vibration of the molecules. $E_{m,n}$ is the energy of the state having m and n as its rotation and vibration quantum numbers, respectively. While $p_{m,n}$ is the corresponding *a priori* probability of the state, $p_{m,n}$ was taken equal to $2m$. A full discussion of the above calculation may be found in connection with the similar calculation for hydrogen chloride.[1]

The values for the various energy levels of the hydrogen bromide molecule were obtained from the work of Czerny[13] on the pure rotation band of this substance and from the earlier work of Kratzer[14] on the first rotation-vibration band.

The value obtained for the entropy of the ideal gas at the temperature of the boiling point is 44.92 or 44.60 cal./deg. per mole, corresponding, respectively, to the use of the Tetrode or Lewis constant for the Sackur equation. The entropy has also been calculated for a temperature of 298.1°K. (25°C.). The results of the above calculations are compared with the third law values in Table VII.

TABLE VII

COMPARISON OF SPECTROSCOPIC AND THIRD LAW VALUES OF THE ENTROPY OF HYDROGEN BROMIDE

	Spectroscopic		Third law	
T, °K.	Tetrode constant	Lewis constant	Actual gas	Corrected to ideal state
206.38	44.92	44.60	44.9 ± 0.1	45.0
298.1	47.53	47.21	......	47.6

The third law value given at 298.1°K. was obtained by adding the spectroscopic difference between 206.38 and 298.1°K. to the 45.0 cal./deg. per mole obtained at 206.38°K.

The value for the chemical constant obtained in the paper of Eucken, Karwat and Fried[15] is given in terms of entropy in the German edition of Lewis and Randall[16] as $S_{\mathrm{HBr}} = 48.99 \pm 0.3$ E. U. at 298°K., which is 1.5 E. U. higher than the value obtained with the assistance of spectroscopic data.

Our measurements support the Tetrode rather than the Lewis constant for the Sackur equation. The close agreement supports the third law of thermodynamics.

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[13] Czerny, *Z. Physik*, 44, 235 (1927); 45, 476 (1927).

[14] Kratzer, *ibid.*, 3, 289 (1920).

[15] Eucken, Karwat and Fried, Z. *Physik*, 29, 1 (1924).

[16] "Thermodynamik und die freie Energie chemischer Substanzen," von Lewis und Randall, übersetzt von Redlich, Julius Springer, Wien, 1927.

Summary

The heat capacity of solid and liquid hydrogen bromide has been measured from 14.7 °K. to its boiling point.

Three regions of very high heat capacity were found in the solid state. These appear to be transitions of an internal molecular nature which do not occur at a definite temperature. The melting point is **186.24 ± 0.05° K.** The boiling point is **206.38** ± 0.05°K.

Calorimetric determinations of the heat of fusion and of the heat of vaporization have been made.

The entropy of hydrogen bromide has been calculated from the experimental data and the third law of thermodynamics.

The entropy due to the rotational-vibrational energy has been calculated from the energy levels of the molecule as obtained from band spectra. This amount added to the entropy as given by the Sackur equation with the Tetrode constant agrees with the value obtained from the third law thus supporting this law.

BERKELEY, CALIFORNIA

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

THE HEAT CAPACITY AND ENTROPY OF CESIUM ALUM FROM 18 TO 300° ABSOLUTE. THE ENTROPY OF ALUMINUM ION. THE POTENTIAL OF THE ALUMINUM ELECTRODE FROM THERMAL DATA

BY WENDELL M. LATIMER AND BERNARD S. GREENSPELDER

RECEIVED JUNE 19, 1928 PUBLISHED AUGUST 4, 1928

The direct measurement of the potential of the aluminum electrode is a task of singular difficulty. The literature[1] abounds in discordant results and contradictory explanations of their disparity. It has therefore seemed desirable to make an independent evaluation from thermal data with respect to the reaction

$$Al + 3H^+ = Al^{+++} + 3/2H_2$$

employing values for the entropies of aqueous ions in the manner developed by Latimer and Buffington.[2]

The heat of this reaction, AH, is known from the precise work of Richards

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[1] (a) **Buff,** *Ann.*, **102,265 (1857);** (b) Neumann, *Z. physik. Chem.*, **14,217 (1894);** **(c) Kahlenberg and Montgomery,** *Trans. Am. Electrochem. Soc.*, **36, 285 (1919); (d)** Kremann **and** Müller, *Z. Metallkunde*, **12, 289 (1920); (e) Heyrovsky, J.** *Chem. Soc.*, **117, 27 (1920);** (f) Müller **and** Hölz, *Z. anorg. Chem.*, **121, 103 (1921);** (g) **Dhar,** *Z. anorg. Chem.*, **119, 75 (1921); (h)** Smits **and Gerding,** *Z. Elektrochem.*, **31, 304 (1925);** (i) **de Gruyter,** *Rec. trav. chim.*, **44,937 (1925).**

[2] **(a)** Latimer **and Buffington,** THIS JOURNAL, **48, 2297 (1926); (b)** Latimer, **ibid., 48,2868 (1926); (c)** Latimer, **J.** *Phys. Chem.*, **31, 1267 (1927).**

and Burgess[3] on the heat of solution of aluminum in acid. Then in order to get the free energy, ΔF, and the electromotive force from the relation $\Delta F = -nEF = \Delta H - T\Delta S$, it is necessary to determine the entropy change, ΔS, for the reaction. The entropies of metallic aluminum and hydrogen gas are known and the experimental portion of this article consists in the determination of the entropy of Al^{+++} with respect to that of H^+. In order to accomplish this, the entropy, at 25°, of some aluminum salt and its entropy of solution must be measured. To permit an accurate evaluation of the free energy of solution, the salt must have a low solubility, must be capable of existing in stable equilibrium with its ions and should be definitely crystalline in character. An extended investigation indicated that no simple aluminum salt possessed such qualifications; amorphous modifications in metastable equilibrium with basic hydrates were predominant. However, the alkali metal alums, which have been thoroughly described in the literature, offered promise. Of these, the cesium alum, $CsAl(SO_4)_2 \cdot 12H_2O$, has the lowest solubility ($M/70$ at 25°). It is easily obtained in a high degree of purity, is stable at room temperature with respect to its full quota of water,[4] and has been the subject of several solubility determinations over a wide temperature range.

The following measurements were made: (1) the heat capacity of cesium alum from 18 to 300° K.; (2) the freezing points of solutions of cesium and rubidium alums; and **(3)** the heat of solution of cesium alum.

The values in (1) were employed to calculate the entropy by the relation $S_{298} = \int_0^{298} C_p d \ln T$. The freezing point data were necessary in order to calculate the free energy of solution from the solubility. This free energy combined with the experimental heat of solution (3) sufficed to give the entropy of the aqueous solution of the salt.

Heat Capacity and Entropy of Cesium Alum

Material.—C. P. cesium alum was obtained from Eimer and Amend, containing 37.98% of H_2O; theoretical, 38.05%. Pycnometer determinations gave $d_4^{20} = 1.978$. The reported values are 1.984,[5a] 1.911[5b] and 1.93–1.96.[5c]

Apparatus.—Considerable attention was given to the design of a vacuum calorimeter suitable for measuring the heat capacity of solids from the triple point of hydrogen to room temperature. The present apparatus is expected to be so employed in this Laboratory over a period of years and it was eminently desirable to unite mechanical durability with ease of manipulation and delicacy of control. The general disposition of the apparatus is similar to that of Latimer and Hoenshel,[6] but the dimensions have been approximately doubled. This change decreases the possibility of electrical or

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[3] Richards and Burgess, THIS JOURNAL, **32,** 1176 (1910).

[4] Ephraim and Wagner, *Ber.*, **50,** 1103 (1917).

[5] (a) Spring, Ber., 17,408 (1884); (b) Soret, *Compt. rend.*, 99,867 (1884); (c) Hart and Huselton, THIS JOURNAL, 36,2682 (1914).

[6] Latimer and Hoenshel, *ibid.*, 48, 19 (1926).

mechanical breakdown, increases the constancy of temperature control, accelerates evacuation by reason of the larger lead-in tubing, and facilitates assembly and take-down.

The more important newer characteristics are as follows (see Fig. 1). The calorimeter A of 115cc. capacity was wound with 300 turns of No. 40 D. S. C. gold wire (215 ohms at 25°). This wire was made by the Shreve Gold Products Company of San Francisco, from proof gold alloyed with 0.1% silver and drawn to No. 30 B. and S. gage through steel dies, washing with hot concentrated sulfuric acid after each draw. Diamond dies effected reduction to No. 40, and thorough annealing at 375° followed. This process is similar to that described by Giauque and Wiebe.[7] The entire winding gave a dR/dT of approximately 0.6 ohm/deg. from room temperature to 40°K. At 25° K. it fell to 0.4 and then rapidly diminished to 0.14 at 14°K.

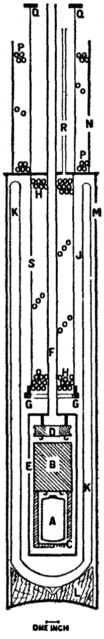

Fig. 1.

Manganin exhibits a nearly constant dR/dT at these lower temperatures, offering a means of eliminating the error introduced in estimating the mean dR/dT of the gold winding for a given ΔT in this region. The gold winding was therefore spaced at the center and $16^1/_2$ turns of No. 40 D. S. C. manganin (192 ohms at 25°) wound in the gap. The wire was further insulated from the calorimeter shell by a single layer of porous tissue paper saturated with bakelite lacquer and slowly baked to dryness, overheating being carefully avoided to prevent crackling. Exchange of thermal radiation was reduced by sheathing the calorimeter with 0.0005-inch gold foil.

For temperature calibration a copper–constantan thermocouple was located on the bottom of the calorimeter, the body of the junction entering a $^1/_{16}$-inch copper tube filled with Rose metal. For temperature control both the 4.6-kg. lead block B and the 1.4-kg. copper radiation shield C were equipped with resistance heaters proportioned to give an equal temperature rise at 80°K. The auxiliary lead block D was secured to the outer brass container E by three No. 10 brass machine screws. The evacuating tube F was of 0.75-inch Monel tubing 3.5 ft. long and carried the electrical leads. A vacuum of 10^{-6} mm. of mercury was maintained during the runs.

The built-in hydrogen liquefier consisted of a double-wound regenerative liquefying coil H, by-passed at the middle thirds, using 300 ft. of copper tubing (0.070 in. I. D., 0.125 in. O. D.). The superposed liquid air immersion pre-cooling coil P consisted of 40 ft. of copper tubing (0.125 in. I. D., 0.188 in. O. D.). Two special blow-out tubes were affixed thereto to clean out obstructions. Duplicate expansion valves G were provided, the valve stems extending to the hand wheels Q. The valves were connected by a circular 0.25-inch copper tube, designed to act as a trap for solid oxygen particles, thereby preventing plugging of the valve bore. The accumulated oxygen presents the hazard of electrostatic discharge due to crystal cleavage, igniting the hydrogen gas and solid oxygen. A recent explosion in one of the older liquefiers in this Laboratory might be so explained, although it is possible that the ignition was due to the sudden fracture of a circular steel tube leading to the valve. Copper is superior to steel under these conditions of repeated stress; its use offers a possible safeguard. Duplicate valves are advantageous; in case of "plugging" by solid oxygen or "freezing" by thermal contraction of the valve seat, the spare valve will as a rule be found free. Whether the accumulation of solid oxygen in the tube joining the valves is more likely to ignite than the constant stream of solid oxygen particles ejected through the valve at the beginning of liquefaction is most

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[7] Giuque and Wiebe, This Journal, 50,101 (1928).

uncertain, and indeed the amount, location and physical state of this troublesome impurity varies capriciously during each run. The hydrogen analyzed **0.03** ±0.01% of O_2 on leaving the compressor.

In operation, 3 or 4 liters of liquid hydrogen could be produced in two hours from a total circulation of 1270 cu. ft. of hydrogen gas at 1200 lb. pressure, sufficient to maintain a temperature below 18°K. for fourteen hours. The coil *H* was wrapped in a sheet S of Monel metal, this in turn being surrounded by a wool blanket in the space J. Thermal insulation was provided by the 36-inch Pyrex Dewar K, seated in a felt-lined wood block L. A vacuum-tight Monel can M served as container; when assembled the entire apparatus was lowered into a silk floss insulating case 4.5 ft. deep, 7 in. I. D., 14 in. O. D. Inlet and outlet tubes similar to the hydrogen return line R were provided for liquid air intake and blow-out, evacuation and outside control thermocouples. These are not shown for the sake of clarity.

All of the electrical measurements were made with the set-up described by Gibson and Giauque.[8]

Thermocouples.—Nine thermocouples measuring **305** cm. from ice to cold junction were made up of three parallel No. 30 D. S. C. constantan wires and one No. 36 D. S. C. copper. They were then calibrated against the laboratory standard couple No. 179 with Mr. R. T. Milner. All nine couples showed similar characteristics, the average deviation from the standard being +2.5 microvolts at 16° K., rapidly falling to +0.5 microvolt at 100° K. and maintaining such a value to room temperature. **A** couple designated as No. 109 was selected for its particularly uniform behavior and used as standard throughout the measurements. All temperatures are expressed in terms of the hydrogen thermometer.[9,10]

Operation of Calorimeter.—The specific heat measurements were made as follows. The block and radiation shield were adjusted to the mean temperature of the run; sufficient energy was then supplied over a period of several minutes (usually ten) to heat the calorimeter five or six degrees. The method of measurement and calculation was similar to that of Gibson and Giauque,[8] and included the smaller correction terms for apparent heat effect in the resistance thermometer winding described by Giauque and Wiebe.[11] Over half of the runs were timed with the automatic device described by Johnston[12] with an accuracy of 0.003 sec. The remainder were timed with a stop watch, the observer's error averaging ±0.2 sec.

Results.—The data are summarized in Table I.

The points fall on a smooth curve (Fig. 2) with an average deviation of less than 0.25%, excepting (1) those in the range 210–230° K., where water vapor adsorbed on the metallic surfaces of the apparatus always causes a temporary disturbance while being pumped off; and (2) the two measurements at the ice point, where the presence of 0.05 g. of uncombined water would completely account for the observed deviation from the smooth curve. The effect of this amount of water on the observed heat capacity at any other point is less than one-tenth the estimated experimental error. It is important to be aware of this phenomenon when investigating hydrated salts.

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

[9] Giauque, Buffington and Schulze, *ibid.*, 49, 2343 (1927).

[10] Giauque, Johnston and Kelley, *ibid.*, 49, 2367 (1927).

[11] Giauque and Wiebe, ibid., 50, 101 (1928).

[12] Johnston, to be published.

TABLE I

HEAT CAPACITY OF CESIUM ALUM

$CsAl(SO_4)_2 \cdot 12H_2O = 568.10$

T, °K.	Spec. ht. cal./g./-deg.	Molal ht. cap., cal./mole/-deg.	T, °K.	Spec. ht., cal./g./-deg.	Molal ht. cap., cal./mole/-deg.	T, °K.	Spec. ht., cal./g./-deg.	Molal ht. cap., cal./mole/-deg.
18.71	0.0129	7.35	94.20	0.1051	59.69	192.82	0.1882	106.91
21.26	.0146	8.29	99.62	.1098	62.38	198.19	.1925	109.36
23.70	.0214	12.16	104.61	.1150	65.33	205.72	.1955	111.08
27.23	.0244	13.84	109.24	.1189	67.54	210.20	.1980	113.47
30.25	.0291	16.50	113.61	.1254	71.24	215.83	.2091	118.81
31.31	.0308	17.49	117.80	.1270	72.14	221.86	.2124	120.69
32.65	.0329	18.68	122.52	.1323	75.13	227.88	.2122	120.56
36.13	.0379	21.53	127.68	.1363	77.42	233.78	.2208	125.44
39.77	.0434	24.68	132.57	.1379	78.36	239.29	.2247	127.67
44.17	.0494	28.05	137.90	.1428	81.13	245.25	.2275	129.22
48.60	.0546	31.03	143.63	.1488	84.54	251.62	.2321	131.88
52.87	.0606	34.40	149.03	.1518	86.23	257.77	.2356	133.86
57.71	.0663	37.64	154.17	.1569	89.12	263.77	.2409	136.83
62.68	.0721	40.93	159.43	.1603	91.06	(269.44)	(.2530)	(143.75)
67.57	.0780	44.31	164.62	.1642	93.28	(275.30)	(.2522)	(143.25)
72.63	.0834	47.35	169.46	.1684	95.68	281.30	.2521	143.24
75.88	.0868	49.28	176.26	.1745	99.15	286.73	.2544	144.50
80.07	.0912	51.80	181.56	.1796	102.04	292.42	.2578	146.45
84.84	.0956	54.30	187.12	.1840	104.54	297.84	.2586	146.91
89.26	.0996	56.58						

The entropy of cesium alum at 298° K. was found by plotting C_p against log T, multiplying the area under the curve by 2.3026 (Fig. 3).

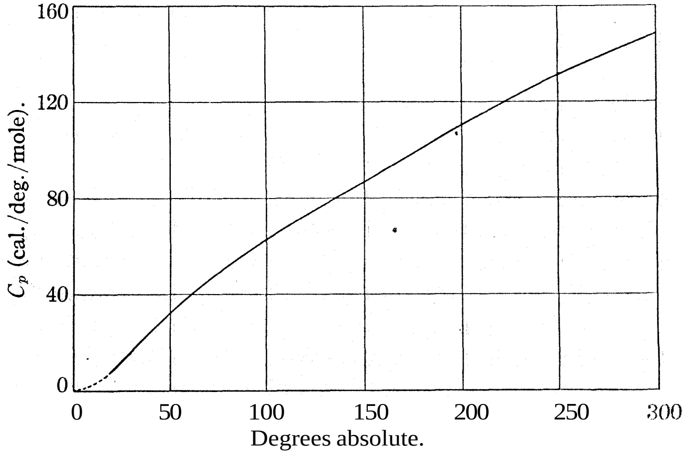

Fig. 2.—Molal heat capacity of cesium alum.

The curve was graphically extrapolated from the lowest measurement at 18.71 down to 10° K. A large scale plot was then drawn for this region and composite "Debye curves" were computed for the entropy due to Cs^+, Al^{+++}, $SO_4^=$ and $12H_2O$. The cesium alum curve was then extended parallel to the sum of the latter, giving the heat capacity to 3°. Below this point the Debye T^3 rule was assumed to be valid. These figures are summarized in Table II. The estimated accuracy is to within 0.5%.

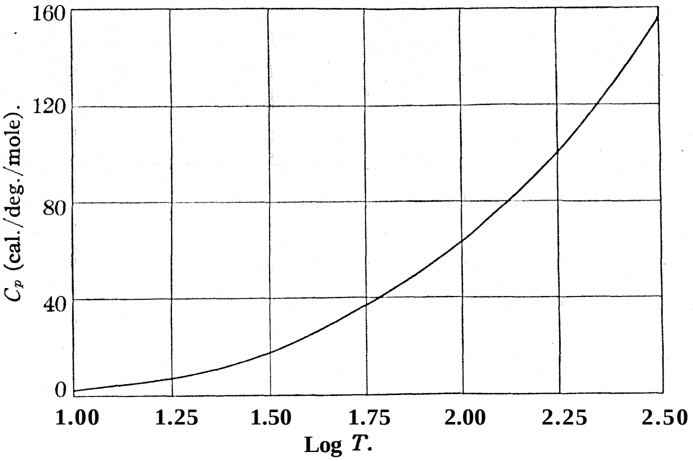

Fig. 3.—Molal entropy of cesium alum.

TABLE II

ENTROPY OF CESIUM ALUM

	T, °K.	E. U.
0–3	Debye T^3 Rule	0.067
3–10	Calcd. extrapolation	1.082
10–18	Graphical extrapolation	2.647
18–298.1	Graphical from data	160.051
		163.847

Entropy of cesium alum at 298.1° K. = 163.85 E. U.

Activity and Free Energy of Solution of Cesium Alum

The freezing point lowering of dilute solutions of cesium and rubidium alum was measured in the apparatus of Randall and Vanselow,[13] using the fifty junction thermo-element. In this way a temperature difference of 0.00005° could easily be observed. The measurements were carried out on a nearly saturated solution, gradually diluted over the desired range. The concentrations were determined by gravimetric analysis.

To evaluate the free energy of solution at 298.1°K., the activity of the aqueous salt must be determined for the corresponding concentration. The freezing points of dilute solutions of cesium alum were first measured, the results being shown in Fig. 4 and Table III. As a check both upon

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[13] Randall and Vanselow, THIS JOURNAL, 46, 2418 (1924).

the method and the behavior of cesium alum, a similar series of determinations was made on rubidium alum. The points fall smoothly on the same straight line within the limits of experimental error. The activity coefficient at the 25° saturation concentration is then obtained without extrapolation, since saturated rubidium alum at 0° has about the same molality as cesium alum at 25°.

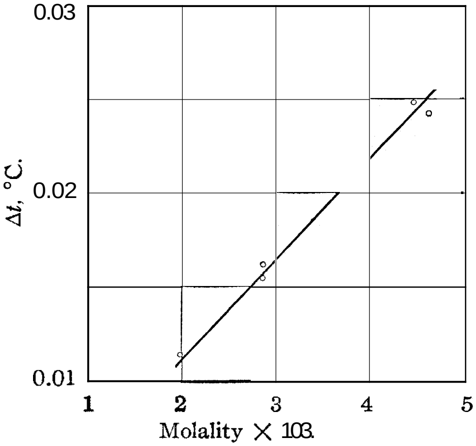
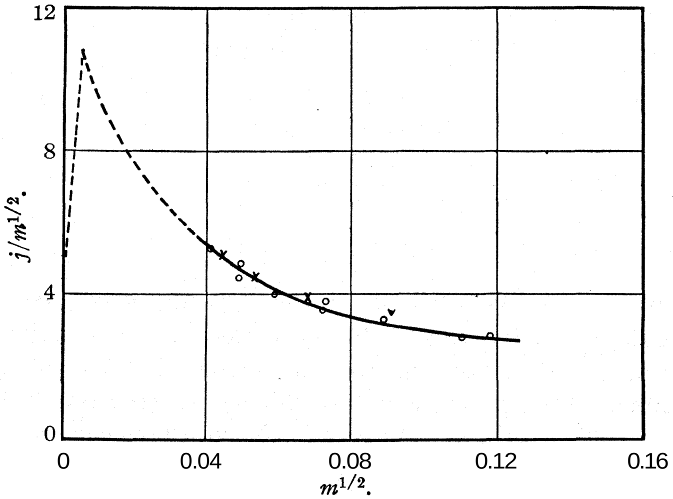


Fig. 4.—Freezing point lowering of cesium alum.

The activity coefficient was graphically calculated from the expression $\ln \gamma = -j - 2\int_0^m (j/m^{1/2})d(m^{1/2})$, which may be simply derived from the Duhem equation.[14] The limit, $j/m^{1/2} = 5.05$ when $m^{1/2} = 0$, was deduced from the Debye-Hückel theory; the segment of the curve between this point and that corresponding to the mast dilute solution capable of measurement was drawn in agreement with the best data available for comparable valence types, as shown in Fig. 5. The sharp maximum in



O Rubidium alum; X cesium alum.

Fig. 5.—Activity function.

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[14] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, 1923, p. 286.

this curve should, of course, be rounded off, but as the area difference is not large we have left it in this limiting form.

The activity coefficients so established are valid at 25° if the heat of dilution is negligible. Experimental verification was made by diluting 200 cc. of saturated solution at 25° to one-tenth its concentration. A Beckmann thermometer sensitive to 0.001° indicated no measurable temperature difference.

The results are shown in Table III. It may be noted that the freezing points are somewhat lower than those obtained for potassium alum and sodium alum by Jones and Mackay.[15] No definite interpretation can be made in view of the uncertainty of the values of these investigators. The values of γ for rubidium alum and cesium alum fall about 25% below the curve calculated from the table of individual ionic activities given by Lewis and Randall,[16] using their figures for Cs^+, Al^{+++} and SO_4^{--}. The two curves are nearly identical in shape; the numerical agreement is adequate, taking cognizance of the specific differences entering into any given combination of ions.

TABLE III

FREEZING POINT LOWERING

Cesium Alum Molality	Cesium Alum F. p. lowering, °C.	Rubidium Alum Molality	Rubidium Alum F. p. lowering, °C.
0.00456	0.0243	0.01236	0.0598
.00287	.0158	.00787	.0413
.00197	.0108	.00527	.0286
		,00343	.0198
		.00242	.0139
		.00170	.0099

Activity Coefficients for Rubidium and Cesium Alum

Molality	0.001	0.002	0.004	0.006	0.008	0.010	0.01167	0.01403	0.01690
γ	.462	.406	.353	.310	.276	.251	.233	.217	.200

The last three values of γ correspond to the saturated cesium alum at 20, 25 and 30°, respectively. An additional check was obtained from the experimental heat of solution (see below). Assuming a constant second derivative of the curve ln γm against $1/T$ between 20 and 30°, it is found that $\gamma\ 0.01690/\gamma\ 0.01167 = 0.84$; from Table III, $\gamma\ 0.01690/\text{-}\gamma\ 0.01167 = 0.86$.

The effect of the solute on the activity of the water, a twelfth-power factor, was calculated to be less than 25 cal./mole in terms of ΔF.

Heat of Solution of Cesium Alum.—Since it is a difficult matter to evaluate accurately ΔH of solution from the temperature solubility curve, even where activity corrections are applied, the direct experimental determination was carried out with Dr. F. D. Rossini in the accurately

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[15] Jones and **Mackay,** *Am. Chem.* J., **19,** 83 (1897).

[16] Ref. 14, p. 382.

calibrated apparatus described by Randall and Rossini.[17] It was found that $\Delta H_{298.1} = +13{,}560$ cal./mole, the estimated accuracy being ±25 cal./mole.

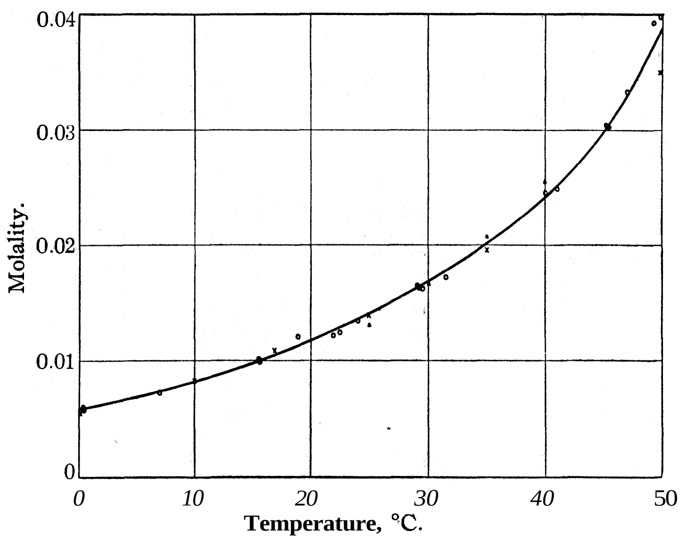
Entropy of Aluminum Ion

The entropy of aluminum ion may now be calculated. Writing the solubility reaction as

$$\mathrm{CsAl(SO_4)_2{\cdot}12H_2O = Cs^+ + Al^{+++} + 2SO_4^{--} + 12H_2O}$$

$\Delta F^\circ_{298.1} = -\mathrm{RT\ ln\ K} = -1363.7 \log 4(\gamma m)^4 = -5454.8 \log (1.4142)(0.217)(0.01403) = +12{,}910$ cal./mole.

The solubility, m, of cesium alum[18] has been accurately determined by Berkeley and confirmed by others, as illustrated by Fig. 6.



Berkeley; ○ Hart and Huselton; △ Locke; × Setterberg.

Fig. 6.—Solubility of cesium alum.

Then employing our experimental value for the heat of solution, $\Delta H_{298.1} = +13{,}560$ cal./mole, we obtain for the entropy of solution

$$\Delta S^\circ_{298.1} = \frac{\Delta H - \Delta F}{T} = +2.18 \text{ E. U.}$$

We may now write for the entropy of $\mathrm{Al^{+++}}$

$$S_{\mathrm{Al^{+++}}} = \Delta S_{(\mathrm{sol})} + S_{\mathrm{Cs\ alum\ (solid)}} - 12S_{\mathrm{H_2O\ (liq)}} - 2S_{\mathrm{SO_4^{--}}} - S_{\mathrm{Cs^+}}$$

The first two terms on the right have been obtained above. The entropy of H_2O has been computed from the specific heat of ice given from 9 to

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[17] Randall and Rossini, *to be published.*

[18] (a) Berkeley, *Trans. Roy. Soc. London,* **203A,** 189 (1904); (b) Setterberg, *Ann.,* **211,** 100 (1882); (c) Locke, *Am. Chem. J.,* **26,** 180 (1901); (d) Hart and Huselton, THIS JOURNAL, **36,** 2082 (1914).

273.1°K. by Simon[19] in a tabulation in advance of formal publication. His measurements at the ice point show the influence of pre-melting. The extraordinarily precise data of Dickinson and Osborne[20] is used in this range. At lower temperatures the two series coincide exactly. Callendar's work[21] on the specific heat of water has been used for the range 0–25°.

The Simon curve compares favorably up to 210°K. with that derived from the earlier work of Nernst and of Pollitzer.[22] The value of Dickinson and Osborne is used for the heat of fusion, $\Delta H = 1436.6$ cal./mole. The calculation of the entropy of water at 298.1°K. follows in Table IV.

TABLE IV

ENTROPY OF WATER

	E. U.
0–10°K. Debye T^3 Rule	0.02
10–273.1 Graphical	9.06
Entropy of fusion, 1436.6/273.1	5.26
273.1–298.1 Graphical	1.58
$S°_{298.1}$ =	15.92 ±0.02 E. U.

For the entropy of sulfate and cesium ions we have 9 and 27.9, respectively. The sulfate value is from the paper by Latimer and Buffington[2"] and that for cesium is calculated from the expression deduced by these authors relating the entropy of solution of gas ions and the ionic radius. Although this expression is empirical, the excellent agreement shown by the other alkali metal ions warrants confidence in its accuracy.

Substituting these values in the equation given above, we find for the entropy of Al^{+++} at 298.1°K. in a hypothetical one-molal solution, $S_{Al^{+++}298.1} = -70.9$ cal./deg./mole.

Potential of the Aluminum Electrode

The entropies of $^1/_2H_2$ and Al, as calculated by Lewis, Gibson and Latimer,[23] are 14.7 and 6.82, respectively. The recent work of Cornish and Eastman[24] changes the hydrogen value to 14.6. Using our value for the entropy of aluminum ion, we find for the reaction,

$$Al + 3H^+ = Al^{+++} + 3/2H_2;\quad AS = -70.9 + 43.8 - 6.8 = -33.9 \text{cal./deg.}$$

AN° from the work of Richards and Burgess[3] is −127.0 k. cal., whence $\Delta F°_{298} = \Delta H°_{298} - T\Delta S°_{298} = -116{,}900$ cal./mole and $E° = -\Delta F/NF = 116{,}900/(3 \times 23{,}074) = +1.69$ v.

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[19] Simon, "Handbuch der Physik," Julius Springer, Berlin, **1926**, Vol. X, p. 363.

[20] Dickinson and Osborne, *U. S. Bur. Stand. Sci. Papers*, 248, **1915**.

[21] Callendar, *Proc. Roy. Soc. London*, **86A**, 254 (1912).

[22] (a) Nernst, *Sitzb. preuss. Akad. Wiss.*, 1910, 262; (b) Pollitzer, *Z. Elektrochem.*, 19,513 (1913).

[23] Lewis, Gibson and Latimer, THIS JOURNAL, 44, 1008 (1922).

[24] Cornish and Eastman, *ibid.*, 50, 627 (1928).

Discussion of Results

The probable error is rather difficult to estimate. The electrode potential changes about 0.01 volt per 700 cal. change in ΔF, and we believe the free energy is known with this accuracy. The largest uncertainty appears to exist in the extrapolation of the freezing point data to obtain the activity coefficient. The largest numerical quantity is evidently the heat of solution of aluminum metal in acid. For Richards' determination, —127.0 k. cal., with hydrochloric acid in 200 moles of water a correction might be made for the heat of dilution, but this is certainly much less than other errors involved in the determination. Richards' value, -126.0 k. cal., for a more concentrated solution, that is, for $HCl \cdot 20H_2O$ is substantiated by the work of Biltz and Hohorst,[25] who give 125.1 k. cal. for $HCl \cdot 8.8H_2O$.

Among the direct determinations of the aluminum electrode, that of Heyrovsky[26] appears to be the most reliable. He employed the electrode sat. Al amalg. || X *m* $AlCl_3$, and obtained the value $+1.337$ volts, which he believed corresponded to the reaction, $Al + 3H_2O = Al(OH)_3 + 3/2H_2$. This could be checked against our value if the solubility product of aluminum hydroxide were accurately known. For this quantity we find 4×10^{-18} by Remy and Kuhlmann[27] and 10^{-33} by Heyrovsky.[28] Whence we may write

		Volts
$Al + 3H_2O$	$= Al(OH)_3 + 3/2H_2$	1.337
$Al(OH)_3$	$= Al^{+++} + 3OH^-$	-0.344 or -0.650
$3H^+ + 3OH^-$	$= 3H_2O$	0.828
$Al + 3H^+$	$= Al^{+++} + 3/2H_2$	$+1.821$ or $+1.515$

Our value, $+1.69$ volts, falls as a close mean.

The free energy of the reaction $Al + 3H_2O = Al(OH)_3 + 3/2H_2$, has been calculated by Drossbach[29] from the reaction heats and entropies, and agrees with the potential found by Heyrovsky.

A correction, estimated from the data of Denham[30] as \$0.004 volt, might be applied on the assumption of hydrolysis to $Al(OH)^{++}$. However, the stoichiometrical hydrolysis may be considered as due to the distributed polarization of the water molecules, and it then would be as unsuitable to attempt to specify an appropriate equilibrium constant as it is to define a dissociation constant for a strong electrolyte. For this reason no correction has been made and the hydrolysis effect is thus included in the standard state of hypothetical unit molal aluminum ion which corresponds to the experimental activities.

[25] Biltz and Hohorst, *Z. anorg. allgem. Chem.*, 121, 18 (1922).

[26] Heyrovsky, *J. Chem. Soc.*, 117, 27 (1920).

[27] Remy and Kuhlmann, *Z. and. Chem.*, 65, 167 (1924).

[28] Heyrovsky, *J. Chem. Soc.*, 117, 11 (1920).

[29] Drossbach, *Z. Elektrochem.*, 33, 114 (1927).

[30] Denham, *J. Chem. Soc.*, 93, 41 (1908).

The authors wish to express their appreciation of the helpful suggestions of Professor W. F. Giauque pertaining to the specific heat measurements, the skilful execution of the mechanical design by Mr. G. F. Nelson, the work on the heat of solution of cesium alum by Dr. F. D. Rossini, and the laboratory assistance of Mr. J. E. Ahlberg.

Summary

The heat capacity of cesium alum, $CsAl(SO_4)_2 \cdot 12H_2O$, has been measured from 18 to 300°K.; the molal entropy at 298.1°K. is computed to be 163.8 cal./deg.

The activity of dilute solutions of rubidium and cesium alums has been determined from freezing point measurements.

The entropy ($H^+ = 0$) of Al^{+++} in hypothetical 1 M solution at 298.1°K. has been determined as −70.9 cal./deg./mole.

The electrode potential at 298.1°K. of aluminum, $Al = Al^{+++} + 3E^-$, has been calculated from thermal data to be +1.69 ± 0.01 volts.

BERKELEY, CALIBORNIA

[CONTRIBUTION FROM SEVERANCE CHEMICAL LABORATORY OF OBERLIN COLLEGE]

THE TRANSITION TEMPERATURE OF CARBON TETRACHLORIDE AS A FIXED POINT IN THERMOMETRY

BY JAMES C. MCCULLOUGH AND HARRIS E. PHIPPS[1]

RECEIVED JUNE 22, 1928 PUBLISHED AUGUST 4, 1928

An enantiotropic or reversible transition has been discovered when carbon tetrachloride is cooled below its freezing point. This solid–solid transition is a change from the cubic to the monoclinic system and takes place at −48.54 ± 0.02°. The hold in the time–temperature curve (Fig. 1) is of approximately the same duration as that at the freezing point. With proper precautions the transition temperature is as constant as the freezing temperature. Since the freezing point of carbon tetrachloride is given as a fixed point in thermometry,[2] the transition point should be equally valuable. The purification of one substance would thus serve to fix two points on the thermometer scale, saving the purification of *a* second material, such as chlorobenzene.

No reference has been found in the literature indicating that more than one solid form of carbon tetrachloride has been known at atmospheric pressure. Tammann,[3] working with high pressures, at one time believed that he had found three solid forms. Later, in "Kristallisieren und Schmel-

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[1] This paper represents part of the work done by Mr. Phipps in meeting the requirements for the degree of Master of Arts.

[2] (a) "International Critical Tables," Vol. I, p. 54; (b) Timmermans and Martin, *J. chim. phys.*, **23**, 747–787 (1926).

[3] Tammann, "Kristallisieren und Schmelzen," E. Barth, Leipzig, 1903, p. 222.

zen," he retracted his former statements, and explained the irregularities which he had observed when carbon tetrachloride solidified at various temperatures and pressures by assuming the existence of two polymorphic forms. Bridgman,[4] using very high pressures, found three solid forms of carbon tetrachloride. Extension of his curves indicates that the second form should exist below − 48° with one atmosphere pressure. In this connection Bridgman says: "It should be possible to realize the phase II at atmospheric pressure at low enough temperatures. Such an attempt was made by cooling CCl_4 in carbon dioxide snow to − 80°, but the depression of temperature was not sufficient to overcome the viscous resistance to the reaction." There are two possible explanations as to why Bridgman did not observe the solid–solid transition: (1) he may have failed to identify it and (2) the solid may have supercooled. If the third phase recorded by Bridgman exists at atmospheric pressure, the transition temperature would probably be close to absolute zero.

The transition was first observed by us with a polarizing microscope equipped with a cold stage. Samples of carbon tetrachloride from three different sources were examined. Each exhibited the same behavior. The first crystal form is cubic, as is well known. The form existing below —48.54' appears to be monoclinic, for it exhibited a biaxial interference figure and both parallel and oblique extinction with polarized light.

Apparatus

The apparatus used in measuring the transition temperature consisted of two large test-tubes, made from heavy walled Pyrex tubing, one of which slipped inside the other. These were then placed in a one-quart thermos bottle of the wide-mouthed type which was filled with solid carbon dioxide and ether. A four-terminal, compensated lead, platinum resistance thermometer and Mueller type bridge, made by the Leeds and Northrup Company were used for the major portion of the work. This pyrometer was calibrated at the sulfur boiling point by the method of Mueller and Burgess,[5] at the steam and ice points, and at the sublimation point of solid carbon dioxide.[6] Since no information could be found regarding the calibration at the sublimation point of solid carbon dioxide, the technique is here given in detail.

The solid carbon dioxide was purchased from the Dry-Ice Corporation in the usual form of a dense cube about ten inches on an edge. The resistance thermometer was placed in a one-quart thermos bottle of the wide-mouthed type which was filled with small pieces of solid carbon dioxide. The bottle was closed with a cork which fitted the thermometer loosely. The cork had a second hole about 4 mm. in diameter so as to ensure atmospheric pressure without undue circulation of air. Equilibrium was reached in about two hours. The readings could be checked by this method. The temperature of the solid carbon dioxide in the thermos bottle was also measured by a pentane thermometer which had been calibrated at −40° and other temperatures by the U. S. Bureau of Standards. The value obtained with this thermometer agreed with the published value for carbon dioxide in the solid state, as given in the "International

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[4] Bridgman, Phys. *Rev.*, (2) **3, 126–141, 153–203** (1914).

[5] Mueller and Burgess, *Bureau of Standards Scientific Paper,* **339.**

[6] Ref. 2 a, p. **53.**

Critical Tables."[6] It was first thought that the sublimation temperature of the solid carbon dioxide could best be obtained by placing the thermometer in a deep hole drilled in the cake of Dry-Ice. This was done and after equilibrium was established, which took about seventeen hours, a temperature of −97° was obtained. It appears that this must be due to the escape of carbon dioxide gas and the rapid sublimation of the solid. If the solid carbon dioxide were not in equilibrium with its vapor, the temperature at the surface of the block would naturally fall. This point was tested by placing some pieces of solid carbon dioxide in a thermos bottle and rapidly drawing off the carbon dioxide gas by means of a suction tube extending nearly to the bottom of the bottle. A temperature of −102° has been obtained by this method and further study of it is under way.

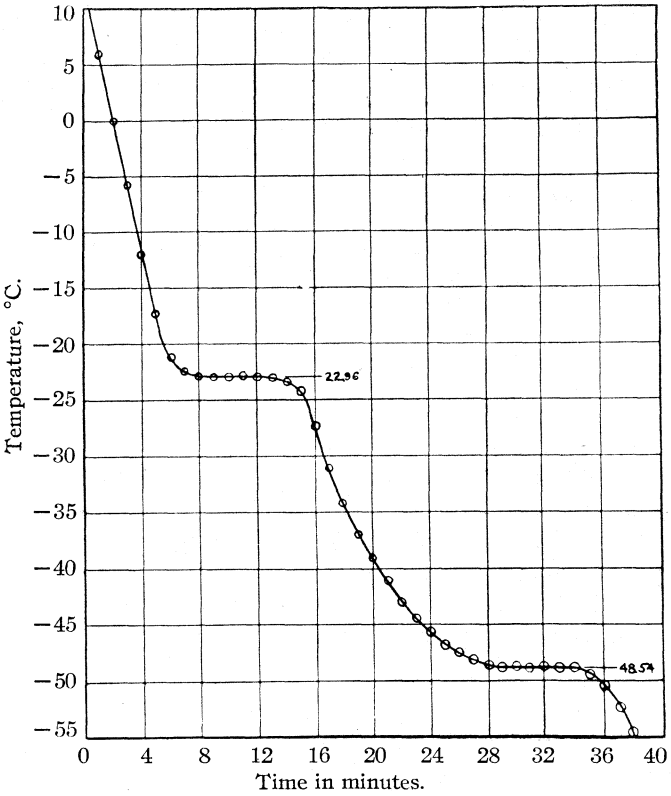

Fig. 1.—Enantiotropic transition of carbon tetrachloride. E. K Co., 444-A.

Procedure and Results

Time–temperature curves were made by cooling various samples of carbon tetrachloride, some of which were purified by fractional distillation. A Young pear-head fractionating column was used and the temperature of the condensing vapor was taken with a mercury thermometer calibrated by the U. S. Bureau of Standards. The boiling point was calculated to atmospheric pressure (760 mm.) by the method of Smith and Menzies.[7] When freezing, the liquid carbon tetrachloride was vigorously stirred until it was nearly all in the solid state. After it had all solidified and the temperature was again falling, the tube containing the solid carbon tetrachloride was occasionally removed from the freezing bath and gently tapped. When this was done the temperature was fairly constant even with an impure sample. The temperatures recorded in the table below are the average temperatures obtained, plus or minus the fluctuations observed during the hold. The platinum resistance thermometer was accurate to 0.006'.

TABLE I

BOILING, FREEZING AND TRANSITION POINTS OF CARBON TETRACHLORIDE

Thermometer	Sample of CCl_4	B. p., °C.	F. p., °C.	Transition point, °C.
Resistance	444	....	−22.946±0.008	−48.563±0.006
	444	....	−22.967±0.01	−48.551±0.007
Pentane	444	....	−22.97	−48.5
Resistance	444-A	76.8	−22.968±0.005	−48.541±0.005
	444-B	76.8	−22.973±0.006	−48.531±0.008
	444-C	76.8–77.3	−22.889±0.02	−48.395±0.02
	P.W.R.	....	−23.225±0.3	−48.925±0.3
	P.W.R.-A.	76.6–76.8	−23.14±0.2	−48.71±0.3
Pentane	P.W.R.-A.	76.6–76.8	−23.0 to −23.2	−48.7 to −48.9
	Stock		−22.9 to −23.5	−48.6 to −49.2

Sample 444 was obtained from the Eastman Kodak Company and is listed as E. K. Co. 444 carbon tetrachloride; 444-B was a sample obtained by fractional distillation; 444-C was a small amount of the higher boiling fraction; 444-A was obtained in the same way as 444-B but a more efficient pear-head fractionating column was used. The P.W.R. was a sample of the Powers-Weightman-Rosengarten Company product marked purified. The sample marked stock was a cheap commercial grade.

Summary

The results obtained show quite definitely that carbon tetrachloride has a solid–solid transition. The change from the cubic to the monoclinic system takes place at −48.54 * 0.02 when pure material is used. It is suggested as a fixed point in thermometry, since the hold is as constant and as fixed as the freezing point which is given as a fixed point in "International Critical Tables" and elsewhere.

OBERLIN, OHIO

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[7] Smith and Menzies, THIS JOURNAL, 32, 907 (1910).

NOTE

A Simplified Method of Differential Potentiometric Titration.—The excellent differential method of MacInnes and Jones[1] requires the use of a glass device of a certain complexity for temporarily withholding from reaction a small portion of the titrated solution while at the same time electrolytic contact is maintained between this portion and the remainder. The construction of this apparatus becomes unnecessary if the following modification is used. The electrodes may be two identical wires, one (A) enclosed in a dropper or syringe of the form shown in the figure, the other (B) wound around the stem of the dropper. B may be thrust through the rim of the bulb to hold it in place.

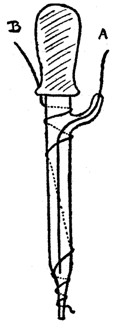

Fig. 1.—Double electrode for differential potentiometric titration.

Simply by squeezing the bulb a small part of the liquid is withdrawn and caused to surround the inner electrode, while electrolytic contact is maintained through the capillary tip. After the measurement, repeated squeezing of the bulb causes rapid mixing of the entire liquid. The method has been tested by students both in neutralization and oxidation reactions with entirely satisfactory results, the curves of $\Delta E/\Delta V$ against the percentage titration showing extremely sharp maxima when the reaction was of suitable type. The double maxima reported by MacInnes and Jones have also been observed. The apparatus may, of course, be used with a galvanometer and high resistance instead of a potentiometer and is extremely cheap and easy to prepare. Even an ordinary medicine dropper, with the inner electrode wire thrust directly through the rubber bulb, is quite satisfactory for temporary use.

CONTRIBUTION FROM THE
CHEMICAL LABORATORY OF
HARVARD UNIVERSITY
CAMBRIDGE, MASSACHUSETTS

NORRIS F. HALL
MARK A. JENSEN
SVEN A. BAECKSTRÖM

RECEIVED MAY 23, 1928
PUBLISHED AUGUST 4, 1928

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[1] MacInnes and Jones, THIS JOURNAL, 48, 2831–2836 (1926).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF STANFORD UNIVERSITY]

BENZYLIDENE ANILINE AND BENZYLIDENE PARA-TOLUIDINE AS AMMONO ALDEHYDE-ACETALS

BY HAROLD H. STRAIN

RECEIVED MARCH 7, 1928 PUBLISHED AUGUST 4, 1928

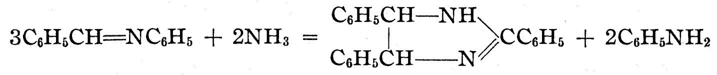
Introduction

According to the views of Franklin and his co-workers, the Schiff's bases are aldehyde-acetals of an ammonia system of compounds.[1] Moreover benzylidene aniline and benzylidene *p*-toluidine, typical aromatic Schiff's bases, are known to form addition compounds with hydrocyanic acid[2] and with Grignard reagents[3] which are analogous to the familiar addition products formed from aquo aldehydes and these same reagents. Benzylidene aniline is also reduced by nascent hydrogen to a secondary amine[4] which is a primary ammono alcohol.

As ammono aldehyde-acetals the aromatic Schiff's bases should be expected to undergo the Cannizzaro reaction and the benzoin condensation. These ammono compounds should also be nitridized to ammono acids and ammonolyzed to ammono aldehydes and ammono alcohols.

The reactions outlined in the previous paragraph have all been found to take place. In addition, a reaction resulting in the formation of a possible polymerized ammono aldehyde-acetal has been observed.

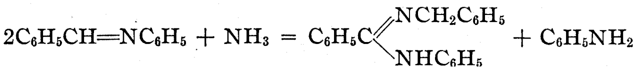
Ammonolysis.—When benzylidene aniline is ammonolyzed, amarine and aniline are the reaction products.



$$3C_6H_5CH{=}NC_6H_5 + 2NH_3 = \begin{array}{l} C_6H_5CH{-}NH \\ \quad | \\ C_6H_5CH{-}N \end{array}\!\!\!>\!CC_6H_5 + 2C_6H_5NH_2$$

The benzylidene imine which one should expect to find as a product of the reaction must condense to form amarine, a reaction known to take place.[5] Benzylidene *p*-toluidine is ammonolyzed to amarine and *p*-toluidine.

Cannizzaro Reaction.—The Cannizzaro reaction of the ammono aldehyde-acetals takes place readily when these compounds are treated with an excess of an ammono base. In this reaction, however, the ammono acids and the ammono alcohols which are formed are found in the form of ammono esters; namely, benzylphenylbenzamidine and benzyl-*p*-tolylbenzamidine.[6]



$$2C_6H_5CH{=}NC_6H_5 + NH_3 = C_6H_5C\begin{array}{l} {\nearrow}NCH_2C_6H_5 \\ {\searrow}NHC_6H_5 \end{array} + C_6H_5NH_2$$

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[1] Franklin, *Am. Chem. J.*, **47**, 285 (1912); *Proc. Eighth Int. Cong. Appl. Chem.*, *6*, 119 (1912); THIS JOURNAL, **46**, 2137 (1924); Strain, *ibid.*, 49, 1559 (1927).

[2] Cech, *Ber.*, 11, 246 (1878).

[3] Busch and Rinck, *Ber.*, **38**, 1764 (1905).

[4] Schiff, *Ann. Suppl.*, **3**, 354 (1864).

[5] Strain, THIS JOURNAL, 49, 1566 (1927).

[6] The formation of benzylyhenylbenzamidinc can perhaps be best explained by

Benzoin Condensation.—When treated with an alkaline cyanide in liquid ammonia the ammono aldehyde-acetals undergo the benzoin condensation forming ammono benzoin-acetals; namely, benzoin-anil-anilide and benzoin-*p*-tolyl-*p*-toluide.[7] This reaction, which is analogous to the benzoin condensation of aquo aldehydes, is illustrated by the following parallel equations

$$2C_6H_5CH{=}O \quad = \quad \begin{array}{l} C_6H_5CH{-}OH \\ \quad | \\ C_6H_5C{=}O \end{array}$$

(aquo aldehyde) (aquo benzoin)

$$2C_6H_5CH{=}NC_6H_5 \quad = \quad \begin{array}{l} C_6H_5CH{-}NHC_6H_5 \\ \quad | \\ C_6H_5C{=}NC_6H_5 \end{array}$$

(ammono aldehyde-acetal) (ammono benzoin-acetal)

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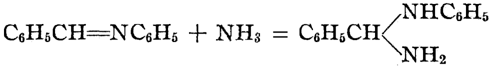
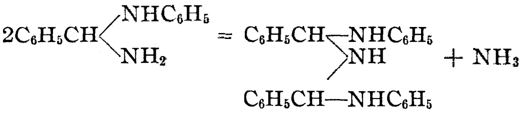
the following series of equations



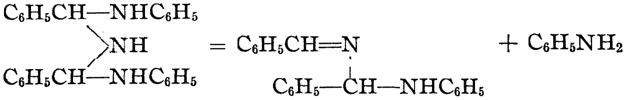
$$C_6H_5CH{=}NC_6H_5 + NH_3 = C_6H_5CH\begin{cases} NHC_6H_5 \\ NH_2 \end{cases}$$

(ammono aldehyde-acetal) (ammono acetal)



$$2C_6H_5CH\begin{cases} NHC_6H_5 \\ NH_2 \end{cases} = \begin{array}{l} C_6H_5CH{-}NHC_6H_5 \\ \qquad \rangle NH \\ C_6H_5CH{-}NHC_6H_5 \end{array} + NH_3$$

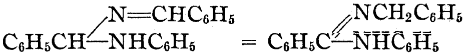
(ammono acetal) (ammono acetal)



$$\begin{array}{l} C_6H_5CH{-}NHC_6H_5 \\ \qquad \rangle NH \\ C_6H_5CH{-}NHC_6H_5 \end{array} = \begin{array}{l} C_6H_5CH{=}N \\ \qquad\quad | \\ C_6H_5{-}CH{-}NHC_6H_5 \end{array} + C_6H_5NH_2$$

(ammono acetal) (ammono aldehyde-acetal)

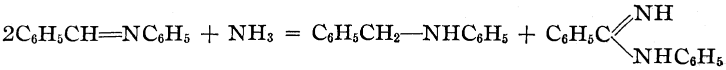
The ammono aldehyde-acetal last written may undergo intramolecular oxidation and reduction, the aldehyde group being reduced to an ammono alcohol, the acetal group being nitridized (oxidized) to an ammono acid. This reaction, obviously an example of the Cannizzaro reaction, is shown herewith.



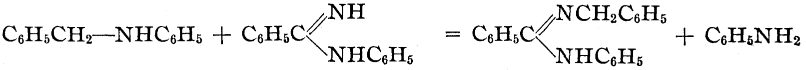
$$C_6H_5CH\begin{cases} N{=}CHC_6H_5 \\ NHC_6H_5 \end{cases} = C_6H_5C\begin{cases} {=}NCH_2C_6H_5 \\ NHC_6H_5 \end{cases}$$

(ammono aldehyde-acetal) (ammono acid-ester)

The formation of benzylphenylbenzamidine from benzylidene aniline can also be explained by assuming the Cannizzaro reaction to take place before the ester formation, as follows



$$2C_6H_5CH{=}NC_6H_5 + NH_3 = C_6H_5CH_2{-}NHC_6H_5 + C_6H_5C\begin{cases} {=}NH \\ NHC_6H_5 \end{cases}$$



$$C_6H_5CH_2{-}NHC_6H_5 + C_6H_5C\begin{cases} {=}NH \\ NHC_6H_5 \end{cases} = C_6H_5C\begin{cases} {=}NCH_2C_6H_5 \\ NHC_6H_5 \end{cases} + C_6H_5NH_2$$

It is interesting to note that these reactions take place in accordance with the theories proposed by Lachman [THIS JOURNAL, 45, 2356 (1923)] who observed the aquo ester benzylbenzoate as an intermediate product when benzaldehyde undergoes intermolecular oxidation and reduction.

[7] Evidence will be presented in a following paper to show that these compounds undergo a number of reactions which substantiate the view that they are related to ammonia as the familiar benzoin and acetals are related to water.

Nitridation.—Benzylidene aniline is nitridized with difficulty with the result that tar-like decomposition products are formed along with small quantities of benzonitrile (benzoic anammonide).

Polymerization.—When treated with small quantities of alkali in liquid ammonia the ammono aldehyde-acetals form polymerized compounds whose structure has not been definitely established. The proposed formulas will therefore be described in the experimental part.

Experimental

Ammonolysis.—The ammonolysis reaction was carried out by allowing the ammono aldehyde-acetals to stand in liquid ammonia solution for thirty to thirty-five days. The ammonia was then evaporated and the residue extracted with alcohol which was then diluted with water, whereupon an oil separated. The clear liquid was then decanted from the oily layer, the latter was dissolved in a little concentrated hydrochloric acid, the solution diluted with an equal volume of water and cooled. When crystals ceased to form, the mixture was filtered and the crystals removed to a flask, where they were boiled with alcoholic ammonium hydroxide until a clear solution was obtained. Upon cooling and diluting this solution with water, large crystals of amarine were obtained. The identity of the crystals was established by a mixed melting point. The yields varied from 60 to 91% of the theoretical. The aniline and p-toluidine were identified in the respective filtrates.

It was also found that the ammonolysis reaction could be completed in ten to fourteen hours by heating the ammono aldehyde-acetals with liquid ammonia in the presence of ammonium chloride to a temperature of 120–150°.[8]

Cannizzaro Reaction.—Benzylidene aniline, or benzylidene p-toluidine, was treated with two or more molecular equivalents of potassium amide in liquid ammonia solution at room temperature. A considerable quantity of heat was evolved, indicated by the vigorous boiling of the solution, and a deep blue color was produced. This color disappeared upon the addition of more of the respective ammono aldehyde-acetal and reappeared upon the further addition of potassium amide. The reaction products could not be induced to crystallize from this dark blue solution even when the latter was concentrated and cooled to −35°. The ammonia was, therefore, allowed to escape, when a flaky blue residue was obtained. This material was dissolved in hot 95% alcohol (the blue color immediately disappeared) and the alcoholic solution then diluted with water until a slight turbidity appeared. Upon cooling, the solution was found to deposit beautiful, colorless, needle-shaped crystals of benzylphenylbenzamidine, or benzyl-p-tolylbenzamidine. A considerable quantity of aniline or *p*-toluidine was always found in the mother liquor. The yield of the ammono acid esters usually amounted to 60% of the weight of the ammono aldehyde-acetals used in the reaction.

The benzylphenylbenzamidine melted at 99–100° and when mixed with benzylphenylbenzamidine prepared by the action of phosphorus pentachloride and aniline on benzanilide[9] the mixture melted at 99–100°.

The crystals were analyzed and their molecular weight was determined in benzene solution by the cryoscopic method.

Anal. Calcd. for $C_{20}H_{18}N_2$: C, 83.9; H, 6.3; N, 9.8. Found: C, 83.8, 83.6; H, 6.7, 6.6; N, 9.8, 9.7. Mol. wt. Calcd. for $C_{20}H_{18}N_2$: 286. Found: 271, 282.

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[8] For method of heating, see Blair, THIS JOURNAL, **48,** 87 (1926).

[9] (a) Beckmann and Fellrath, *Ann.,* 273, 9 (1893); (b) Pechmann and Heinze, *Ber..* 30, 1787 (1897).

In order to make more certain of the structure of the benzylphenylbenzamidine, the benzenesulfonyl derivative was prepared by treating some finely pulverized crystals with benzenesulfonylchloride and alkali. The white, crystalline derivative thus obtained was insoluble in alkalies and melted at 148°. It was analyzed by the method of Carius.

And. Calcd. for $C_{26}H_{22}O_2N_2S$: S, 7.5. Found: S, 7.1.

The benzyl-*p*-tolylbenzamidine prepared from benzylidene p-toluidine melted at 127–127.5°. The molecular weight in benzene solution was determined by the cryoscopic method.

Mol. wt. Calcd. for $C_{21}H_{20}N_2$: 300. Found: 294,259. *Anal.* Calcd. for $C_{21}H_{20}N_2$: C, 84.0; H, 6.7; N, 9.3. Found: C, 83.9, 84.1; H, 7.0, 6.9; N, 9.1, 8.9.

Since benzyl-p-tolylbenzamidine was not known it seemed advisable to prepare this compound in order to compare it with the material obtained by the Cannizzaro reaction. The synthesis was accomplished by heating benz-p-toluide with phosphorus pentachloride and benzylamine. The crystals thus obtained melted at 127° and when mixed with those obtained from benzylidene *p*-toluidine, the mixture melted at 127°. The two preparations appeared to be identical in crystalline form and solubility, being insoluble in water, moderately soluble in alcohol and acetone, and readily soluble in ether and benzene.

Benzoin Condensation.—From 3 to *5* g. of ammono aldehyde-acetal and ***0.5*** to 1.0 g. of freshly pulverized potassium cyanide were dissolved in about ***20*** cc. of liquid ammonia and the clear solution was allowed to stand at room temperature. After several hours a heavy, viscous liquid separated from the solution. Twenty-four hours later a few crystals had formed in this liquid, but due to its high viscosity the growth of the crystals was retarded to such an extent that it seemed best to repeat the experiment, using the crystals first formed to seed the reaction product before any large quantity of the viscous material could be formed. Accordingly, the crystals were drained of the mother liquor and uncrystallized oil, dried and transferred to a freshly prepared solution of the aldehyde-acetal and potassium cyanide in liquid ammonia. After standing for several hours the solution was found to be filled with crystals.

The crystals formed from benzylidene aniline were hexagonal yellow prisms having a greenish fluorescence. These crystals were washed, dried and analyzed.[10]

Anal. Calcd. for $C_{26}H_{22}N_2$: C, 86.2; H, 6.1; N, 7.7. Found: C, 85.9, 85.9; H, 6.2, 6.2; N, 7.5. *Mol. wt.* (Benzene). Calcd. for $C_{26}H_{22}N_2$: 362. Found: 321, 331.

The yellow crystals of benzoin-anil-anilide are insoluble in water, moderately soluble in boiling alcohol and very soluble in hot benzene and toluene, from which they may be recrystallized. When heated these crystals begin to soften at 185° but do not melt completely until a temperature of 200° is reached. At a higher temperature the benzoin-anil-anilide distils with only slight decomposition.

The ammono benzoin obtained from benzylidene p-toluidine is slightly soluble in liquid ammonia, separating as a clear, colorless, viscous liquid or as colorless crystals. It is moderately soluble in hot alcohol and crystallizes from a concentrated solution in

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[10] It is interesting to note at this time that Schiff reported a compound having the empirical formula $C_{26}H_{22}N_2$ which he obtained by heating benzylidene aniline in a sealed tube [*Ann.* Suppl., **3**, 354 (1864); *Ann.*, **148**, 336 (1868)]. However, Voigt, [*J. prakt.* Chem., ***[2]*** **31**, 544 (1885); [2] 34, *2* (1886)] and v. Miller and Plöchl ***[Ber.,*** 25, ***2020*** (1892)], and the writer were unable to duplicate Schiff's results. In attempting to prepare benzoin-anil-anilide by the action of aniline on benzoin, Lachowicz [*Monatsh.*, 15, 402 (1894)], found that benzoin-anil was the sole product of the reaction, the ammonolysis failing to go to completion.

beautiful colorless prisms. After recrystallization this compound was found to melt at 122°.[11]

Anal. Calcd. for $C_{28}H_{26}N_2$: C, 86.2; H, 6.7. Found: C, 86.2, 86.3; H, 6.8, 6.8.

Nitridation.—Benzylidene aniline (1 g.) in solution in liquid ammonia was treated with an excess of iodine and the temperature of the solution maintained at 0° until the iodine color had completely disappeared (eight hours). During this time a considerable quantity of nitrogen was evolved while the solution became quite dark in color. Upon evaporation of the ammonia, a dark, tarry mass was obtained which smelled strongly of phenylisocyanide. Neither benzamidine or phenylbenzamidine could be detected in the aqueous and dilute acid extracts of the residue. From the ether extract a few drops of an oily liquid which smelled strongly of benzonitrile were obtained; boiling point of benzonitrile, 191°; found, 180°.

Polymer from Benzylidene Aniline.—After standing in a solution of potassium amide in liquid ammonia containing less than one molecular equivalent of potassium amide, benzylidene aniline is converted into a very soluble material which is best obtained by evaporating the ammonia and recrystallizing the residue from alcohol. The time necessary for this reaction varies from five to fifteen days. The yields vary between 10 and 60% of the weight of benzylidene aniline used.

The crystals obtained from alcohol grow very slowly and take the form of prisms. They melt at 132–134°. After digestion with dilute alcoholic potassium hydroxide, the crystals melt at 136°, but upon recrystallization from alcohol they melt again at 132–134°.

This new substance is insoluble in acids, alkalies and water, but is moderately soluble in benzene and toluene. It is only slowly attacked by aqueous hydrochloric acid at the boiling temperature, a blue-green coloring matter being produced. Ammono hypoiodous acid failed to nitridize the material in liquid ammonia solution.

When treated with an excess of potassium amide, 0.4 g. of the unknown crystals produced 0.3 g. of phenylbenzylbenzamidine and when heated with a solution of ammonium chloride in liquid ammonia the crystals gave rise to another compound which melted at 168° and which has not as yet been identified.

The composition and the molecular weight of the crystals melting at 132–134° were determined, the latter in benzene solution by the cryoscopic method.

Anal. Calcd. for $C_{33}H_{29}N_3$: C, 84.8; H, 6.2; N, 9.0. Found: C, 85.1, 85.0, 85.1; H, 6.5, 6.2, 6.5; N, 8.6, 8.6. *Mol.* wt. Calcd. for $C_{33}H_{29}N_3$: 467. Found: 418, 438.

When this compound obtained by the action of potassium amide on benzylidene aniline is treated with alcoholic hydrochloric acid, it forms a soluble hydrochloride which separates as a white, finely crystalline mass when the solution is diluted with water. Upon heating this hydrochloride with ammonium hydroxide, the original base is regenerated. Two preparations of the hydrochloride were made.

Anal. Calcd for $C_{33}H_{29}N_3 \cdot HCl$: Cl, 7.1. Found: Cl, 6.9, 7.4.

Polymerization of three molecules of benzylidene aniline to a six membered heterocyclic ring with the subsequent elimination of one molecule of aniline by ammonolysis would yield a compound whose hydrochloride would have the formula $C_{33}H_{29}N_3 \cdot HCl$.

Polymer from Benzylidene *p*-Toluidine.—When treated with potassium amide,

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[11] Schiff [*Ann.*, 140, 96 (1866)] reported a compound having the formula $C_{28}H_{26}N_2$ and melting at 120–125°, which he obtained by heating benzylidene p-toluidine in a sealed tube at 180° for twenty-four hours. However, v. Miller and Plochl [*Ber.*, 25, 2020 (1892)] and, more recently, the writer were unable to duplicate Schiff's results. Nevertheless, the melting point of Schiff's compound agrees fairly well with that of the ammono benzoin obtained as a result of the benzoin condensation in liquid ammonia.

as just described above for benzylidene aniline, benzylidene *p*-toluidine forms a compound which melts at 136–137° when recrystallized from alcohol. The crystals thus obtained are much more difficult to purify than those obtained from benzylidene aniline. Furthermore, they are very easily converted into benzyl *p*-tolylbenzamidine, this reaction taking place when less than one molecular equivalent of potassium amide is present in the ammonia solution.

Anal. Calcd. for $C_{35}H_{33}N_3$: **C,** 84.8; **H, 6.7.** Found: C, 84.6, 84.3; H, 6.7, 6.3. *Mol. wt.* Calcd. for $C_{35}H_{33}N_3$: **495.** Found: **399,401.**

It is with the greatest pleasure that the writer takes this opportunity to express his thanks to Dr. E. C. Franklin for the care which he exercised in directing the experimental work and in reading this manuscript.

Summary

Experimental evidence has been presented to show that the aromatic Schiff's bases, benzylidene aniline and benzylidene *p*-toluidine, are aldehyde-acetals of the ammonia system of compounds.

The ammonolysis of ammono aldehyde-acetals has been accomplished.

Benzylphenylbenzamidine and benzyl-p-tolylbenzamidine have been prepared by the Cannizzaro reaction.

Benzoin-anil-anilide and benzoin-*p*-tolyl-*p*-toluide have been prepared by the benzoin condensation.

STANFORD UNIVERSITY, CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OR IOWA STATE COLLEGE]

THE REACTION BETWEEN ORGANOMAGNESIUM HALIDES AND ALKYL SULFONATES

BY HENRY GILMAN AND LLOYD L. HECK

RECEIVED MARCH 7, 1928 PUBLISHED AUGUST 4, 1928

Introduction

Alkyl esters of sulfonic acids differ from aryl esters of sulfonic acids in their reaction with organomagnesium halides. With alkyl esters, alkylation takes place, and this reaction has generally been formulated as follows[1]

$$2RSO_2O\text{–Alkyl} + 2R'MgX \longrightarrow 2R'\text{–Alkyl} + (RSO_2O)_2Mg + MgX_2 \qquad (1)$$

With aryl esters, sulfones and phenols are formed, as follows

$$RSO_2\text{–OAryl} + R'MgX \longrightarrow RSO_2R' + \text{ArylOMgX} \qquad (2)$$

When molecular equivalents of alkyl sulfonate and Grignard reagent are used, according to Reaction 1, the yield of alkylation product does not generally exceed 50%.[2] This prompted a further investigation of the

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[1] Gilman, Robinson and Beaber, THIS JOURNAL, 48, **2715 (1926).** References to earlier studies are contained in this paper.

[2] Gilman and Beaber, *ibid.*, **47,518 (1925).** The only exception to the **18** alkylation reactions reported by them was in the reaction between benzyl *p*-toluenesulfonate and benzylmagnesium chloride. In this case a 55% yield of dibenzyl was obtained, but it is quite probable that part of this high yield is due to some dibenzyl that is generally

reaction. The results described here show that Reaction 1 is only partly correct. In addition to the alkylation product an alkyl halide is formed, the alkyl group coming from the ester and the halogen from the Grignard reagent.

The following reactions are proposed to account for the formation of these compounds.

$$\mathrm{RSO_2O\text{-}Alkyl + R'MgX \longrightarrow R'\text{-}Alkyl + RSO_2OMgX} \qquad (3)$$

$$\mathrm{RSO_2OMgX + RSO_2O\text{-}Alkyl \longrightarrow Alkyl\,X + (RSO_2O)_2Mg} \qquad (4)$$

In strict accordance with these reactions the yield of alkylation product should be increased when two moles of alkyl sulfonate are used with one mole of Grignard reagent. This is supported by experiment. Also it has been shown that when two moles of ester are used for one of RMgX compound, the R-Alkyl and RX compounds are formed in essentially equivalent quantities. It is obvious that after some RSO_2OMgX has been formed according to Reaction **3,** this salt would react with ester to give the RX compound according to Reaction 4 even when equivalent molecular quantities of ester and Grignard reagent are used. This, too, has been found to be the case.

The correctness of Reaction 4 has been established by treating anhydrous @-naphthalenesulfonic acid with methylmagnesium iodide to form β-$C_{10}H_7SO_2OMgI$, and then treating this salt with n-butyl *p*-toluenesulfonate to form n-butyl iodide and magnesium β-naphthalenesulfonate, as follows

$$\beta\text{-}\mathrm{C_{10}H_7SO_2OH + CH_3MgI \longrightarrow} \beta\text{-}\mathrm{C_{10}H_7SO_2OMgI + CH4} \qquad (5)$$

$$\beta\text{-}\mathrm{C_{10}H_7SO_2OMgI} + p\text{-}\mathrm{CH_3C_6H_4SO_2OC_4H_9}\,(n) \longrightarrow n\text{-}\mathrm{C_4H_9I} + (\beta\text{-}\mathrm{C_{10}H_7SO_2O})_2\mathrm{Mg} \qquad (6)$$

Kenyon, Phillips and Turley[3] obtained ethyl a-bromopropionate and not ethyl a-phenylpropionate (as might have been expected in accordance with Reaction 1) when the *p*-toluenesulfonic ester of optically active ethyl lactate was treated with phenylmagnesium bromide. Also, Rossander and Marvel,[4] in a study of the lengthening of carbon chains by three carbon atoms wherein y-chloropropyl *p*-toluenesulfonate was treated with various RMgX compounds, obtained not only the normal reaction[5] leading to the introduction of the chloropropyl group but also the dihalide formed from the γ-chloropropyl group and the halogen of the Grignard reagent.

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formed in significant quantities in the preparation of benzylmagnesium chloride. Two other yields in excess of 50% have been reported by Gilman and Beaber with halogen alkyl sulfonates, ibid., **45,** 839 (1923). The high yields obtained with dialkyl sulfates may be due to the presence of two alkyl groups in these esters in contrast with the one alkyl group in alkyl p-toluenesulfonates.

[3] Kenyon, Phillips and Turley, J. *Chem. Soc.,* 127, 399 (1925). They also obtained ethyl a-bromopropionate from the lactyl ester and ethylmagnesium bromide. With ethoxymagnesium iodide (C_2H_5OMgI) and the lactyl ester they got ethyl a-iodopropionate. No other products from these three reactions were reported by them.

[4] Rossander and Marvel, THIS JOURNAL, **50,** 1491 (1928).

[5] Gilman and Beaber, *ibid.,* **45,** 839 (1923).

In some of their reactions where one mole of ester was used with one mole of Grignard reagent, they obtained significant quantities of the hydrocarbon that would be expected from the hydrolysis of the RMgX compound. An explanation for the formation of these hydrocarbons is to be found in Reactions 3 and 4. From these reactions it will be noted that the ester is competing for the RMgX and the RSO_2OMgX compounds, and inasmuch as these reactions probably take place concurrently (R-alkyl and RX are both formed from one mole of ester and one mole of RMgX) some of the RMgX compound will remain unused. This unused Grignard reagent would then give the corresponding hydrocarbon when the reaction mixture is subsequently hydrolyzed in the course of working up the reaction products.

In connection with the formation of hydrocarbon when equimolecular proportions of ester and Grignard reagents are used,[6] it is possible to formulate other reactions to account for the alkylation product and the alkyl halide. Kenyon, Phillips and Turley, and Holmberg[7] have proposed the following reaction to account for the formation of the ethyl a-bromopropionate

$$RSO_2O\text{–Alkyl} + R'MgX \longrightarrow \text{Alkyl X} + RSO_2OMgR'. \qquad (7)$$

Unless this reaction is peculiar to the lactyl ester of *p*-toluenesulfonic acid, and there is no reason at present to believe so in view of the several diverse alkylations that have been reported,[2] it should account for general alkylations involving the Grignard reagent. Their scheme of Reaction (7) accounts for the formation of alkyl halide; it can also explain the formation of hydrocarbon observed in some cases by Rossander and Marvel[4,6]; but it offers no satisfactory explanation for the alkylation action that is so common with alkyl sulfonates. It can account for the formation of hydrocarbon, because the RSO_2OMgR' compound postulated there has the highly reactive $-MgR'$ group that should show many, if not all, of the reactions of RMgX compounds. Hydrolysis of it, for example, should yield the hydrocarbon R'H.

A series of reactions has been proposed,[4] independently of the formulation just considered, to account for all of the products so far obtained in the reaction between alkyl sulfonates and RMgX compounds. This scheme admits Reaction 3 to account for a part of the alkylation; it admits Reaction 7 to account for the alkyl halide, and then with Reaction 7 as a basis it accounts for the formation of the remainder of the alkylation product and the hydrocarbon by the following reactions that assume the intermediate formation of RSO_2OMgR'

$$RSO_2O\text{–Alkyl} + RSO_2OMgR' \longrightarrow R'\text{–Alkyl} + (RSO_2O)_2Mg \qquad (8)$$

$$RSO_2OMgR' + HOH \longrightarrow R'H + RSO_2OMgOH \qquad (9)$$

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[6] When Marvel and Rossander (ref. 4) used two moles of ester with one of Grignard reagent they isolated a hydrocarbon in only one experiment.

[7] Holmberg, ***Ber.***, 59, 1560 (1926).

Admittedly this series of Reactions (3, 7, 8 and 9) offers not only an explanation for all of the products so far observed, but also accounts for the improvement of yield in the alkylation reaction when two moles of ester are used for one mole of Grignard reagent. There are, however, some objections to such a scheme of reactions. First, it calls for a manner of scission of the RMgX molecule that is unusual. Grignard reactions generally have been explained as involving, at some stage, a scission or dissociation of the molecule to give R– and –MgX and not RMg– and –X. Second, Reactions 7, 8 and 9 postulate a compound (RSO_2OMgR') which is unknown, so that it is impossible at present to verify these three reactions by the use of the RSO_2OMgR' compound about which all three reactions turn. Over and against such a proposal that has no confirmation in experiment is Reaction 4, which has found support in experiment. Reactions 3 and 4 account for (1) alkylation, (2) alkyl halide, (3) magnesium sulfonate, (4) hydrocarbon corresponding to the RMgX when insufficient ester is used and (5) the improvement in alkylation yield noted when an excess of ester is used.

The alkyl halides formed in accordance with Reaction 4 may also be prepared from the alkyl sulfonate when the –MgX group is attached to practically all elements, and not only to carbon as in the Grignard reagent. This was shown when n-butyl halides were obtained from n-butyl *p*-toluenesulfonate and ethoxymagnesium iodide (C_2H_5OMgI), phenoxymagnesium iodide (C_6H_5OMgI), *p*-tolylsulfinylmagnesium bromide (*p*-$CH_3C_6H_4S(=O)OMgBr$), methylanilinomagnesiumbromide (C_6H_5N-(CH_3)-$MgBr$), thiophenylmagnesium iodide (C_6H_5SMgI), magnesium iodide and magnesium bromide.

The formation of RX from the alkyl sulfonate and the magnesium halides is of more than passing interest. Some magnesium halide is formed in the ordinary preparation of all Grignard reagents, but the extent of this side reaction is altogether too slight to account for the high yield of RX compound obtained in the several experiments with alkyl sulfonates. Of much greater significance is its bearing on the constitution of the Grignard reagents. Very recently a renewed interest has been shown in Jolibois'[8a] formula for oganomagnesium halides. He suggested that RMgX compounds are really magnesium dialkyls or diaryls with magnesium halide, and that the correct formulation is $R_2Mg + MgX_2$ instead of RMgX. For our present purposes it is of no great significance whether we ascribe

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[8] (a) Jolibois, *Compt. rend.*, 155, 353 (1912); 183, 971 (1926); (b) Kierzek, *Bull. soc. chim.*, *41*, 1299 (1927); (c) Grignard, *Compt. vend.*, 185, 507 (1927); Terentiev, *Z. anorg. allgem. Chem.*, 156, 73 (1926); Job, *Bull. soc. chim.*, *39*, 583 (1926); Ivanoff, *Compt. rend.*, 185, 505 (1927). Meisenheimer and Schlichenmaier, *Ber.*, 61, 720 (1928), have just reported on the molecular weight and the constitution of the Grignard reagent. In dilute solutions the organomagnesium halides are apparently monomolecular and therefore best represented as RMgX and not as $R_2Mg + MgX_2$.

to the Grignard reagents the "mixed molecule" formula or whether we designate this complex as being in equilibrium with the RMgX form.

$$2RMgX \rightleftharpoons R_2Mg + MgX_2 \qquad (10)$$

Gilman and Schulze[9] have shown that the following equilibrium under certain conditions exists between beryllium dialkyls and alkylberyllium halides.

$$2RBe \rightleftharpoons R_2Be + BeX_2 \qquad (11)$$

In this connection it is interesting to note that other inorganic halides have split alkyl sulfonates to give alkyl halides. Kenyon, Phillips and Turley,[3] for example, used lithium chloride, sodium bromide and potassium iodide with their lactyl sulfonate to get the corresponding ethyl α-halogenopropionates. Further studies[10] of the chemistry of R_2Mg compounds should throw more light on this problem.

The formation of sulfones (Reaction 2) is not restricted to aryl esters of sulfonic acids. n-Butyl *p*-toluenesulfonate and phenylmagnesium bromide gave, in addition to large amounts of normal products that would be expected from Reactions 1, **3** and 4, a small quantity of phenyl *p*-tolyl sulfone. A corresponding reaction was reported some years before by Ferns and Lapworth,[1] and Strecker,[1] who showed that ethyl ethanesulfonate and phenylmagnesium bromide underwent reactions in accordance with 1 and 2.

Experimental

In general, stock solutions of the appropriate Grignard reagent in ether were used. These solutions were filtered free of any unused magnesium and aliquots[11] and were slowly added to the ester until a positive color test[12] was obtained. In a few cases the ester was added to the Grignard reagent, but no essential differences were noted. After refluxing for one to two hours, the mixture was hydrolyzed by iced acid. The ether layer, after washing with water, was steam distilled in order to effect a more ready separation of alkyl halide and hydrocarbon from any unused ester. All of the alkyl halides were identified by conversion to the alkylmercuric halides,[13] and these in turn were identified by a mixed melting point determination made with authentic specimens.

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[9] Gilman and Schulze, *J. Chem. Soc.*, **131**, 2663 (1927); THIS JOURNAL, 49, 2904 (1927). In the latter reference (p. 2907) attention is directed to the possibility of the same equilibrium with RMgX compounds. The same idea has been suggested by Grignard (see ref. 8*c* of this paper).

[10] Gilman and Schulze, THIS JOURNAL, 49, 2328 (1927). This paper reports a study of the reaction between magnesium diethyl and acetyl chloride.

[11] The yields of Grignard reagent were assumed to be those determined by Gilman and McCracken, *ibid.*, 45, 2462 (1923).

[12] Gilman and Schulze, THIS JOURNAL, 47, 2002 (1925); *Bull. soc. chim.*, 41, 1479 (1927).

[13] Marvel, Gauerke and Hill, THIS JOURNAL, 47, 3009 (1925); also, Hill, *ibid.*, 50, 167 (1928).

The magnesium sulfonates were obtained from the water layer by crystallization after concentration. They are much less soluble in water than the magnesium halides. Some of the magnesium sulfonates were analyzed for water of crystallization as well as for magnesium in the anhydrous salt.

TABLE I

Ester	G.	Mole	–MgX compound	Hydrocarbon	G.	%	RX compound	G.	%
$(C_2H_5)_2SO_4$	16	0.1	MgI_2	....			C_2H_5I[a]	1.5	10
$(C_2H_5)_2SO_4$	38	.25	C_2H_5MgBr	......	..	..	C_2H_5Br	..	..
C_2H_5-*p*-$OSO_2C_7H_7$	20	.1	C_6H_5MgI	$C_2H_5C_6H_5$	3	45	C_2H_5I	2.5	32
n-C_4H_9-*p*-$OSO_2C_7H_7$	91.2	.4	$MgBr_2$	......	..	..	*n*-C_4H_9Br[b]	38	71
n-C_4H_9-*p*-$OSO_2C_7H_7$	91.2	.4	*n*-C_3H_7MgI	......	..	..	*n*-C_4H_9I[c]	20	67
n-C_4H_9-*p*-$OSO_2C_7H_7$	91.2	.4	$C_6H_5CH_2MgCl$	*n*-$C_5H_{11}C_6H_5$	20	67	*n*-C_4H_9Cl[d]	....	
n-C_4H_9-*p*-$OSO_2C_7H_7$	91.2	.4	C_6H_5MgBr	*n*-$C_4H_9C_6H_5$	17	64	*n*-C_4H_9Br[e]	18	67
n-C_4H_9-*p*-$OSO_2C_7H_7$	23	.1	C_2H_5OMgI	......	..	..	*n*-C_4H_9I	12	67
n-C_4H_9-*p*-$OSO_2C_7H_7$	23	.1	C_6H_5OMgI	......	..	..	*n*-C_4H_9I[f]	10	54
n-C_4H_9-*p*-$OSO_2C_7H_7$	186	.8	C_6H_5SMgI	.....	..	..	*n*-C_4H_9I[g]	43	67
n-C_4H_9-*p*-$OSO_2C_7H_7$	228	1.0	$C_6H_5N(CH_3)MgBr$	......	..	..	*n*-C_4H_9Br[h]	22	30

[a] In studies where esters other than those of the halogen acids (or RX compounds) were treated in ether with magnesium, diethyl sulfate gave a positive color test when a trace of iodine was added. Unquestionably this was due to the formation of some magnesium iodide, which split the diethyl sulfate to form ethyl iodide and this then reacted with the magnesium present to give ethylmagnesium iodide.

[b] An 85–87% yield of magnesium p-toluenesulfonate was obtained.

[c] The quantity of n-propylmagnesium bromide required for a positive test was 0.2 mole. No attempt was made to separate the low boiling n-heptane. The yield of magnesium p-toluenesulfonate was 65 g. or 70%.

[d] n-Butyl chloride was not isolated here; however, qualitative tests showed it to be present. The large quantity of ether used in this experiment was undoubtedly responsible for the difficulty in separating the butyl chloride. This was shown in a blank experiment where 18 g. of butyl chloride was added to the same volume (550 cc.) of ether and fractional distillation with the same column gave no separation. From a corresponding reaction, using one mole of ester and one mole of benzylmagnesium cloride, Marvel[4] succeeded in separating butyl chloride. The yield of magnesium p-toluenesulfonate from this experiment was 70%.

[e] In this experiment 0.22 mole of phenylmagnesium bromide was required to give a positive color test that persisted after two hours of refluxing. The yield of magnesium *p*-toluenesulfonate was 86 g. or 86.5%. The anhydrous salt was analyzed for magnesium after drying to constant weight at 110°. Anal. Calcd. for $(C_7H_7SO_3)_2Mg$: Mg, 6.64. Found: 6 65, 6.64. A sodium hydroxide extraction of the ether layer gave some phenol. The residue from steam distillation gave 2.0 g. of phenyl-*p*-tolyl sulfone. This was identified by a mixed melting point determination with an authentic specimen.

[f] The yield of magnesium p-toluenesulfonate was 67%. In another run a special search failed to reveal any n-butylphenyl ether. The phenol was almost quantitatively recovered as 2,4,6-tribromophenol.

[g] The *p*-thiophenylmagnesium iodide was prepared from 44 g. or 0.4 mole of *p*-thiophenol and an equivalent quantity of n-propylmagnesium iodide. Subsequent to hydrolysis the ether layer when extracted with sodium hydroxide yielded no thiophenol. The yield of n-butylphenyl sulfide was 39 g. or 52%.

[h] The methylanilinomagnesium bromide was prepared from 55 g. or 0.5 mole of methylaniline and ethylmagnesium bromide. Twenty *g.* of an amine boiling at 225–230" was obtained. This was very probably the expected methyl-n-butylaniline, $C_6H_5N(CH_3)(n\text{-}C_4H_9)$. The boiling point agrees with that reported by Komatsu, J.

Coll. *Sci.* Imperial University *of* Tokio, **3,** 371 (1912), *C. A.*, 7, 1021 (1913), but not with that reported by Frohlich and Wedekind, Ber., 40, 1648 (1907). Accordingly, the picrate was prepared and found to melt at 93° and not at 141–142°, as reported by Komatsu. There is a possibility of a typographical error in Komatsu's work, because among the large number of picrates reported by him is a related one melting at 93–94°, namely, methyl-iso-amylaniline.

p-Toluenesulfonic Ester of Ethyl Lactate and Phenylmagnesium Bromide.—From 12 g. or 0.04 mole of the ester and 0.05 mole of phenylmagnesium bromide, there was obtained 4 g. or a 55% yield of ethyl a-bromopropionate. Its identity was confirmed by the preparation of the ammonium salt prepared from m-nitraniline according to the method of Bischoff.[14] A mixed melting point determination was then made with an authentic specimen and the observed melting point was 247–248°.

Because of the small size of the experiment none of the expected ethyl α-phenylpropionate was isolated. Probably some of the phenyl ester, if formed, reacted with the excess of Grignard reagent to give some of the corresponding ketone or ester. These products are to be sought in a larger run, for they should be present if Reactions 3 and 4 are correct and if the lactyl ester is not an exceptional compound.

Ethyl Cyclohexylsulfonate and Phenylmagnesium Bromide.—From 35 g. or 0.18 mole of ester and a slight excess (color reaction) of phenylmagnesium bromide, there were obtained 3.5 *g.* of ethylbenzene, some ethyl bromide (characterized as ethylmercuribromide) and 1 g. of a compound melting at 107°. It was thought that this solid was cyclohexylphenyl sulfone. However, this could not be confirmed because when experiments were carried out to synthesize such a sulfone by standard procedures, the melting point of the synthetic compound was 73°. This latter compound was prepared by the oxidation of the sulfide obtained from sodium thiophenate and bromocyclohexane. The properties of the cyclohexylphenyl sulfide are: b. p. 145° (11 mm.); $d^{20}_{20} = 1.0031$; $n_{25} = 1.5663$. The magnesium cyclohexylsulfonate was analyzed.

Anal. Calcd. for $(C_6H_{11}SO_3)_2Mg\cdot6H_2O$: H_2O, 24.88. Found: 24.28, 24.25. Calcd. for $(C_6H_{11}SO_3)_2Mg$: Mg, 7.45. Found: 7.34, 7.45.

This experiment with ethyl cyclohexylsulfouate shows that alkyl alicyclic sulfonates alkylate after the manner of alkyl arylsulfonates according to Reaction 1.

n-Butyl *p*-Toluenesulfonate and Ethylmagnesium Bromide with Water.—By means of the color test[11] it was shown that 0.1–0.12 mole of water in ether was required to destroy 0.1 mole of ethylmagnesium bromide. To this mixture, which may be magnesium bromide and magnesium hydroxide and not basic magnesium bromide,[8b] there was added 23 g. or 0.1 mole of n-butyl p-toluenesulfonate. After refluxing for two hours and then working up in the customary manner, there were obtained 2 g. or 14% of n-butyl bromide and 18 g. or 40% of magnesium p-toluenesulfonate.

n-Butyl p-Toluenesulfonate and Bromomagnesium *p*-Tolylsulfinate (p-$CH_3C_6H_4S(=O)OMgBr$).—The bromomagnesium sulfinate was prepared by the addition of sulfur dioxide to a 0.4 mole solution of p-tolylmagnesium bromide until there was no color reaction.[11] After reaction with 92.4 g. or 0.4 mole of n-butyl *p*-toluenesulfonate, there were obtained 32 g. or 58% of n-butyl bromide and 80 g. of a mixture of the magnesium salts of *p*-toluenesulfinic and *p*-toluenesulfonic acids. From another run, 7 g. of *p*-toluenesulfinic acid was obtained.

n-Butyl p-Toluenesulfonate and Iodomagnesium β-Naphthalenesulfonate, β-$C_{10}H_7SO_2OMgI$.—The anhydrous β-naphthalenesulfonic acid was prepared according to the directions of Kraft and Roos[15] and was chesked by a melting point determination

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[14] Bischoff, Ber., 30, 2766 (1897).

[15] Kraft and Roos, Ber., 26, 2823 (1893).

in vacuo[16] and a neutralization equivalent. Sufficient anhydrous acid was used to react with 0.2 mole of methylmagnesium iodide until no color test was obtained. From the iodomagnesium sulfonate obtained in this manner and 46 g. or 0.2 mole of n-butyl *p*-toluenesulfonate, there was obtained 12 g. or 33% of *n*-butyl iodide.

A part of the magnesium β-naphthalenesulfonate, which incidentally is less soluble in water than magnesium p-toluenesulfonate, was analyzed after drying to constant weight at 110°.

Anal. Calcd. for $(\beta\text{-}C_{10}H_7SO_3)_2Mg$: Mg, 5.99. Found: 6.09.

Phenyl *p*-**Toluenesulfonate** and Magnesium Bromide.—An ether–toluene solution containing 50 g. or 0.2 mole of phenyl p-toluenesulfonate and 0.25 mole of magnesium bromide etherate was refluxed for two hours at 100°. After hydrolysis, an ether extract of the steam distillate gave no test for halogen and there was no indication of the formation of magnesium p-toluenesulfonate. This experiment illustrates a difference between aryl and alkyl sulfonates (see Reactions 1 and 2).

Summary

Alkylation is not the only reaction that takes place when alkyl sulfonates are treated with organomagnesium halides. Alkyl halides are also formed. The reactions proposed to account for these products have a direct bearing on the formula for the Grignard reagent proposed some time ago by Jolibois.

AMES, IOWA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WASHINGTON SQUARE COLLEGE, NEW YORK UNIVERSITY, NEW YORK, N. Y.]

NEW CONDENSATIONS OF KETONES WITH PHENOLS. THE PHORONE DI-META-CRESYL ETHER

BY JOSEPH B. NIEDERL

RECEIVED MARCH 28, 1928 PUBLISHED AUGUST 4, 1928

Introduction

The importance of the condensations occurring between aldehydes and phenols gave the impulse to a number of investigations of the behavior of ketones toward phenols under the influence of dehydrating agents.

Previously the following four types of condensations of ketones with phenols had been established: (1) the formation of diphenylmethane derivatives,[1,2] (2) the formation of ketals,[2,3,4] (3) the formation of molecular addition compounds and (4) the formation of oxygen heterocyclics.[5]

It has now been found that diaryl derivatives of di-iso-butyl ketone

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[16] Witt, *Ber.*, **48**, 743 (1915).

[1] Dianin, *J. Russ. Phys.-Chem. Soc.*, **1**, 488–517 (1891).

[2] Mackenzie, *J. Chem. Soc.*, **121**, 1695 (1922).

[3] Claisen, *Ber.*, **29**, 1005 (1896); *Ber.*, **31**, 1010 (1898).

[4] Clough, *J. Chem. Soc.*, **89**, 771 (1906); *ibid.*, **26**, 170 (1910); Schmidlin and Lang, *Ber.*, 43,2806 (1910).

[5] Chem. Fabriken vorm. Weiler ter Mer, Ger. pat., 367,765.

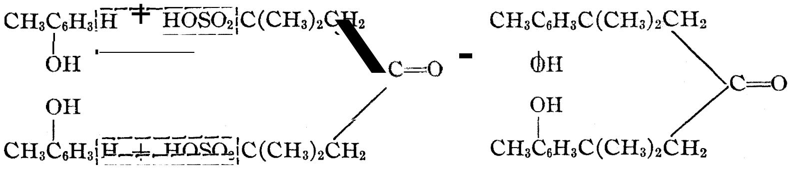
result on treatment of phenols with acteone in the presence of concentrated sulfuric acid.

The discussion of this condensation is the purpose of the present communication.

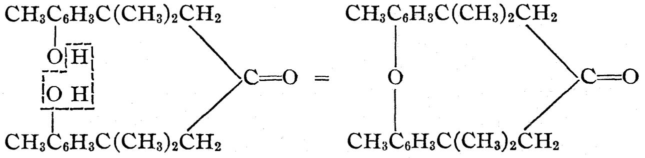
Discussion

The first condensation product of this type, phorone di *m*-cresyl ether, was obtained by the author[6] by treating a mixture of m-cresol and acetone with concentrated sulfuric acid.

It apparently formed in four steps: (1) the formation of phorone from 3 molecules of acetone, with mesityl oxide as intermediate;[7,8] (2) the addition of 2 molecules of sulfuric acid, forming phorone di-sulfuric acid, analogous to the addition of halogen acids, which has already been observed;[9] (3) the re-elimination of 2 molecules of sulfuric acid and subsequent addition of 2 molecules of *m*-cresol.



(4) ether formation, yielding the final reaction product, the phorone di-m-cresyl ether.



$C_{23}H_{28}O_2$: Mol. wt., 336

The assigned structure is in harmony with the fact that the same product was also obtained when phorone was treated with 2 moles of m-cresol in the presence of concentrated sulfuric acid under the same reaction conditions.

Derivative.—The phorone di-m-cresyl ether very readily forms a bromine derivative, the phorone di-bromo-m-cresyl ether; it is also easily nitrated, whereby the phorone di-(di-nitro)-m-cresyl ether results.

Oxidation Products.—In order to substantiate more fully the assigned structure of the compound, its oxidation products were studied. On oxidation with chromic acid two simpler products were isolated. One of them was shown to be dimethyl malonic acid; the other appears to

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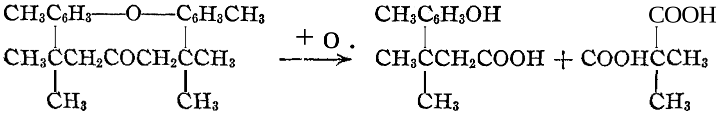
[6] Niederl, *Inaugural Dissertation*, University of Graz, Austria, April, 1925.

[7] Claisen, *Ann.*, **180,** 22 (1875).

[8] Orndorff and Young, THIS JOURNAL, 15,255 (1893).

[9] Vorlander and Hayakawa, *Ber.*, 36, 3536 (1903).

be m-cresyl isovaleric acid. Their formation may be represented as follows.



$$\begin{array}{c} \mathrm{CH_3C_6H_3{-}O{-}C_6H_3CH_3} \\ |\qquad\qquad | \\ \mathrm{CH_3CCH_2COCH_2CCH_3} \\ |\qquad\qquad | \\ \mathrm{CH_3}\qquad\quad \mathrm{CH_3} \end{array} \xrightarrow{+\,\mathrm{O}} \begin{array}{c} \mathrm{CH_3C_6H_3OH} \\ | \\ \mathrm{CH_3CCH_2COOH} \\ | \\ \mathrm{CH_3} \end{array} + \begin{array}{c} \mathrm{COOH} \\ | \\ \mathrm{COOHCCH_3} \\ | \\ \mathrm{CH_3} \end{array}$$

Dimethyl malonic acid is one of the oxidation products of phoronic acid;[10] its formation in the present case indicates that the compound under discussion is also a derivative of phorone.

Of the m-cresyl isovaleric acid, its di-bromo and mono-nitro derivative and di-sodium salt could be isolated and identified.

Experimental Part

Phorone Di-m-cresyl Ether, **2,6-Dimethyl-2,6-di-(4-oxy-2-methyl)-phenyl heptanone-(4) Ether, Di-(*m*-tolyl)-*iso*-butyl** Ketone Ether, $C_{23}H_{28}O_2$.—For the preparation of this compound use was made at first of Baeyer's[11] aldehyde condensation process. Later the following procedure was adopted as being most effective.

Three moles of concentrated sulfuric acid was added to an ice-cold mixture of three moles of acetone and two moles of m-cresol, keeping the temperature at 0°.

This reaction mixture was allowed to stand at room temperature for forty-eight hours, precautions being taken to exclude all moisture, and was then heated on a water-bath for one hour.

On cooling a solid red mass was obtained. This was washed successively with cold and hot water, to remove the sulfuric acid, the m-cresol sulfonic acid-(4) and the m-cresol di-sulfonic acid, which formed in the reaction as by-products.

The remaining tar was then treated with hot potassium or sodium hydroxide in order to extract any unchanged m-cresol and again with water until free of alkali.

The tar was then dissolved in hot ethyl alcohol and on cooling the phorone di-*m*-cresyl ether crystallized out.

The tar, as obtained after purification with water and alkali, yielded on distillation a fraction boiling between 270 and 300°, from which the ether could be obtained on dilution with ethyl alcohol.

The treatment of either acetone or m-cresol separately with concentrated sulfuric acid under identical conditions yielded no new products.

However, when 1 mole of phorone was mixed with two moles of m-cresol and then subjected to the action of concentrated sulfuric acid, as before, the phorone di-m-cresyl ether also formed. The yields obtained by this method were as high as 80% of the theoretical, while in the previous experiment only about 15% could be isolated.

Phorone di-m-cresyl ether crystallizes in various forms, depending on the conditions and the solvents. Usually it is obtained in cubes, 2 to 3 mm. in diameter; on slow crystallization it forms prismatic aggregates or large hexagonal crystals; m. p. 127° (uncorr.); b. p. 270° (uncorr.) with partial decomposition.

It is insoluble in hot and cold water, dilute and concentrated alkalies and dilute acids. It is sparingly soluble in cold ethyl alcohol but dissolves easily on warming;

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[10] Pinner, Ber., 14, 1072, 1077 (1881); *Ber.*, 15,585 (1882).

[11] Baeyer, Ber., 5,280, 1095 (1872).

it dissolves in hot concentrated sulfuric and nitric acids and is very soluble in ether, chloroform, carbon tetrachloride and glacial acetic acid.

Anal. Calcd. for $C_{23}H_{28}O_2$: C, **82.14**; H, 8.33. Found: **C, 81.92, 82.04;** H, **8.26,** 8.29.

Mol. **wt.** Calcd.: **336.** Found (cryoscopic method): **325, 329;** found (ebullioscopic method): 318, 322.

Qualitative tests show that the compound is saturated and that the two oxygen atoms in this compound are neither hydroxylic nor carboxylic in nature.

Dibromo Derivative, $C_{23}H_{26}O_2Br_2$.—Phorone di-m-cresyl ether was dissolved in carbon tetrachloride, an excess of bromine in carbon tetrachloride added and the mixture left standing in the dark at room temperature for twenty-four hours.

After this time the evolution of hydrogen bromide had completely ceased. The carbon tetrachloride was then distilled off, the residue dissolved in boiling glacial acetic acid and allowed to crystaliize.

It crystallizes in large, colorless, prismatic rosets. It melts at 215° (uncorr.). It is insoluble in cold and hot water, cold and hot mineral acids and alkalies. It dissolves slightly in boiling alcohol and is freely soluble in ether, chloroform and carbon tetrachloride. It dissolves also in boiling glacial acetic acid and concentrated sulfuric acid.

Anal. Calcd. for $C_{23}H_{26}O_2Br_2$: C, **55.86;** H, **5.26;** Br, **32.39.** Found: C, **55.61;** H, **5.59;** Br, **32.51.**

Tetranitro Derivative, $C_{23}H_{24}O_{10}N_4$.—By treating the phorone di-m-cresyl ether with boiling concentrated nitric acid and diluting the resulting solution with cold water, a yellow, crystalline solid separated out. This substance was freed from adhering oxidation products formed simultaneously by repeated washings with alkalies and recrystallization from ethyl alcohol. Yellow crystals were obtained which melt at **243"** (uncorr.).

The product is insoluble in cold and hot water and alkalies, but dissolves in ethyl alcohol, ether, chloroform, carbon tetrachloride and glacial acetic acid.

Anal. Calcd. for $C_{23}H_{24}O_{10}N_4$: C, **53.49;** H, **4.65;** N, **10.85.** Found: C, **53.48;** H, **4.44;** N, **10.87.**

Oxidation Products

m-Cresyl Isovaleric Acid, $HO(CH_3)C_6H_3C(CH_3)_2CH_2COOH$.—The phorone di-m-cresyl ether was dissolved in hot glacial acetic acid and to this mixture an equal amount of chromic acid anhydride, dissolved in the same solvent, was added in small portions.

The mixture was refluxed for six hours and the solution then poured into cold water. A white precipitate consisting chiefly of the m-cresyl isovaleric acid separated. It was repeatedly dissolved in alkalies and reprecipitated with mineral acids. Finally it was crystallized from acetone.

It melts at 107° (uncorr.). It is soluble in alkalies, forming dark red solutions, and in organic solvents such as acetone, ethyl alcohol, ether, chloroform, carbon tetrachloride, etc.

Anal. Calcd. for $C_{12}H_{16}O_3$: C, **69.23;** H, 7.69. Found: **C, 68.94, 69.70;** H, **7.24, 7.73.**

Dibromo-*m*-cresyl Isovaleric Acid, $C_{12}H_{14}O_3Br_2$.—This substance was prepared by treating the solution of the m-cresyl isovaleric acid in glacial acetic acid with bromine water. The di-bromo-m-cresylisovaleric acid precipitated out immediately.

It was purified by repeated precipitation from its solution in aqueous alkali (potassium or sodium hydroxide) and finally crystallized from ethyl alcohol; m. p. 140° (uncorr.).

Anal. Calcd. for $C_{12}H_{14}O_3Br_2$: C, 39.30; H, 3.82. Found: C, 39.67; H, 3.65.

Nitro-m-cresyl **Isovaleric** Acid, $HO(CH_3)C_6H_2(NO_2)C(CH_3)_2CH_2COOH$.—This acid was obtained as the oxidation by-product in the nitration of the phorone di-m-cresyl ether.

When the solution of the nitration and oxidation products in concentrated nitric acid was diluted with water, both the phorone di-(dinitro) m-cresyl ether and the nitro-m-cresyl isovaleric acid separated out. Subsequent treatment with aqueous alkalies dissolved the acid, which could be precipitated again easily from the colored alkaline solutions by mineral acids. It was finally crystallized from benzene; m. p. 108° (uncorr.). It is insoluble in water and dilute mineral acids but dissolves readily in alkalies and organic solvents.

Anal. Calcd. for $C_{12}H_{15}NO_5$: C, 56.92; H, 5.93; N, 5.53. Found: C, 57.13; H, 6.10; N, 5.44.

Its disodium salt could be obtained by neutralizing an alcoholic solution of the acid with sodium alcoholate. On standing a finely divided precipitate formed. It was isolated and finally crystallized from dilute methyl alcohol.

Anal. Calcd. for $C_{12}H_{13}O_5NNa_2$: Na, 15.48. Found: Na, 15.50, 15.35.

Dimethyl Malonic Acid.—This acid was obtained together with the m-cresyl isovaleric acid.

When the aqueous filtrate obtained after the removal of the m-cresyl isovaleric acid was treated with lead acetate, a heavy, white precipitate formed, which proved to be the insoluble lead salt of dimethyl malonic acid. It was purified by repeated precipitations and washings with water, alcohol and ether.

Anal. Calcd. for $C_5H_6O_4Pb$: C, 17.77; H, 1.78; Pb, 61.42. Found: C, 17.57; H, 1.51; Pb, 61.26, 61.32.

This lead salt was decomposed with hydrogen sulfide and the lead-free filtrate on evaporation left a residue which, when purified, corresponded for the tests (m. p., solubility) of dimethyl malonic acid as recorded in the literature.

All the quantitative determinations were carried out micro-analytically according to Pregl[12] and the author desires here to thank Miss Edith P. Silbert for her assistance in carrying out these analyses.

The author wishes to acknowledge here his appreciation for laboratory facilities placed at his disposal and repeated courtesies extended by Professors John A. Mandel of the University and Bellevue Hospital Medical College and William C. MacTavish of the Washington Square College, New York University.

Summary

(1) New condensations of ketones with phenols were investigated, resulting in the formation of aryl substituted ketones, the phorone di-*m*-cresyl ether being the first one isolated; (2) the mechanism of their formation is explained, and *(3)* the proof for their structure is given.

Further investigations of the condensation possibilities of phorone and

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[12] Pregl, "Die quantitative org. Mikro Elementar Analyse," Julius Springer, Berlin, 1923.

mesityl oxide with other phenolic compounds and of their oxidation products are being carried on.

NEW YORK CITY

[COMMUNICATION FROM THE DEPARTMENT OF INDUSTRIAL AND CELLULOSE CHEMISTRY, McGILL UNIVERSITY]

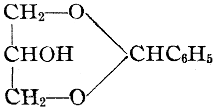
STUDIES ON THE REACTIONS RELATING TO CARBOHYDRATES AND POLYSACCHARIDES.

XV. THE ISOMERIC BENZYLIDENE GLYCEROLS

BY HAROLD S. HILL,[1] MYRON S. WHELEN[2] AND HAROLD HIBBERT[2a]

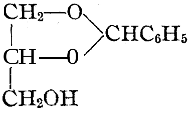
RECEIVED APRIL 14, 1928 PUBLISHED AUGUST 4, 1928

Fischer[3] was the first to describe a definite condensation product from the interaction of glycerol with benzaldehyde and the molecular structure of the cyclic acetal formed was represented as being



I

or



II

The same reaction product was more thoroughly investigated by Irvine, Macdonald and Soutar[4] with a view to determining its structure, and by methods of direct synthesis the material in hand was shown to possess the five membered cyclic configuration (II). While these authors pointed out the possibility of the existence of the isomeric form (I), they were unable to detect its presence in their product. It is because of this fact, together with the generally accepted finished character of their research, that their results have been interpreted as indicating the absence of the six membered benzylidene derivative, and the conclusion that the condensation of benzaldehyde with a poly-alcohol takes place only through *adjacent* hydroxyl groups.

This is especially true since the formula for monobenzylidene a-methyl glucoside was given earlier as containing a five membered acetal ring[5] (A),

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[1] Research Fellow, Canadian Pulp and Paper Association.

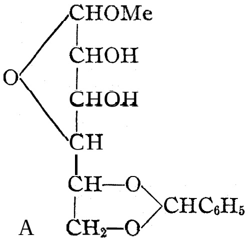
[2] Holder of Bursary, Canadian National Research Council.

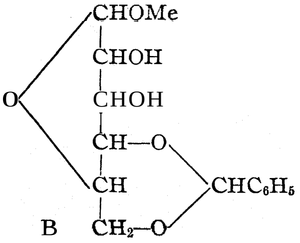
[2a] This work was carried out under the auspices of the cooperative research organization embracing the Canadian Pulp and Paper Association, the Pulp and Paper Division of the Forest Products Laboratories of Canada, and the Department of Industrial and Cellulose Chemistry, McGill University. The authors wish to express their thanks for the generous support accorded them. One of them (M. S. W.) is also indebted to the Canadian National Research Council for the award of a Bursary for which he desires to express his thanks.

[3] Fischer, Ber., 27, **1536 (1894).**

[4] Irvine, Macdonald and Soutar, J. *Chem. Soc.*, **107, 337 (1915).**

[5] Irvine and Scott, *ibid.*, 103, **575 (1913).**


A


B

a conclusion based partly on the assumption of α-methyl glucoside containing the five membered butylene oxide structure. More recent investigations,[6] however, have brought forth considerable evidence that the transformations of α-methyl glucoside are best explained on the basis of the six membered oxidic form. If the latter view be correct, then formula (A) for the benzylidene derivative becomes less probable than that of a six membered acetal ring (B). The question of the possibility of the formation of the latter grouping is, therefore, of interest.

In view of the great ease of formation of both five and six membered cyclic acetals in general, as shown by various partition experiments carried out by Hibbert and co-workers,[7] it was concluded by these authors that benzylidene glycerol should exist not only in both isomeric forms, but also that in the condensation of benzaldehyde with glycerol a "partition" should take place to give a reaction product consisting of a mixture of a five and six membered cyclic benzylidene glycerol, (I) and (II). The present investigation shows this to be the case and deals with the actual separation and identification of the isomers. The assumption that benzaldehyde condensations involve only adjacent hydroxyl groups is, therefore, unjustified.

Separation of the Isomeric Benzylidene Glycerols.—Glycerol was condensed with benzaldehyde essentially as described by Gerhardt[8] and a product obtained, b. p. 142–147° (2.5 mm.), which proved to be a mixture of the two benzylidene glycerols. A fortunate difference in solubility of the isomers in a mixture of cold ligroin and benzene permitted a fairly quantitative separation, the 1,3-benzylidene glycerol crystallizing out and leaving the 1,2-derivative in solution. The former product melts sharply at 83.5°.

Distillation and fractionation of the mother liquor yields 1,2-benzylidene glycerol as an oil, b. p. 143–144° (2 mm.) which presumably still holds a small amount of the 1,3-isomer in solution.

The benzoate of the crystalline isomer, prepared by means of benzoyl chloride in dry pyridine solution, is a well crystallized product, m. p. 103°, whereas that from the liquid 1,2-benzylidene glycerol is an oil.

It is of interest to compare the above results with those obtained by Irvine and co-workers, who also followed Gerhardt's patent in their prepa-

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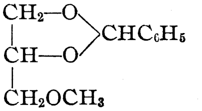
[6] A review of the subject by W. N. Haworth is to be found in Chem. *Soc.* Annual Reports, 1926, pp. 74–92.

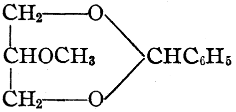
[7] Hill and Hibbert, THIS JOURNAL, 45, 3117 (1923).

[8] Gerhardt, German patent 255,083 (1913).

ration of benzylidene glycerol. They obtained only one product, a benzylidene glycerol whose melting point was originally 65°, but which rose on standing to 76° and which was proved beyond question to be the 1,2-derivative. In the present investigation it is shown that the crystalline benzylidene glycerol, m. p. 83.5°, is a pure 1,3-isomer and that the liquid product is a mixture of a small amount of this with the 1,2-derivative as the main product. The liquid isomer would not crystallize even on long cooling either alone or from solvents. This difference from Irvine's 1,2-benzylidene glycerol may be due to the fact that although it has the same ring system, it represents the alternate *cis* or *trans* geometric isomer. On the other hand, the small amount of the 1,3-derivative present may prevent crystallization.

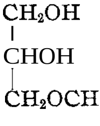
Determination of Structure.—For the identification of the isomeric benzylidene glycerols the methylation–hydrolysis method of Irvine and co-workers was followed. The use of dimethyl sulfate and sodium hydroxide as a methylating agent[9] proved to be unsuitable, owing to extensive hydrolysis of the acetal group. Methylating with silver oxide and methyl iodide, however, gave satisfactory yields of the corresponding benzylidene glycerol methyl ethers

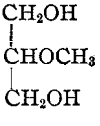

III


IV

the crystalline benzylidene glycerol, m. p. 83.5°, giving exclusively the new six membered acetal ether (IV) as a crystalline product, whereas the liquid isomer yielded an oil identical with Irvine's benzylidene glycerol methyl ether which was shown by him to have the five membered cyclic structure (III).

Hydrolysis of the latter product gave glycerol a-methyl ether (V), identical with that described by Irvine. Hydrolysis of the isomeric benzylidene glycerol ether (IV) yielded a new glycerol monomethyl ether, VI, quite different from the a-derivative and which must, therefore, be glycerol β-methyl ether,


$$\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OCH_3 \end{array} \quad V$$


$$\begin{array}{l} CH_2OH \\ | \\ CHOCH_3 \\ | \\ CH_2OH \end{array} \quad VI$$

It is now possible to assign definitely to the crystalline benzylidene glycerol, m. p. 83.5°, the six membered cyclic acetal structure (I) and to the liquid isomer the alternate formula (II). It should be noted that while the liquid benzylidene glycerol, by the above methylation–hydrolysis method,

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[9] Haworth, *J. Chem. Soc.*, **107**, 8 **(1915)**.

yielded for the most part glycerol a-methyl ether, it also gave a small amount of the β-ether, showing that the liquid acetal still holds some of its isomer in solution.

Glycerol β-methyl ether, as isolated above, marks the first definite β-derivative of glycerol to be recorded in the literature, and for this reason it should prove to be a reference compound of some importance. Its physical constants in comparison with glycerol a-methyl ether are given in the following table.

TABLE I

PHYSICAL PROPERTIES OF ETHERS

Glycerol a-methyl ether (Irvine)	Glycerol a-methyl ether (The authors)	Glycerol β-methyl ether (The authors)
B. p., 110–111° (13 mm.)	**B. p., 110–111° (13 mm.)**	**B. p., 123° (13 mm.)**
$d_{4°}^{17°}$ = **1.1197**	$d_{4}^{17°}$ = **1.1202**	$d_{4}^{17°}$ **1.1306**
$n_{D}^{17°}$ = **1.4460**	$n_{D}^{17°}$ = **1.4449**	$n_{D}^{17°}$ **1.4505**

Partition and Interconversion of the Isomeric Benzylidene Glycerols.—Taking advantage of the fact that the crystalline 1,3-benzylidene glycerol is practically insoluble in a strongly cooled mixture of ligroin and benzene, while the other isomer remains in solution, it is possible by carefully controlled conditions to determine the relative amounts of the isomers present in the primary reaction product. In the material isolated by the use of Gerhardt's method, it was found that the five membered cyclic form (II) exceeds that of the six membered (I) in the ratio of 7.5 to 1. On the other hand, if the preparation of benzylidene glycerol was carried out by a different method, namely, by heating glycerol and benzaldehyde with a small amount of 40% sulfuric acid, a mixture was obtained in which the same isomers were present in a ratio of 3 to 1.

Obviously the "partition" varies somewhat with the conditions used in the preparation, and it is even possible that in some cases the above ratio might be reversed. The fact remains, however, that both isomers are always formed and that in all cases investigated the smaller ring structure predominates.

In this connection it seemed desirable to ascertain whether the "partition" was the result of chance formation of varying amounts of the isomers, or whether it represented a state of equilibrium between the two forms. If the latter interpretation be correct, then, as shown previously in other cases, either isomer, when treated with a trace of acid, should be transformed into the other until an equilibrium mixture results, and for a given set of conditions the same ratio of products should be obtained, regardless of which isomer is used, and this is found to be the case. When 1,3-benzylidene glycerol is treated with a trace of dry hydrogen chloride and heated at 100° for one hour, a mixture is obtained in which the ratio of the five membered cyclic acetal to the six is 5:1. Starting with 1,2-benzylidene glycerol, the ratio of these isomers found in the equilibrium product is 5.5:1.

This transformation is rapid and takes place even under very mild conditions. Thus crystalline 1,3-benzylidene glycerol treated with a trace of dry hydrogen chloride and warmed to 30° liquefies immediately as a result of its partial conversion into the 1,2-isomer.

On the other hand, 1,2-benzylidene glycerol, when allowed to stand for one month at room temperature with a trace of dry hydrogen chloride, reaches approximately the same equilibrium with its 1,3-isomer as when heated to 100°, the ratio being 5.7 to 1.

These interconversion experiments are to be considered as being more of a qualitative than an exact quantitative nature, since it is admittedly impossible to separate all of the crystalline isomer from the liquid. The possibility of cis-trans interconversions in the same ring system must also be considered as a complicating factor.

These results are significant, however, since they bring out the labile character of these carbon-oxygen cyclic structures, many closely related examples of which exist in various sugar and polysaccharide derivatives. The marked ease of transformation of one form into the other emphasizes the need for great caution in assigning a definite structure to an original compound on the basis of the structure of one of its derivatives, especially if the latter has been prepared under conditions involving an acid medium as, for example, in the case of the two different cellobiosans obtained by Bergmann and Knehe, *Ann.*, 448, 76 (1926), and Hess and Friese, Ann., **450,** 40 (1926); **456,** 38 (1927), respectively.

It is believed that the formation of isomeric glycerol methyl ethers by the methylation–hydrolysis method, as applied to the corresponding ethylidene glycerols, lends considerable support to the claims of Irvine and coworkers regarding their method of methylation technique based on Purdie's original observations.

Their procedure of complete methylation, subsequent hydrolysis and identification of the resulting methylated sugars is taken as indicating the positions of the free hydroxyls and of the point of union in the original polysaccharide. In such reasoning there is always the possibility that a rearrangement in the oxide ring of the sugar residues may take place under the conditions of methylation. The present investigation with the simpler glycerol derivatives shows that under these same conditions the relatively sensitive five and six membered acetal rings involved undergo no change, one into the other, and that the methylated products obtained are an authentic proof of the constitution of the parent substances.

Experimental Part

Preparation and Separation of Isomeric Benzylidene Glycerols.—One hundred fifty g. of pure benzaldehyde and 120 g. of glycerol were heated in an atmosphere of carbon dioxide with stirring for one hour at 145–155°, and then for thirty minutes at 165°. The product upon fractionation under reduced pressure yielded 170 g. of a crude mixture,

b. p. 140–149° (3 mm.). This was taken up in ether, washed several times with water to remove traces of glycerol, dried over solid potassium carbonate and refractionated; yield, 120 g. of mixed benzylidene glycerols, b. p. 142–147° (2.5 mm.); $d^{17°}_{4°}$, 1.19838; n_D, 1.5400.

Anal. Subs., 0.2244: CO_2, 0.5464; H_2O, 0.1340. Calcd. for $C_{10}H_{12}O_3$: C, 66.67; H, 6.67. Found: C, 66.41; H, 6.66.

Sixty g. of mixed benzylidene glycerols from the above preparation was dissolved in a mixture of 150 cc. of ligroin (b. p. 60–70°) and 90 cc. of benzene and cooled to −15° until crystallization had taken place. Enough benzene was slowly added, with shaking, until there was no longer undissolved oil present with the precipitated crystals. After standing at −15° for one hour, the crystals were filtered from the cold solution and washed with 40 cc. of a cold mixture of equal parts of ligroin and benzene; yield, 7 g. Recrystallization from ligroin-benzene mixture with practically no loss gave pure 1,3-benzylidene glycerol, m. p. 83.5°.

Anal. Subs., 0.2020: CO_2, 0.4947; H_2O, 0.1182. Calcd. for $C_{10}H_{12}O_3$: C, 66.67; H, 6.67. Found: C, 66.79; H, 6.50.

Benzylidene glycerol was also prepared using sulfuric acid as a catalyst.

Method.—One hundred fifty-nine g. of benzaldehyde, 150 g. of glycerol and 2 cc. of 40% sulfuric acid were heated on a steam-bath for eight hours in an atmosphere of carbon dioxide. The product was taken up in ether, neutralized with potassium carbonate and dried over this reagent. Fractionation yielded 105 g. of mixed benzylidene glycerols, b. p. 163–168° (11 mm.).

Fifty g. of this mixture, separated as described above, gave 13 g. of crystalline 1,3-benzylidene glycerol, m. p. 83°. In another experiment 28 g. of the mixture yielded 7 g. of 1,3-benzylidene glycerol.

1,2-Benzylidene Glycerol.—The ligroin–benzene mother liquor from the above separation of 1,3-benzylidene glycerol was evaporated under reduced pressure, taken up in ether, washed with concentrated potassium carbonate solution to remove traces of acid and dried over the solid carbonate. Fractionation gave pure 1,2-benzylidene glycerol, b. p., 143–144° (2 mm.); $d^{17°}_{4°}$, 1.1916; n_D, 1.5389. This product showed no tendency to crystallize.

Anal. Subs., 0.2170: CO_2, 0.5295; H_2O, 0.1301. Calcd. for $C_{10}H_{12}O_3$: C, 66.67; H, 6.67. Found: C, 66.55; H, 6.66.

Benzoates of Benzylidene Glycerol.—The respective benzylidene glycerols were benzoylated by dissolving each of them at room temperature in four times the weight of dry pyridine containing the theoretical amount of benzoyl chloride and allowing the reaction, with development of heat, to proceed spontaneously for about twenty minutes. On pouring into water, the product from 1,3-benzylidene glycerol crystallized at once, while that from 1,2-benzylidene glycerol remained as an oil. The benzoate of 1,3-benzylidene glycerol was recrystallized from ligroin, m. p. 103°.

Analysis of the Benzoate from **1:2-Benzylidene** Glycerol.—Subs. 0.2153: CO_2, 0.5674; H_2O, 0.1103. Calcd. for $C_{17}H_{16}O_4$: C, 71.83; H, 5.63. Found: C, 71.87; H, 5.69.

Methylation of **1,3-Benzylidene** Glycerol.—Fifty-four g. of crystalline 1,3-benzylidene glycerol was recrystallized from ligroin–benzene solution (1:1), pressed as dry as possible on a suction filter and methylated immediately in the usual manner, using 115 g. of silver oxide and 230 g. of methyl iodide. The reaction mixture was thoroughly extracted with ether from which, on partial evaporation and cooling, benzylidene glycerol methyl ether separated. Recrystallization from mixture of ligroin–benzene (1:1) yielded 31 g. of long, coarse, transparent needles, m. p. 52°. No other substance could be isolated from the reaction product.

Anal. Subs., 0,1446: CO_2, 0.3570; H_2O, 0.0878. Calcd. for $C_{11}H_{14}O_3$: C, 68.04; H, 7.22. Found: C, 67.38; H, 6.79.

Hydrolysis of Benzylidene Glycerol &Methyl Ether.—Twenty-seven g. of benzylidene glycerol β-methyl ether (m. p. 52°) was hydrolyzed by boiling under reflux for seventy minutes with 220 cc. of 75% aqueous ethyl alcohol containing 3 cc. of concd. hydrochloric acid; 65 cc. of water was added and the alcohol removed under reduced pressure. Three or four extractions with ether removed benzaldehyde. The aqueous solution was neutralized by shaking with lead carbonate, filtered, concentrated and fractionated under diminished pressure. Redistillation yielded 9 8 g. (64%) of pure @-methyl glycerol ether, b. p. 123° (13 mm.); $d^{17°}_{4°} = 1.1300$; $n^{17°}_{D} = 1.4505$.

Anal. Subs., 0.1419: CO_2, 0.2350; H_2O, 0.1176. Calcd. for $C_4H_{10}O_3$: C, 45.28; H, 9.27. Found: C, 45.17; H, 927.

Methylation of **1,2-Benzylidene Glycerol.**—Seventy-five g. of the liquid 1,2-benzylidene glycerol was methylated in the usual manner with 145 g. of freshly prepared silver oxide and 290 g. of methyl iodide. Extraction of the reaction mixture with ether and fractionating gave 50 g. of a mixture, b. p. 139–145° (10 mm.).

Fraction I	28 g.	b. p. 138–139° (10 mm.)	$n^{17°}_{D} = 1.5128$
Fraction II	12 g.	b. p. 139–141° (10 mm.)	$n^{17°}_{D} = 1.5135$
Fraction III	8 g.	b. p. 141–145° (10 mm.)	$n^{17°}_{D} = 1.5159$

Analysis of the lower and higher fractions showed both to be benzylidene glycerol methyl ether.

Anal. Fraction *I*. Subs., 0.2281: CO_2, 0.5678; H_2O, 0.1472. Calcd. for $C_{11}H_{14}O_3$: C, 68.04; H, 7.22. Found: C, 67.89; H, 7.17.

Anal. Fraction III. Subs., 0.2180: CO_2, 0.5127; H_2O, 0.1408. Calcd. for $C_{11}H_{14}O_3$: C, 68.04; H, 7.22. Found: 67.92; 7.19.

Hydrolysis of Benzylidene Glycerol a-Methyl Ether.--Twenty-eight g. of benzylidene glycerol a-methyl ether (fraction (I) above), hydrolyzed in the same manner as the @-derivative yielded 13.4 g. (87%) of glycerol a-methyl ether, b. p. 110° (13 mm.), $d^{17°}_{4°} = 1.1202$; $n^{17}_{D} = 1.4449$.

Anal. Subs., 0.2073: CO_2, 0.3424; H_2O, 0.1747. Calcd. for $C_4H_{10}O_3$: C, 45.28; H, 9.43. Found: C, 45.05; H, 9.36.

Hydrolysis of the higher boiling fractions from the preparation of 1,2-benzylidene glycerol or-methyl ether gave for the most part glycerol a-methyl ether, b. p. 112° (13 mm.), $n^{17°}_{D} = 1.4446$, but also a smaller fraction, b. p. 112–118°, indicating the presence of a small amount of the higher boiling β-methyl glycerol ether.

Interconversion of the Benzylidene **Glycerols.**—Several bubbles of dry hydrogen chloride were passed into 3 g. of 1,2-benzylidene glycerol contained in a tube so small that there was very little free air space when stoppered. This was heated for one hour at 100°, allowed to stand at room temperature for twelve hours and taken up with 10 cc. of ether. The solution was shaken with 0.5 g. of solid potassium carbonate to neutralize the acid, filtered and evaporated under reduced pressure. The residue was taken up with 15 cc. of a 50% mixture of ligroin (b. p. 60–70") and benzene and cooled to −15° for one hour. The crystals of 1,3-benzylidene glycerol which separated were filtered from the cold solution, washed with 10 cc. of the cold ligroin-benzene mixture and dried in a vacuum; yield, 0.5 g. (m. p. 81°). It was recrystallized with practically no loss and then melted at 83.5°.

Three g. of 1,3-benzylidene glycerol, when subjected to an as nearly as possible parallel treatment, as above, yielded 0.46 g. of unchanged 1,3-benzylidene glycerol, m. p. 80–82°.

An experiment carried out with 3 g. of 1,2-benzylidene glycerol, similarly treated with dry hydrogen chloride but without any preliminary heating and allowed to stand for one month at room temperature, yielded 0.45 g. of 1,3-benzylidene glycerol.

Summary

1. The preparation, isolation, quantitative separation and interconversion of the isomeric 1,2- and 1,3-benzylidene glycerols are described.

2. The corresponding methyl ethers have been prepared and their physical constants determined.

3. The remarkably labile character of the oxygen ring is shown by the ease of partial transformation of either of the acetals into the corresponding isomer at a low temperature under the influence of traces of gaseous hydrochloric acid. The bearing of this on polysaccharide investigations is pointed out.

4. Glycerol 8-methyl ether has been isolated for the first time in a pure state. It is apparently the first pure 8-derivative of glycerol to be reported in the literature.

MONTREAL, CANADA

[COMMUNICATION FROM THE DEPARTMENT OF INDUSTRIAL AND CELLULOSE CHEMISTRY, McGILL UNIVERSITY]

STUDIES ON THE REACTIONS RELATING TO CARBOHYDRATES AND POLYSACCHARIDES.

XVI. SEPARATION AND IDENTIFICATION OF THE ISOMERIC ETHYLIDENE GLYCEROLS[1]

BY HAROLD S. HILL,[2] ALLAN C. HILL[3] AND HAROLD HIBBERT[4]

RBCEIVED APRIL 14, 1928 PUBLISHED AUGUST 4, 1928

The importance of the cyclic acetal and ketal glycerols has long attracted the interest of investigators in the field of carbohydrate chemistry. Such workers as Tollens,[5] Fischer,[6] Karrer,[7] Irvine,[8] and more recently

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[1] This work was presented by Mr. Allan C. Hill to the Graduate Department, McGill University, in April, 1927, in partial fulfilment of the requirements for the degree of Master of Science.

[2] Research Fellow, Canadian Pulp and Paper Association,

[3] Research Chemist attached to Pulp and Paper Division, Forest Products Laboratories of Canada.

[4] This paper represents the second of a forthcoming series of publications carried out under the joint auspices of the Canadian Pulp and Paper Association, the Pulp and Paper Division of the Forest Products Laboratories of Canada and the Department of Industrial and Cellulose Chemistry, McGill University. The authors wish to express their keen appreciation of the generous facilities placed at their disposal by the three cooperating agencies.

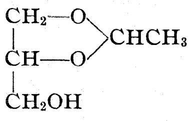
[5] Schulz and Tollens, *Ann.*, 289, 29 (1896).

[6] Fischer, *Ber.*, 27, 1536 (1897).

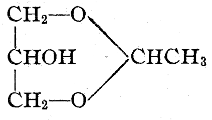
[7] Karrer, *Helv. Chim. Acta*, *4*, 728 (1921).

[8] Irvine, Macdonald and Soutar, *J. Chem. Soc.*, 107,337 (1915).

Hibbert and his pupils[8] have studied or used this class of compounds in their efforts to explain, by analogy, certain features of the chemical behavior of the more complex polysaccharides. It is remarkable, therefore, that up to the present time the molecular structure of one of the simplest glycerol acetals, namely, ethylidene glycerol, has remained undetermined, its formula being given as either, or both, of the two possible isomeric forms


(A)

or


(B)

Schulz and Tollens,[5] working with the lower homolog, methylidene glycerol, indicated the existence of both of the corresponding isomeric forms since, under different experimental conditions, they were able to obtain products which, in one case, yielded a benzoate as *a* crystalline product, in the other as an oil. The isomers were not identified, however, and the method used in their preparation left some doubt as to their existence as different chemical individuals.[9a]

With respect to the structure of ethylidene glycerol, however, there has been no evidence brought forward as to which of the two forms, A or B, should be assigned as its molecular constitution. This is due in large part to the extreme ease of hydrolysis of this product and the consequent difficulty of obtaining any derivative not involving rupture of the acetal ring.

Ethylidene glycerol was first prepared by Harnitzky and Menschutkine[10] and later, in much purer form, by Nef,[11] the formula being given as either A or B.

Recent work[12] has shown that in benzaldehyde condensations with glycerol a "partition" occurs, both the five and the six membered cyclic acetals being formed simultaneously. In view of these results, as well as those from earlier experiments in this field,[9] it was concluded that ethylidene glycerol would also prove to be a mixture of the two ring systems (A) and (B). The present investigation deals with the separation and identification of these isomers, and of several of their derivatives.

The isomeric ethylidene glycerols are obtained as a mixture in either of the two recognized methods of preparation.[9] The crude product in both

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[9] Hill and Hibbert, THIS JOURNAL, 45, 3121 (1923).

[9a] Neal Carter has recently succeeded in isolating and identifying the two pure methylidene glycerols and their corresponding benzoates. An account of this work is to be published in the immediate future. (H. H.)

[10] Harnitzky and Menschutkine, Ann., 136, 126 (1865).

[11] Nef, Ann., 335, 216 (1904).

[12] Hill, Whelen and Hibbert, THIS JOURNAL, 50,2235 (1928).

cases boils at 176–187° (760 mm.), the rise in temperature during distillation, even with a fractionating column, being very gradual. Operating under reduced pressure, however, it is possible, by several fractionations, to obtain two distinct products, Fraction I, b. p. 86–88° (21 mm.), and Fraction II, b. p. 101–103.5° (20 mm.), neither of which, however, can be considered as a pure material.

The acetylene method of preparation yielded the sharpest boiling low fraction, while that from the paraldehyde method gave the most definite high boiling product. From this observation it would appear that the partition between the two isomeric forms of ethylidene glycerol may vary considerably, according to the method and conditions of preparation.

The fractions from either method have the same percentage composition and each, upon hydrolysis with dilute phosphoric acid, yields the same theoretical amount of acetaldehyde. Differences in the densities and refractive indices, however, further indicate the presence of isomers.

Many unsuccessful attempts were then made, using the low boiling fraction from the acetylene method and the high boiling from the paraldehyde process (as representing the purest samples), to isolate an acylated product, and this was finally achieved by the use of benzoyl chloride in dry pyridine solution. This reagent causes no hydrolysis of the acetal ring and readily yields two well defined glycerol-acetal-benzoates, that from the low boiling fraction being crystalline (m. p. 86°) and that from the high boiling product an oil, b. p. 163 (11 mm.).

The isolation of these benzoates in a pure state proved to be the key to this research, especially since a fortunate difference in solubility in ligroin permitted of an almost quantitative separation.

Employing the mixture of isomers obtained by the acetylene method, benzoylating the product and separating the mixed benzoates by the use of cold ligroin, it was possible to isolate the isomeric benzoates, the ratio of the amounts of the crystalline to the liquid form being 1:1.8. This ratio may be regarded as an approximately accurate value of the extent of the partition between the low and high boiling ethylidene glycerols, respectively, as prepared by this method.

Applying the same procedure to the mixture of ethylidene glycerols obtained from the reaction of paraldehyde with glycerol, the relative amounts of the low and high boiling isomers were found to be 1:4.

Two conclusions may be drawn from these partitions. 1. The formation of the high boiling isomer—later shown to have the five membered cyclic configuration (A)—is definitely favored over that of the six membered derivative (B). *2.* The partition ratio is a variable one, the relative amounts of each isomer formed depending on experimental conditions such as temperature, concentration of acid, etc. There is no reason to suppose that the actual mechanism of ring closure is any different in the preparation from acetylene than from paraldehyde. Furthermore, it is to be expected, as found in the preceding paper[12] (Part XV) on the isomeric benzylidene glycerols that under standard conditions, there will always exist a final equilibrium mixture which should be the same irrespective of whether this is approached from the side of the five or from that of the six membered acetal.

Structural Identification of the Isomers.—Since the isomeric ethylidene glycerol benzoates may thus be separated and isolated in a pure condition, these derivatives were used as the starting point to determine the structure of the original acetals. It was found possible to hydrolyze off the benzoyl group, leaving the acetal ring intact.

In this way, starting with the pure benzoates, two isomeric ethylidene glycerols were obtained for the first time, as pure individual compounds.

The structures of these acetals were determined essentially as in the case of the benzylidene glycerols, namely, by the methylation–hydrolysis method developed by Irvine and co-workers. Silver oxide and methyl iodide was used as the methylating agent, since Haworth's methyl sulfate method proved unsatisfactory.

Each of the two ethylidene glycerols yielded an isomeric ethylidene glycerol methyl ether which, in turn, on hydrolysis, gave an isomeric glycerol monomethyl ether.

The low boiling ethylidene glycerol (purified through its crystalline benzoate) gave only glycerol β-methyl ether, identical with that isolated for the first time from 1,3-benzylidene glycerol, while the higher boiling ethylidene glycerol (from its liquid benzoate) yielded only the glycerol α-methyl ether.

In the latter case, while the α-ether was the main product, there was also a small amount of the β-derivative present. This was due to its imperfect removal in the purification of the benzoate, since it is admittedly impossible to separate completely all of the solid from the liquid benzoate, but this fact does not affect the conclusions drawn as to the structure of the products.

It is considered proved, therefore, that in the preparation of ethylidene glycerol, a partition occurs between the five and six membered rings, and also that the low boiling acetal has definitely the 1,3-configuration (B) while the higher boiling isomer has the alternate 1,2-structure (A).

Comparative Properties of the Isomers.—Four pairs of isomeric glycerol derivatives, namely, 1,2- and 1,3-ethylidene glycerols, their corresponding benzoates, their methyl ethers and α- and β-glycerol methyl ethers, have now been synthesized and it is believed that their properties offer an interesting physico-chemical study. For purposes of comparison some properties and physical constants are collected in the following table.

Certain generalizations may be drawn from the results in Table I. In all

TABLE I

PHYSICAL CONSTANTS OF COMPOUNDS

Compound	B. p., °C.	$d^{17°}_{4°}$	$n^{17°}_{D°}$
1,3-Ethylidene glycerol	52 (1 mm.)	1.1477	1.4532
1,2-Ethylidene glycerol	68–70 (1 mm.)	1.1243	1.4413
1,3-Ethylidene glycerol benzoate	(86")	....	....
1,2-Ethylidene glycerol benzoate	144–145 (2 mm.)	1.1618	1.5145
1,3-Ethylidene glycerol methyl ether	80 (23 mm.)	1.0705	1.4375
1,2-Ethylidene glycerol methyl ether	56–58 (23 mm.)	1.0224	1.4177
Glycerol @-methylether	125 (14 mm.)	1.1300	1.4500
Glycerol α-methyl ether	111 (13 mm.)	1.1191	1.4460
Glycerol β-methyl ether from 1,3-(benzylidene glycerol)	123 (13 mm.)	1.1305	1.4505
Glycerol a-methyl ether from 1,2-(benzylidene glycerol)	110–111 (13 mm.)	1.1197	1.4462

[a] Melting point, crystalline compound.

cases the more symmetrical 1,3-derivatives have higher densities, higher refractive indices and show greater tendency to crystallize (also noted in the benzylidene series) than their isomeric 1,2-forms.

There is one anomaly, however, for which no explanation can be offered. It is seen that the boiling point of the 1,3-ethylidene glycerol is considerably lower than that of the 1,2-derivative, but that when these products are methylated the relative boiling points are reversed, the six membered cyclic form having the higher boiling point. In this connection it should be noted that ethylidene 1,3-propylene glycol, b. p. 108°, and ethylidene 1,2-propylene glycol, b. p. 92°, agree with the relationship of the methylated ethylidene glycerols rather than with the acetals themselves. The various isomers exhibit almost identical properties.

An attempt was made to prepare glycerol a- and β-monobenzoates starting from the purified isomeric benzoates of ethylidene glycerol and hydrolyzing off the acetal groups with dilute acid but only negative results were obtained.

Experimental Part

Preparation of Ethylidene Glycerol from Acetylene.—The directions given by Hill and Hibbert[8] for the preparation of cyclic acetals from acetylene were followed. Eight g. of mercuric sulfate was triturated in a mortar with 8 cc. of concentrated sulfuric acid, and the resulting paste added, with stirring, to 184 g. (2 moles) of pure glycerol in the reaction flask. After sweeping out the air with acetylene, 45 liters (2 moles) of the latter gas was led in under slight hydrostatic pressure from a gasometer. The reaction flask was surrounded by a water-bath maintained at 70°. After the required amount of acetylene had been absorbed (during about two hours) the reaction product was taken up in ether, filtered and neutralized with solid potassium carbonate. The ether was removed and the product fractionated under reduced pressure. Two hundred and thirty-four g. of mixed ethylidene glycerols was obtained, b. p. 86–101" (20 mm.).

Preparation of Ethylidene Glycerol from Paraldehyde.—Two hundred and seventy-six g. of glycerol was mixed with 5 cc. of 50% sulfuric acid in a three-necked flask fitted with a reflux condenser and a stirrer with a mercury seal. While heating to 100° in a water-bath, 144 g. of paraldehyde was gradually added during the course of one-half hour and the mixture heated for three hours. After cooling, ether was added, the small glycerol layer separated and the ether solution dried over potassium carbonate. Fractionation under reduced pressure yielded 233 g. of mixed ethylidene glycerols, b. p. 79–89 (13 mm.).

Fractional Distillation of Ethylidene Glycerol.—Using a long bead fractionating column and diminished pressure, it was possible, by repeated fractionations, to effect a partial separation of the isomeric acetals. From the mixture obtained by the paraldehyde method the sharpest high boiling fraction was obtained, b. p. 80–81° (8 mm.); 187–188 (760 mm.). The mixture from the acetylene method, on the other hand, gave the sharpest low boiling fraction, b. p. 86–88 (20 mm.); 176–177 (760 mm.).

Although these fractions still do not represent completely separated isomers, it was from them that the first definite indication of isomerism was obtained. From them also the benzoates of the isomers were first obtained (using benzoyl chloride with dry pyridine), the low boiling ethylidene glycerol yielding a crystalline product, m. p. 86°, and the high boiling acetal an oil, b. p. 163° (11 mm.). After the properties of these benzoates had been studied the separation of the isomers became a relatively simple matter.

Determination of Relative Amounts of 1,2- and 1,3-Ethylidene Glycerol Formed by Paraldehyde and Acetylene Methods

The method of isolating and determining the relative amounts of the 1,2- and 1,3-ethylidene glycerols formed depends on the difference in physical character of their benzoates, particularly the difference in solubility in cold ligroin.

Forty-five g. of benzoyl chloride was mixed with 90 cc. of pure, anhydrous pyridine (which had been carefully dried by boiling over barium oxide for 24 hours) and 39 g. of mixed ethylidene glycerols (prepared by the acetylene method, b. p. 94–100" (24 mm.)) added. The reaction was accompanied by the evolution of a large amount of heat. The mixture was allowed to stand for 20 minutes and then added slowly, with constant stirring, to a liter of cold water. The precipitated oil was dissolved in ether, the ether solution washed with 5% sodium hydroxide, then with 3% sulfuric acid, finally with water and dried with potassium carbonate. The ether was removed and the remaining oil heated for two hours at 100° under vacuum to remove traces of pyridine. To this mixture of benzoates was added 100 cc. of ligroin, b. p. 60–70°, and the solution cooled to 0°. Crystals separated out which were washed with cold ligroin and weighed. The remaining oil was fractionated under reduced pressure, yielding the α-benzoyl derivative. In this way 17 g. of crystalline benzoate (from 1,3-ethylidene glycerol) and 30 g. of liquid benzoate (from 1,2-ethylidene glycerol) were obtained, representing a combined yield of 47 g. or 70%.

The crystalline benzoate melted at 86°. The liquid product boiled at 163° (11 mm.); n_D, 1.5146; $d_{4°}^{20°}$, 1.1618. The relative amounts of the low boiling isomer (1,3-ethylidene glycerol) and the high boiling isomer (1,2-ethylidene glycerol) are thus in the ratio of 1 to 1.8.

In the same manner 39 g. of the mixed ethylidene glycerols, prepared by the paraldehyde method, gave a yield of 49 g. (71%) of the mixed benzoates, of which 10 g. was ethylidene glycerol β-benzoate (m. p. 86°) and 39 g. ethylidene glycerol a-benzoate (b. p. 164° (12.5 mm.); n_D, 1.5145). The amounts of 1,3-ethylidene glycerol and 1,2-ethylidene glycerol in this case are in the ratio of 1 to 4.

A carefully refractionated sample of ethylidene glycerol, obtained from the low boiling fraction of the acetylene method, and a similarly purified fraction from the high boiling fraction of the paraldehyde method were benzoylated in a similar manner. In the first case the product was almost exclusively the crystalline benzoate, m. p. 86°.

Anal. Subs., 0.2200: CO_2, 0.5230; H_2O, 0.1245. Calcd. for $C_{12}H_{14}O_4$: C, 64.86; H, 6.31. Found: 64.83; 6.33.

In the second case the product obtained was an oil, b. p., 164° (12.5 mm.); n_D, 1.5146; $d_{4°}^{20°}$, 1.1618.

Anal. Subs., 0.1936: CO_2, 0.4603; H_2O, 0.1090. Calcd. for $C_{12}H_{14}O_4$: C, 64.86; H, 6.31. Found: 64.84; 6.30.

Preparation of Pure 1,3-Ethylidene Glycerol by Hydrolysis of 1,3-Ethylidene Benzoate.—Fifty-four g. of 1,3-ethylidene benzoate, m. p. 86°, was treated with 15 g. of sodium hydroxide in 150 cc. of water by shaking vigorously and warming until it had melted and completely dissolved. The clear solution was cooled at once and, after adding 100 g. of potassium carbonate, extracted with ether during four hours by means of a continuous extraction apparatus. The ether solution, dried over potassium carbonate and fractionated yielded, besides the solvent, only one product, namely, 17 g. of 1,3-ethylidene glycerol, b. p. 52° (2 mm.); $n_D^{17°} = 1.4532$; $d_{4°}^{17°} = 1.1477$; yield, 59% of the theoretical. The product was a colorless, nearly odorless oil completely miscible in water.

Anal. Subs., 0.1859, 0.1837: CO_2, 0.3482, 0.3283; H_2O, 0.1431, 0.1441. Calcd. for $C_5H_{10}O_3$: C, 50.84; H, 8.47. Found: C, 50.35, 50.23; H, 8.62, 8.79.

Preparation of 1,2-Ethylidene Glycerol.—The liquid 1,2-ethylidene glycerol benzoate used for this preparation was freed as far as possible from the crystalline isomer, as described above, and further by standing at −10° for several days after seeding with the crystalline benzoate. Filtration at −10°, followed by fractionation, gave a nearly pure 1,2-derivative, b. p. 144–145° (2 mm.); $n_D^{17°} = 1.5145$; $d_{4°}^{17°} = 1.1618$.

The product was hydrolyzed exactly as in the case of the 1,3-isomer, 140 g. of the benzoate yielding 50 g. of 1,2-ethylidene glycerol, b. p. 68–70' (1 mm.); $n_D^{17°} = 1.4415$; $d_{4°}^{17°} = 1.1243$.

Anal. Subs., 0.2144, 0.1927: CO_2, 0.3965, 0.3555; H_2O, 0.1621, 0.1464. Calcd. for $C_5H_{10}O_3$: C, 50.88; H, 8.47. Found: C, 50.39, 50.32; H, 8.47, 8.51.

Methylation of the Ethylidene Glycerols.—After using methyl sulfate with poor results, this reaction was carried out successfully with methyl iodide and silver oxide. It was found that efficient agitation greatly increased the yield. Fifteen g. of 1,3-ethylidene glycerol, methylated with 105 g. of methyl iodide and 52 g. of silver oxide gave 15 g. (89% of theoretical) of the corresponding ethylidene glycerol methyl ether, b. p. 80" (23 mm.); $n_D^{17°} = 1.4375$; $d_{4°}^{17°} = 1.0705$. The product was a colorless oil completely miscible with water.

In the same way 17 g. of 1,2-ethylidene glycerol treated with 110 g. of methyl iodide and 54 g. of silver oxide yielded 16 g. (85% of theory) of a methylated product, b. p. 53–58° (22 mm.). Refractionation gave 14 g., b. p. 56–58° (23 mm.), and a small higher fraction, b. p. 58-61" (23 mm.), which presumably contains some of the 1,3-derivative. The product was a colorless oil, not completely miscible with water, in contrast with its isomer; $n_D^{17°} = 1.4177$; $d_{4°}^{17°} = 1.0224$.

Hydrolysis of Ethylidene Glycerol Methyl Ethers.—The method used by Irvine and co-workers for the hydrolysis of isopropylidene glycerol methyl ethers was followed except that a smaller volume of aqueous alcohol was used. Fifteen grams of 1,3-ethylidene glycerol methyl ether was refluxed for ninety minutes with 50 cc. of 75% aqueous alcohol containing 0.3 cc. of concd. hydrochloric acid. (The theoretical amount of acetaldehyde was collected in a strongly cooled trap, keeping the reflux condenser at 40–50°.) After neutralizing with lead carbonate, filtering, washing the precipitate with absolute alcohol (adding in all 50 cc. of the latter) and fractionating, 9 g. (72% of theoretical) of pure glycerol β-methyl ether, b. p. 125 (14 mm.), was obtained; $d^{17°}_{4°}$ = 1.1300; $n^{17°}_{D}$ = 1.4500.

In like manner, 17 g. of 1,2-ethylidene glycerol methyl ether yielded 10 g. of glycerol a-methyl ether, b. p. 111–112° (13 mm.), and a small higher fraction containing some β-isomer. That the main fraction was a practically pure a-ether was shown by its refractive index and density, $n^{17°}_{D}$ = 1.4462 and d = 1.1191, compared with $n^{17°}_{D}$ = 1.4460 and $d^{17°}_{4°}$ = 1.1197 reported by Trvine for pure glycerol methyl ether.

Hydrolysis of the Isomeric Ethylidene Glycerols.—Twenty g. of each of the acetals was heated at 130° for one hour with 10 cc. of 5% phosphoric acid, using a reflux condenser maintained at 40°. The latter in turn was connected to a well cooled spiral condenser to collect the acetaldehyde. 20.26 g. of 1,2-ethylidene glycerol (A) gave 7.53 g. of acetaldehyde; yield, 99%. 18.81 g. of 1,3-ethylidene glycerol (B), treated in like manner, gave 6.93 g. of acetaldehyde; yield, 98%.

Summary

1. The preparation, isolation and quantitative separation of the two isomeric ethylidene glycerols are described.
2. The corresponding methyl ethers and benzoates have been prepared and their physical constants determined.

MONTREAL, CANADA

[CONTRIBUTION FROM THE MORLEY CHEMICAL LABORATORY OF WESTERN RESERVE UNIVERSITY]

THE SYNTHESIS OF CERTAIN IODO-ALKOXY ACIDS AND THE MECHANISM OF THE REACTIONS BY WHICH THEY ARE FORMED

BY ERNEST L. JACKSON AND L. PASIUT

RECEIVED APRIL 16, 1928 PUBLISHED AUGUST 4, 1928

The ready substitution of the chlorine atom in α-iodo-β-chlorophenylpropionic acid by the hydroxyl, methoxyl and ethoxyl groups was demonstrated by Erlenmeyer[1] in 1896. The reaction of α-iodo-β-chlorophenylpropionic acid with water was shown to produce α-iodo-β-hydroxyphenylpropionic acid, while its reaction with solutions of potassium hydroxide in absolute methyl and ethyl alcohols gave, respectively, α-iodo-β-methoxyphenylpropionic acid and α-iodo-β-ethoxyphenylpropionic acid.

In applying the procedure of Erlenmeyer to the synthesis of a variety of α-iodo-β-alkoxyphenylpropionic acids, the fact soon came to our attention that the use of potassium hydroxide is unnecessary. When solutions of α-iodo-β-chlorophenylpropionic acid in a number of different alcohols were allowed to stand for several hours, the α-iodo-β-alkoxyphenylpropionic acids resulted. The yields of the iodo-alkoxy acids depend upon the alcohol, being lowest in the case of *iso*propyl and *tert.*-butyl alcohols. The reaction is not precluded by the substitution of the

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[1] Erlenmeyer, *Ann.*, 289, 259 (1896).

a-hydrogen atom in α-iodo-β-chlorophenylpropionic acid by the methyl group, since a-iodo-a-methyl-p-chlorophenylpropionic acid was shown to react with absolute methyl alcohol to yield a-iodo-a-methyl-/3-methoxyphenylpropionic acid. Although the methyl ester of α-iodo-β-chlorophenylpropionic acid does not react with water,[1] it reacts readily with absolute methyl alcohol to give methyl α-iodo-β-methoxyphenylpropionate.

A more suitable method for the preparation of the α-iodo-β-alkoxyphenylpropionic acids was found to be the reaction of iodine monochloride with cinnamic acid and the appropriate alcohol. In order to avoid esterification of the acids, the reaction was carried out in the presence of calcium carbonate. The methoxy and ethoxy acids were also prepared by the introduction of chlorine into solutions of cinnamic acid and iodine, or an alkali iodide, in the appropriate alcohol. The reaction of iodine monochloride and absolute methyl alcohol with crotonic acid yields iodomethoxybutyric acid.

In addition to the synthesis of α-iodo-β-hydroxyphenylpropionic acid by the reaction of water with a-iodo-p-chlorophenylpropionic acid, Erlenmeyer showed that the compound may be prepared by the reaction of the hydrochloride of iodine monochloride with sodium cinnamate in aqueous solution. We have found the introduction of chlorine into a suspension of iodine and cinnamic acid in water to be a convenient procedure for the preparation of the iodohydroxy acid.

For the synthesis of the iodo-alkoxy acids by the reaction of α-iodo-β-chlorophenylpropionic acid with the various alcohols, it was necessary to prepare the iodochloro acid in large quantities. The addition of iodine monochloride to cinnamic acid in carbon tetrachloride[2] solution proved to be more convenient and to produce higher yields than the procedure of Erlenmeyer,[1] who treated cinnamic acid in ether solution with the hydrochloride of iodine monochloride. Also, the reaction of iodine monochloride with a-methylcinnamic acid in carbon tetrachloride solution is a satisfactory method for the preparation of a-iodo-a-methyl-P-chlorophenylpropionic acid.

The yields of the iodo-alkoxy acids by the different methods of preparation are given in Table I.

Erlenmeyer assumed the methoxyl group in the iodomethoxyphenylpropionic acid to be in the β-position by analogy with the corresponding iodohydroxy acid. We confirmed this structure by the reaction of the iodomethoxy acid with zinc and absolute methyl alcohol to give β-methoxyphenylpropionic acid. One would expect the alkoxyl groups in the other acids, which were prepared from a-iodo-p-chlorophenylpropionic acid, to be in the β-position from the method by which the compounds were prepared. It will be shown below, in the discussion of the mechanism

[2] Compare James, *J. Chem. Soc.*, **103, 1372 (1913).**

TABLE I

THE PREPARATION OF IODO-ALKOXY ACIDS

Der. of α-iodo-β-phenylpropionic acid	Method[a]	Cryst. solvent	M. p. (uncorr.), °C.	Yield, %	Analyses		
						Calcd, %	Found, %
β-Methoxy	1	$CHCl_3$	168–169[b]	75	OCH_3,	10.1	9.4
	2	or	.....	88		...	.....
	3	C_6H_6	.....	34–48			
β-Methoxy methyl ester	1	CCl_4	68–69	79	OCH_3,	19 38	18.58
					I,	39.66	39 93, 40 08
α-Methyl-β-methoxy	1	CCl_4	169–170[c]	46	OCH_3,	9.69	9.10
					I,	39.60	39 93
β-Ethoxy	3	C_6H_6	137–138	?		...	......
β-*n*-Propoxy	1	C_6H_6	110–111	28	I,	37.99	37.82
	2	C_6H_6	.....	62		...	......
β-*Iso*propoxy	1	$CHCl_3$	113–114	11	I,	37.99	38.44
	2	$CHCl_3$	.....	22		...	......
β-*n*-Butoxy	1	C_6H_6	93–94	25	I,	36.46	36.55
	2	C_6H_6	.....	42		...	......
β-*Iso*butoxy	2	$CHCl_3$	89–90	38	I,	36.40	30.77
β-*Tert.*-butoxy	1	$CHCl_3$	113–114	8	I,	36.46	36.66
	2	$CHCl_3$	.....	15		...	......
Iodomethoxybutyric acid	2	C_6H_6	83–84	33	OCH_3,	12.71	12 35
					I,	52.01	5205

[a] Methods.—(1) The reaction of the appropriate alcohol with the α-iodo-β-chloro acid, or ester; (2) the reaction of iodine monochloride with the unsaturated acid and the appropriate alcohol in the presence of calcium carbonate; (3) the reaction of chlorine with a solution of the unsaturated acid and iodine, or alkali iodide, in the appropriate alcohol.

[b] Erlenmeyer gives 164–165°.

[c] Obtained by rapid heating (melting point varies with rate of heating).

of the reactions, that the compounds result either from the direct replacement of the chlorine atom by the alkoxyl groups, or from the addition of the alkyl hypoiodites to cinnamic acid. In the first case, there could be no question of the structure of the iodo-alkoxy acids. In the latter case, the alkoxyl groups would be in the β-position, if the mode of addition of the alkyl hypoiodites to cinnamic acid is the same as that of the alkyl hypobromites and hypochlorites.[3] As a check we have proved the compound, prepared with isopropyl alcohol, to be α-iodo-β-*iso*propoxyphenylpropionic acid by the preparation of acetophenone[3c] through its reaction with alcoholic potassium hydroxide, followed by hydrolysis of the product with dilute sulfuric acid solution. By similar reactions, the iodomethoxy acid, obtained from α-iodo-α-methyl-β-chlorophenylpropionic acid, was shown to yield propiophenone. The formation of propiophenone from a-iodo-a-methyl-P-methoxyphenylpropionic acid is shown by the following reactions.

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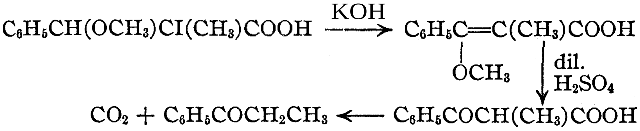
[3] (a) Conant and Jackson, THIS JOURNAL, 46, 1727 (1924); (b) Jackson, *ibid.*, 48,2166 (1926); (c) Jackson and Pasiut, *ibid.*, 49,2071 (1927).



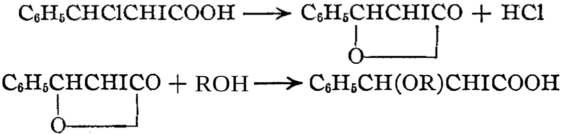
$$C_6H_5CH(OCH_3)CI(CH_3)COOH \xrightarrow{KOH} C_6H_5C(OCH_3)=C(CH_3)COOH \xrightarrow{\text{dil. } H_2SO_4} C_6H_5COCH(CH_3)COOH \longrightarrow CO_2 + C_6H_5COCH_2CH_3$$

The structure of the iodomethoxybutyric acid, which was prepared from crotonic acid, has not yet been established.

The Mechanism of the Reactions

The formation of the α-iodo-β-alkoxy acids from α-iodo-β-chlorophenylpropionic acid could result from any of the following mechanisms

$$C_6H_5CHClCHICOOH + ROH \longrightarrow C_6H_5CH(OR)CHICOOH + HCl \qquad (1)$$



$$C_6H_5CHClCHICOOH \longrightarrow C_6H_5\underbrace{CHCHICO}_{O} + HCl \qquad (a)\ (2)$$

$$C_6H_5\underbrace{CHCHICO}_{O} + ROH \longrightarrow C_6H_5CH(OR)CHICOOH \qquad (b)$$

$$C_6H_5CHClCHICOOH \longrightarrow C_6H_5CH{=}CICOOH + HCl \qquad (a)\ (3)$$

$$C_6H_5CH{=}CICOOH + ROH \longrightarrow C_6H_5CH(OR)CHICOOH \qquad (b)$$

$$C_6H_5CHClCHICOOH \longrightarrow C_6H_5CH{=}CHCOOH + ICl \qquad (a)\ (4)$$

$$ROH + ICl \longrightarrow ROI + HCl \qquad (b)$$

$$C_6H_5CH{=}CHCOOH + ROI \longrightarrow C_6H_5CH(OR)CHICOOH \qquad (c)$$

Erlenmeyer[1] considered the formation of α-iodo-β-hydroxyphenylpropionic acid, as well as the corresponding methoxy and ethoxy acids, to proceed through the β-lactone as shown in mechanism (2). In the case of the hydroxy acid, he regarded the direct replacement of the chlorine atom by the hydroxyl group improbable, since the methyl ester of α-iodo-β-chlorophenylpropionic acid failed to react with water. Mechanism (3), as well as the direct substitution of the chlorine atom by the alkoxyl groups as shown in mechanism (1), was considered unlikely for the lack of analogous examples. Erlenmeyer did not take mechanism (4) into consideration.

By the preparation of methyl α-iodo-β-methoxyphenylpropionate through the reaction of absolute methyl alcohol with the methyl ester of α-iodo-β-chlorophenylpropionic acid, we have shown that a β-lactone need not be an intermediate compound in the formation of the iodo-alkoxy acids. We have also eliminated mechanism (3) by the synthesis of α-iodo-α-methyl-β-methoxyphenylpropionic acid through the reaction of absolute methyl alcohol with α-iodo-α-methyl-β-chlorophenylpropionic acid, which has not the necessary hydrogen atom on the α-carbon atom. The iodo-alkoxy acids are formed, therefore, either according to mechanism (1) or mechanism (4).

Although we have no decisive experiments to distinguish between mechanisms (1) and (4), we nevertheless have obtained certain facts which favor mechanism (4). In the reaction of α-iodo-β-chlorophenylpropionic acid with the various alcohols, there was formed in each instance a certain amount of cinnamic acid, the quantity varying with the alcohol used. In the case of methyl alcohol the amount of cinnamic acid was small, while with *iso*propyl alcohol 75% of the iodochloro acid was converted into cinnamic acid. The data given in Table I show that the yields of the iodo-alkoxy acids, obtained by this method, vary from 75% with methyl alcohol to 8% with *tert.*-butyl alcohol. Erlenmeyer has shown that α-iodo-β-hydroxyphenylpropionic acid is almost completely changed into cinnamic acid by means of 25% hydrochloric acid solution, a reaction which he interprets as proceeding through α-iodo-β-chlorophenylpropionic acid. The production of cinnamic acid in the reaction of the alcohols with a-iodo-p-chlorophenylpropionic acid might, therefore, be attributed to the accumulation of hydrochloric or hydriodic acid in the solution. This, however, seems unlikely in view of the fact that the reactions were carried out in the presence of calcium carbonate. The simplest explanation of the formation of cinnamic acid is the elimination of a molecule of iodine monochloride from α-iodo-β-chlorophenylpropionic acid, as shown in Equation (a) of mechanism (4). This hypothesis is in accord with the usual practice of employing a considerable excess of the reagent in the determination of iodine values by the methods which involve the addition of iodine monochloride. In the presence of methyl alcohol the cinnamic acid, which was formed by the dissociation of iodine monochloride, is almost completely converted into α-iodo-β-methoxyphenylpropionic acid, as shown by Equations (b) and (c) of mechanism (4). When, however, the solvent is isopropyl or *tert.*-butyl alcohol, most of the iodine monochloride, formed in the initial reaction, is used up in side reactions with the alcohols, while a small amount simultaneously reacts to produce the alkyl hypoiodite, which by addition to the double linkage of the unsaturated acid gives a low yield of the α-iodo-β-alkoxy acid. This view is consistent with the results of experiments in which the iodo-alkoxy acids were synthesized by the reaction of iodine monochloride with cinnamic acid and the alcohols. Thus, when cinnamic acid reacts with methyl alcohol and iodine monochloride (1.25 moles), α-iodo-β-methoxyphenylpropionic acid results in 88% yield, while under similar conditions the reactions with isopropyl and *tert.*-butyl alcohols give the iodo-alkoxy acids in only 22 and 15% yields, respectively. In this connection it should be mentioned that the yields obtained in the reaction of an excess of iodine monochloride with cinnamic acid and the various alcohols were in each case higher than resulted in the reaction of a-iodo-p-chlorophenylpropionic acid with the corresponding alcohol. In the latter case a low concentration of iodine monochloride would be maintained throughout the reaction by the gradual elimination of iodine monochloride from the molecule of the iodochloro acid. In order to approximate these conditions, the calculated amount of iodine monochloride was added, a few drops at a time, to a dilute solution of cinnamic acid in isopropyl alcohol over approximately the same period that was used for the reaction of α-iodo-β-chlorophenylpropionic acid with *iso*propyl alcohol. The yield of α-iodo-β-*iso*propoxyphenylpropionic acid thus obtained was comparable to that produced in the reaction with a-iodo-β-chlorophenylpropionic acid.

The formation of the iodo-alkoxy acids according to mechanism (4) involves the assumption that iodine monochloride reacts with the various alcohols to give the alkyl hypoiodites. That iodine monochloride reacts with the alcohols in this manner seems practically certain from our experiments with *tert.*-butyl alcohol. *Tert.*-butyl alcohol was found to be almost without action on α-iodo-β-chlorophenylpropionic acid in the time which was used for the preparation of α-iodo-β-*tert.*-butoxyphenylpropionic acid by the reaction of cinnamic acid with iodine monochloride and *tert.*-butyl alcohol. Also, in the latter reaction no α-iodo-β-chlorophenylpropionic acid was recovered. This indicates that α-iodo-β-chlorophenylpropionic acid is not formed as an intermediate compound in the production of α-iodo-β-*tert.*-butoxyphenylpropionic acid by the reaction of cinnamic acid with iodine monochloride and *tert.*-butyl alcohol. The iodo-*tert.*-butoxy acid is probably formed by the addition of *tert.*-butyl hypoiodite to cinnamic acid, the *tert.*-butyl hypoiodite being a product of the reaction of iodine monochloride with *tert.*-butyl alcohol. The production of the other iodo-alkoxy acids, by the reaction of iodine monochloride with the unsaturated acids and the different alcohols, probably involves a similar mechanism.

Although the facts outlined are in accord with mechanism (4), we do not consider the direct replacement of the chlorine atom excluded. If the iodo-alkoxy acids are formed according to mechanism (1), the slow rate of reaction of *tert.*-butyl alcohol, as well as isopropyl alcohol, with α-iodo-β-chlorophenylpropionic acid would be expected as a consequence of the small reactivity of the hydroxyl hydrogen atoms[4] in these alcohols. However, this slow rate of reaction could equally well be interpreted as a solvent effect on the reactions of mechanism (4).

In previous papers[3a,b,c] it has been shown that bromine and chlorine react with ethylene derivatives and certain alcohols to give bromo and chloro-alkoxyl compounds. This reaction was interpreted as involving the addition of the alkyl hypobromites and hypochlorites to the double linkage of the unsaturated compounds. In connection with the reaction of the different alcohols with α-iodo-β-chlorophenylpropionic acid to give the iodo-alkoxy acids, the question arises whether the bromo and chloro-

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[4] (a) Norris and Ashdown, THIS JOURNAL, 47, 837 (1925); (b) Norris and Cortese, *ibid.*, 49, 2640 (1927).

alkoxyl compounds are formed in a similar manner by the reaction of the alcohols with the appropriate dibromides or dichlorides. The latter possibility is eliminated by the fact that cinnamic acid dibromide was shown by Werner[5] to be unchanged on heating with methyl alcohol, while we have found the dichloride of cinnamic acid in absolute methyl alcohol solution, containing hydrogen chloride, to undergo only the esterification reaction after standing for sixty-five hours. Under similar conditions the high-melting isomer of α,β-dichloro-β-phenylpropiophenone was shown to be unchanged.

Experimental Part

Preparation of the Iodochloro Acids

Ten g. of the unsaturated compound, cinnamic acid, methyl cinnamate or a-methyl cinnamic acid, was dissolved in carbon tetrachloride. To this was added **1.25** moles of iodine monochloride, which was prepared by the method of Hannay.[6] After standing for about fifteen hours, the solid material was filtered off and washed with carbon tetrachloride. The α-iodo-β-chlorophenylpropionic acid, obtained from cinnamic acid, melted with decomposition at 124–126°; yield, 92%. It was further purified by recrystallization from chloroform containing a small amount of petroleum ether. The methyl α-iodo-β-chlorophenylpropionate resulting from methyl cinnarnate was recrystallized from carbon tetrachloride; yield, 77%. It melted at 97–98°, which is the melting point given by Erlenmeyer.' The yield of α-iodo-α-methyl-β-chlorophenylpropionic acid prepared from a-methyl cinnamic acid was 74%. After recrystallization from carbon tetrachloride, the compound melted at 104–105° with decomposition.

Anal. Calcd. for $C_{10}H_{10}ClIO_2$: Cl and I, 50.04. Found: 49.99.

Synthesis of Iodo-alkoxy Acids by the Reaction of Alcohols **with the Iodochloro** Acids.—Two and one-half to 10 g. of the **α-iodo-β-chloro** acid or ester was dissolved in the appropriate alcohol. In order to avoid esterification of the acids, there was added precipitated calcium carbonate **(3** to 12 **g.)**. After standing at room temperature for thirty-five to ninety-eight hours, the calcium carbonate was filtered off and washed with the proper alcohol. The filtrate was poured into a large volume of water. This in some cases precipitated solid material and in others an oil, which crystallized alter standing for several hours. Saturation of the filtrate from this material with sodium chloride gave a small amount of crystals. By dissolving the calcium carbonate in hydrochloric acid, an additional quantity of solid was obtained. For purification the substance was dissolved in sodium carbonate solution and treated with potassium permanganate solution in small excess. By filtering off the manganese dioxide, extracting the filtrate with ether and acidifying, the somewhat impure compound was obtained. Recrystallization from the solvent given in Table I yielded the pure substance.

In the preparation of methyl α-iodo-β-methoxyphenylpropionate and a-iodo-α-methyl-β-methoxyphenylpropionic acid, the general procedure was varied in that the solvent was distilled under diminished pressure at 25–35' instead of pouring into water. The resulting products were purified by recrystallization from the solvents specified.

The principal product in the reaction of isopropyl alcohol with **α-iodo-β-chlorophenylpropionic** acid was cinnamic acid. Thus, from 2.5 g. of **α-iodo-β-chlorophenylpropionic** acid there was obtained 0.9 g. of cinnamic acid melting at 130–131° (75%

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[5] Werner, *Ber.*, 39, 27 (1906).

[6] Hannay, **J.** *Chem. Soc.*, **26, 815** (1873).

of the calculated amount). The substance was shown to be cinnamic acid by a mixed melting point determination and by its complete oxidation by potassium permanganate solution.

The rate of the reaction of *tert.*-butyl alcohol with α-iodo-β-chlorophenylpropionic acid was found to be very slow. After a solution of 10 g. of the iodochloro acid in 75 cc. of *tert.*-butyl alcohol had stood for twenty-two hours, it was poured into water. The solid thus precipitated weighed 7 g. and melted with decomposition at 126–127°. It was shown to be principally unchanged a-iodo-j3-chlorophenylpropionicacid by a mixed melting point determination and by its reaction with methyl alcohol to produce a-iodo-@-methoxyphenylpropionicacid; m. p. 167–168°. However, when a solution of the iodochloro acid in *tert.*-butyl alcohol, containing calcium carbonate in suspension, was allowed to stand for ninety-eight hours, the products were cinnamic acid and α-iodo-β-*tert.*-butoxyphenylpropionic acid (8% yield).

The compounds prepared by this method together with the yields, melting points and analyses are given in Table I.

Structure of the Iodomethylmethoxyphenylpropionic Acid.—To a solution of 4.3 g. of potassium hydroxide in 25 cc. of absolute alcohol there was added 3.6 g. of the iodomethylinethoxyphenylpropionic acid melting at 169–170°. After boiling under a reflux condenser for eight hours, the alcohol was distilled off, the residue dissolved in water and acidified. The oil thus precipitated was extracted with ether. The ether was distilled and to the residue was added 100 cc. of 10% sulfuric acid solution. It was then steam distilled until oil ceased to pass over. By extracting the distillate with ether, drying over sodium sulfate and distillation of the solvent, an oil was obtained which partially crystallized on cooling to about 18°. It was shown to be propiophenone by the preparation of its semicarbazone. To a solution of the substance in alcohol was added a concd. aqueous solution of 0.5 g. of seinicarbazide hydrochloride and 0.8 g. of sodium acetate. After boiling under a reflux condenser for about ten minutes, the solution was set aside overnight. Needle-shaped crystals resembling propiophenone semicarbazone as described by Stobbe[7] had then separated. It is insoluble in water. The crude product melted at 168–171". After recrystallization from alcohol, it melted at 173–174°, which agrees with the melting point of propiophenone semicarbazone given in the literature. The formation of propiophenone by these reactions shows that the methoxyl group is in the @-position to the carboxyl group and the substance is α-iodo-α-methyl-β-methoxyphenylpropionic acid.

Structure of the Iodo-*iso*propoxy Acid.—One g. of the iodo-isopropoxy acid melting at 113–114" was treated with alcoholic potassium hydroxide and sulfuric acid according to the procedure described for the iodomethylmethoxyphenylpropionic acid. The product was an oil (0.3 g.) resembling acetophenone in appearance and odor. It reacted with semicarbazide hydrochloride and sodium acetate to give acetophenone semicarbazone; m. p. 195–196". The melting point was unchanged when mixed with known acetophenone semicarbazone. The formation of acetophenone by these reactions shows that the isopropoxyl group is in the @-position to the carboxyl group.

Synthesis of Iodo-alkoxy Acids by the Reaction of Unsaturated Acids with Iodine Monochloride and Alcohols.—To a solution of 5 to 10 g. of cinnamic acid or crotonic acid in the appropriate alcohol, containing in suspension 7 to 15 g. of calcium carbonate, there was added 1.25 moles of iodine monochloride. After standing for sixteen to forty-two hours, the calcium carbonate was filtered off and washed with the appropriate alcohol. However, in the case of crotonic acid the reaction mixture was stirred for ten hours. The filtrate from the calcium carbonate was poured into a large volume of water and decolorized with sodium sulfite. The products from cinnamic acid were

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[7] Stobbe, *Ann.*, 321, 103 (1902).

precipitated as solids, except those resulting from the reactions with *n*-butyl and *iso*-butyl alcohols. Crotonic acid and methyl alcohol gave material soluble in water. The solids thus precipitated were filtered off and the filtrate saturated with sodium chloride, which yielded a small amount of crystals. Additional substance was obtained by dissolving the calcium carbonate in hydrochloric acid. The compounds were purified by dissolving in sodium carbonate solution and treating with potassium permanganate as previously described. Recrystallization from the solvents given in Table I yielded the pure substances. After recrystallization of α-iodo-β-*tert.*-butoxyphenylpropionic acid from chloroform, it was found to retain the solvent and its correct melting point was obtained only after standing in a vacuum desiccator for about twenty-four hours. The compound also combines with benzene.

The product obtained by pouring into water the solution resulting from the reaction of cinnamic acid, iodine monochloride and *n*-butyl alcohol was an oil which did not crystallize after standing for fifteen hours. The oil was separated from the aqueous solution and dissolved in ether. After drying the ethereal solution over calcium chloride and distillation of the solvent, an oil was recovered which crystallized, in part, on cooling in ice. The substance was partially dissolved in benzene and allowed to stand in an open beaker for several days. The crystals were then separated from the oil by suction filtration and recrystallized from benzene.

Likewise, the product of the reaction of cinnamic acid, iodine monochloride and isobutyl alcohol was an oil which did not crystallize on standing in water for two days. Most of the aqueous layer was decanted from the oil, which was then combined with a small amount of oil obtained by dissolving the calcium carbonate in hydrochloric acid. By extracting the oil with ether, drying over sodium sulfate and distillation of the ether, a solution of the substance in isobutyl alcohol was obtained. The isobutyl alcohol was distilled off under diminished pressure, the bath temperature being 85–95°. The resulting product was dissolved in sodium carbonate solution and treated with potassium permanganate in the usual manner. Acidification of the sodium carbonate solution precipitated colorless crystals which were then recrystallized from chloroform.

The iodine precipitated by pouring the solution obtained in the reaction of crotonic acid, iodine monochloride and absolute methyl alcohol into water was filtered off. The excess of iodine monochloride was removed by precipitation with quinoline.[8] The solution was made distinctly acid with hydrochloric acid and quinoline added until precipitation ceased. The solid material was then filtered off and discarded. The filtrate was strongly acidified with hydrochloric acid and thoroughly extracted with ether. The calcium carbonate was dissolved in hydrochloric acid and the solution extracted with ether, which was then combined with the main portion. After drying over sodium sulfate and distillation of the ether, an oil was obtained which partially crystallized on standing overnight. The crystals were separated from the oil by filtration and recrystallized from benzene.

The reaction of 10 g. of cinnamic acid and 1.25 moles of iodine monochloride in 90 cc. of isopropyl alcohol during forty-two hours produced a 22% yield of α-iodo-β-*iso*-propoxyphenylpropionic acid, as given in Table I. In order to test the effect of the concentration of the reacting substances on the yield of the iodo-isopropoxy acid, one mole of iodine monochloride was added in small portions at intervals of several hours to a more dilute solution of cinnamic acid in isopropyl alcohol. To a solution of 5 g. of cinnamic acid in 105 cc. of isopropyl alcohol, containing in suspension 12 g. of calcium carbonate, there was added two or three drops of iodine monochloride; it was then allowed to stand for several hours. This process was repeated until one mole of iodine monochloride had been added during ninety-seven hours. The product was separated

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[8] German patent, 30,358.

as described under the general procedure and purified by treatment with potassium permanganate solution. The yield of α-iodo-β-*iso*propoxyphenylpropionic acid melting at 108–112° was 0.6 g. or 5.3%.

The reaction of unsaturated acids with iodine monochloride and alcohols in the absence of calcium carbonate produces the esters of the iodo-alkoxy acids. Thus, a solution of 10 g. of cinnamic acid and 11 g. of iodine monochloride in 82 cc. of absolute methyl alcohol, after about forty-eight hours, gave 12 g. of solid melting at 65–74° and a small amount of higher melting material. By recrystallization from carbon tetrachloride, or petroleum ether, the pure methyl ester of a-iodo-@-methoxyphenylpropionic acid melting at 68–69° was obtained.

The compounds prepared by this method and the yields are summarized in Table I.

Synthesis of Certain Iodo-alkoxy Acids by the Reaction of Chlorine with Unsaturated Acids, Iodine and Alcohols.—On chlorinating a solution of cinnamic acid and iodine, or an alkali iodide, in absolute methyl alcohol, a-iodo-@-methoxyphenylpropionic acid results. The introduction of chlorine (about 2 liters) into a vigorously stirred solution of 10 g. of cinnamic acid in 50 cc. of absolute methyl alcohol, to which 9 g. of iodine was added in small portions during ten hours, gave a 34% yield of α-iodo-β-methoxyphenylpropionic acid. In a similar manner, a 48% yield of the iodomethoxy acid was obtained by the reaction of about 2 liters of chlorine with a solution of 10 g. of cinnamic acid and 2.4 g. of potassium iodate in 75 cc. of absolute methyl alcohol, to which 8.2 g. of sodium iodide was added over a period of ten hours. Continuation of the reaction over a relatively long period of time yields the ester of the iodomethoxy acid. Thus, the introduction of about 12 liters of chlorine, during two days, into a solution of 20 g. of cinnamic acid in 190 cc. of absolute methyl alcohol, to which 46 g. of potassium iodide was gradually added, produced methyl α-iodo-β-methoxyphenylpropionate (37% yield).

α-Iodo-β-ethoxyphenylpropionic acid was prepared by the reaction of chlorine with cinnamic acid and sodium iodide in absolute ethyl alcohol solution. To a thoroughly stirred solution of 20 g. of cinnamic acid in 200 cc. of absolute ethyl alcohol was added 20 g. of sodium iodide in small portions, chlorine being simultaneously introduced until the iodine had completely reacted, about 4.5 liters being required. After recrystallization of the product from alcohol, there was obtained 6.5 g. of substance melting at 75–125" and 2.5 g. melting at 70–105°. Another crystallization of the material melting at 75–125° from benzene gave 2 g. of crystals melting at 128–138° and some lower melting substance. By dissolving the material melting at 128–138° in sodium carbonate solution and treating with potassium permanganate in the usual manner, crystals melting at 137–138° resulted. No depression of the melting point was produced on mixing with known a-iodo-j3-ethoxyphenylpropionicacid, which was prepared by the procedure of Erlenmeyer.'

The reaction of chlorine with crotonic acid and iodine in absolute methyl alcohol solution, containing calcium carbonate in suspension, gave iodomethoxybutyric acid. However, the yield by this method was less than that obtained with the use of iodine monochloride and the product was more difficult to purify. When the reaction was carried out in the absence of calcium carbonate, the product was a liquid consisting of esters which could not be obtained in the solid state. To a thoroughly stirred solution of 5 g. of crotonic acid in 50 cc. of absolute methyl alcohol, in which was suspended 7 g. of calcium carbonate, there was added 8 g. of iodine in portions of about 1 g. each. The solution was treated with about 2 liters of chlorine during six hours, the iodine color having then disappeared. The resulting oil was distilled at 5 mm. pressure until the boiling point reached 125°. The residue in the distilling flask partially crystallized on standing overnight. The yield of substance melting at 50–60° was 3 g. After several recrystallizations from benzene, pure iodomethoxybutyric acid was obtained.

α-Iodo-β-hydroxyphenylpropionic acid was prepared by treating a suspension of iodine and cinnamic acid in water with chlorine. To a vigorously stirred suspension of 10 g. of cinnamic acid in 1.3 liters of water, there was added 11 g. of finely powdered iodine in small portions, chlorine being simultaneously introduced until the iodine had completely reacted. About 3.5 liters of chlorine were required. The solid was filtered off and the filtrate extracted with ether. After recrystallization of the product from chloroform, 9 g. of slightly impure α-iodo-β-hydroxyphenylpropionic acid melting at 136–142° resulted. Further recrystallization gave the pure compound; m. p. 141–142°.

Summary

α-Iodo-β-chlorophenylpropionic acid has been shown to react with methyl, n-propyl, isopropyl, n-butyl and *tert.*-butyl alcohols to yield the corresponding α-iodo-β-alkoxyphenylpropionic acids.

A more suitable method for the preparation of the iodo-alkoxy acids was found to be the reaction of iodine monochloride with cinnamic acid and the appropriate alcohol. This reaction has been applied to methyl, n-propyl, isopropyl, n-butyl, isobutyl and *tert.*-butyl alcohols. By the reaction of crotonic acid, iodine monochloride and absolute methyl alcohol, iodomethoxybutyric acid was formed. The iodomethoxy and iodoethoxyphenylpropionic acids were also prepared by reaction of chlorine with solutions of cinnamic acid and iodine, or an alkali iodide, in the appropriate alcohol.

That a β-lactone is not an intermediate compound in the formation of the iodo-alkoxy acids from α-iodo-β-chlorophenylpropionic acid was shown by the preparation of methyl α-iodo-β-methoxyphenylpropionate through the reaction of methyl alcohol with the methyl ester of α-iodo-β-chlorophenylpropionic acid. Also, the iodo-alkoxy acids are not formed by the elimination of hydrogen chloride from α-iodo-β-chlorophenylpropionic acid followed by the addition of the alcohols to the double linkage thus produced, since methyl alcohol reacts with α-iodo-α-methyl-β-chlorophenylpropionic acid to give α-iodo-α-methyl-β-methoxyphenylpropionic acid. The iodo-alkoxy acids are produced either by the direct replacement of the chlorine atom by the alkoxyl groups, or by the dissociation of iodine monochloride from the molecule of the iodochloro acid, followed by its reaction with the alcohols to produce the alkyl hypoiodites, which then add to the double linkage of the unsaturated acid. Facts supporting the latter mechanism have been submitted.

Evidence has been given which indicates that in the reaction of iodine monochloride with the alcohols and unsaturated acids, the iodo-alkoxy acids are probably formed by the addition of the alkyl hypoiodites to the unsaturated acids.

The preparation of α-iodo-β-chlorophenylpropionic acid and α-iodo-α-methyl-β-chlorophenylpropionic acid, by the addition of iodine monochloride to the unsaturated acids in carbon tetrachloride solution, has been found to be more convenient than the procedure of Erlenmeyer,

who used an ether solution of the hydrochloride of iodine monochloride. The introduction of chlorine into a suspension of iodine and cinnamic acid in water proved to be a convenient method for the preparation of α-iodo-β-hydroxyphenylpropionic acid.

CLEVELAND, OHIO

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

REDUCTION OF PYRIDINE HYDROCHLORIDE AND PYRIDONIUM SALTS BY MEANS OF HYDROGEN AND PLATINUM-OXIDE PLATINUM BLACK. XVIII[1]

BY T. S. HAMILTON[2] AND ROGER ADAMS

RECEIVED APRIL 17, 1928 PUBLISHED AUGUST 4, 1928

Although the catalytic reduction of pyridine and pyridine derivatives has been described in the literature,[3] no systematic work has been done which makes possible a prediction of satisfactory conditions for reducing compounds which contain the pyridine nucleus. A study has therefore been made of the reduction with hydrogen and platinum-oxide platinum black, of pyridine hydrochloride and pyridonium salts, quinoline and benzyl quinolonium chloride.

It has been found that pyridine alone in most solvents poisons platinum-oxide platinum black and no reduction takes place. On the other hand pyridine hydrochloride can be reduced readily. The selection of the proper solvent, however, is important. Absolute alcohol proved to be the best of those used, with glacial acetic acid second. Peculiarly enough, water in the alcohol inhibits the reduction very markedly and no satisfactory results were obtained using 95% ethyl alcohol or commercial methyl alcohol as a solvent. Absolute methyl alcohol could be used but it did not give such consistent results as absolute ethyl alcohol. Acetone and ethyl acetate do not dissolve the pyridine hydrochloride readily and, therefore, are not suitable.

As a standard run, 0.1 mole of pyridine hydrochloride in 150 cc. of solvent with 0.15 g. of platinum-oxide platinum black from C. P. chloroplatinic acid was used. The time required for the complete reduction was six to seven hours. In fact 0.15 g. of catalyst was the minimum which would allow complete reduction. Increase of the amount of catalyst to 0.3 g. lowered the reduction time to one hour and using 0.5 g. of catalyst lowered

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[1] The last paper in this series was Adams and Marshall, THIS JOURNAL, 50, 1970 (1928).

[2] This paper is a portion of a thesis submitted by T. S. Hamilton in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.

[3] Skita and Brunner, *Ber.*, 49, 1597 (1916); Darzens, *Compt. rend.*, 149, 1001 (1909); Ipatiew, *Ber.*, 41,992 (1908).

the reduction time to thirty minutes. The yields were essentially quantitative in all instances.

Increasing the temperature increased the rate of reduction. With the standard run the reduction was carried out at room temperature. If the temperature was increased to 50°, the time for reduction dropped from six or seven hours to less than two hours.

Small amounts of ferrous salts and other mineral salts, which acted as promoters in the reduction of aldehydes, did not affect the reduction of pyridine hydrochloride. Oxygen and air, however, revivified a catalyst which had begun to be sluggish, and were employed in reductions which required a good many hours for completion.

Although all of these various conditions were not studied in the reduction of the pyridonium salts, a sufficient number of experiments was completed to show that, qualitatively, the pyridine hydrochloride and pyridonium salts were affected in the same way by changes in conditions. Using 0.1 mole of salt in 150 cc. of absolute alcohol and 0.15 g. of platinum-oxide platinum black, the following substances were reduced quantitatively to the corresponding hexahydro compounds in the following times: pyridine hydrochloride, six to seven hours; phenyl pyridonium chloride, two and one-quarter to two and one-half hours; n-butyl pyridonium chloride, one and one-half to two hours; ethyl pyridonium chloride, one to one and one-quarter hours; benzyl pyridonium chloride, one-half to three-quarters hour; carbo-ethoxymethyl pyridonium chloride, one-half to three-quarters hour; β-hydroxyethyl pyridonium chloride, three to three and one-quarter hours; γ-hydroxypropyl pyridonium chloride, one and three-quarters to two and one-half hours.

It is interesting that the pyridonium salts are in every instance more readily reduced than pyridine hydrochloride.

The quinoline and quinoline derivatives can be reduced to the tetrahydro compounds in exactly a similar manner. The reaction was carried out with quinoline hydrochloride and benzyl quinolonium chloride.

The general method should be of value in the reduction of alkaloids containing pyridine or quinoline nuclei.

Experimental

Catalyst.—The platinum-oxide platinum black was made by the method of Adams and Shriner[4] from C. P. chloroplatinic acid. Platinum oxide prepared by dissolving spent catalyst and reprecipitating without purification was not satisfactory for these reductions. The apparatus was that usually used and the procedure was exactly that which has been described before. Platinum oxide was reduced to platinum black in every instance in the presence of *a* solution of pyridine hydrochloride or pyridonium salt. The lag was approximately three minutes in most cases.

Preparations of Compounds to Be Reduced.—The pyridine used in the preparation of all compounds boiled between 116 and 118°.

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[4] Adams and Shriner, THIS JOURNAL, 45, 2171 (1923).

Pyridine hydrochloride was prepared by passing dry hydrogen chloride into dry pyridine dissolved in dry ether. It was necessary that the mixture be kept cold and that it be stirred constantly. The pyridine hydrochloride precipitated from the ethereal solution in a white, flocculent mass and settled quickly to the bottom of the flask. After the flask had increased to a weight indicating that approximately 85% of the pyridine had been changed to the hydrochloride, the salt was rapidly filtered into a Büchner funnel, taken up twice with absolute ether and the last traces of ether were removed by placing in a desiccator over calcium chloride and repeatedly evacuating. Because of the very deliquescent nature of the pyridine hydrochloride, it was stored in tightly stoppered bottles in a desiccator.

The ethyl and butyl chloride addition compounds of pyridine were made by mixing pyridine and the alkyl chloride in molecular proportions (usually the alkyl chloride in slight excess) and heating the mixture in a sealed tube on a steam-bath for several days or until the entire mixture had solidified. After opening the tube, the contents were washed out with as small as possible a quantity of warm absolute alcohol, the solution was cooled and the addition compound thrown out of the alcoholic solution by the addition of cold absolute ether. The ethyl and butyl chloride addition compounds were amber colored oils.

The phenyl pyridonium chloride was prepared by the method of Weitz, Konig and v. Wistinghausen.[5]

The benzyl chloride, chloroacetic acid, chloroacetic ester, ethylene and trimethylene chlorohydrin addition compounds were all prepared by the interaction of equimolecular quantities of pyridine and the compound to be added. The benzyl chloride, ethylene and trimethylene chlorohydrin derivatives were made by warming the mixture to start the reaction. It was sometimes necessary to cool the flask to prevent too vigorous boiling (especially true of the benzyl chloride compound). The chloroacetic acid and ethyl chloroacetate compounds were made merely by adding these compounds to pyridine and allowing the mixtures to stand in casseroles in a desiccator for a few days. The contents solidified after that time.

The addition compounds were isolated by crystallization from an ether–alcohol solution. Usually the compound was dissolved in a small amount of warm absolute alcohol, the solution cooled and the compound precipitated by the addition of cold ether, and by allowing to stand in a cold place. All compounds are very hygroscopic and the utmost care must be taken in order to obtain the salts in crystalline form, and to eliminate small quantities of water which inhibit the reductions.

Isolation of Products.—For the isolation of the reduced compounds the hydrogen was removed from the reduction bottle by suction and the bottle then shaken with air for ten to fifteen minutes in order to coagulate the platinum black, which was then filtered off. All reduced compounds were less hygroscopic and also less soluble in absolute alcohol than the unreduced. Piperidine hydrochloride may be quantitatively recovered from the alcoholic solution by concentration and crystallization. In all other cases, however, it was better to precipitate the reduced compound by adding ether until a precipitate just failed to appear and allowing to cool.

In the identification of all compounds, both those to be reduced and those reduced, the melting point of the hydrochloride was taken if possible (this was possible in but few cases), or a double salt, usually with platinum chloride, was made, or the free base was obtained by saturating with 40% sodium hydroxide and extracting with ether. In the latter case, after distillation of the ether, the boiling point of the free base was determined.

[5] Weitz, König and v. Wistinghausen, Ber., **57**, 166 (1924).

The compounds prepared in this investigation are listed in Table I.

TABLE I

CONSTANTS OF AND REFERENCES TO UNREDUCED AND REDUCED COMPOUNDS

Compounds to be reduced	Ref.	Reduced products	Ref.	HCl salt, m. p., °C.	Base, b. p., °C.
$C_5H_5N \cdot HCl$	(1)	$C_5H_{11}N \cdot HCl$	(11)	236–237	...
$C_5H_5N \cdot C_2H_5Cl$	(2)	$C_5H_{11}NC_2H_5 \cdot HCl$	(12)	204[a]	127.6
$C_5H_5N \cdot C_4H_9Cl$	(3)	$C_5H_{11}NC_4H_9 \cdot HCl$	(13)	.....	175–177
$C_5H_5N \cdot C_6H_5Cl$	(4)	$C_5H_{11}NC_6H_5 \cdot HCl$	(14)	.....	258–260 (754 mm.)
$C_5H_5N \cdot C_6H_5CH_2Cl$	(5)	$C_5H_{11}NCH_2C_6H_5 \cdot HCl$	(15)	.....	247–251 (750 mm.)
$C_5H_5N \cdot ClCH_2COOH$	(6)	$C_5H_{11}NCH_2COOH \cdot HCl$	(16)	215–216	...
$C_5H_5N \cdot ClCH_2COOC_2H_5$	(7)	$C_5H_{11}NCH_2COOC_2H_5 \cdot HCl$	(17)	.....	209–212 (736 mm)
$C_5H_5N \cdot ClCH_2CH_2OH$	(8)	$C_5H_{11}NClCH_2CH_2OH \cdot HCl$	(18)	.....	200–202 (742 mm.)
$C_5H_5N \cdot ClCH_2CH_2CH_2OH$		$C_5H_{11}NClCH_2CH_2CH_2OH \cdot HCl$	(19)	.....	194–196 (746 mm.)
$C_9H_7N \cdot HCl$	(9)	$C_9H_{13}N \cdot HCl$[b]	(20)	.....	...
$C_9H_7N \cdot C_6H_5CH_2Cl$	(10)	$C_9H_{13}NCH_2C_6H_5 \cdot HCl$[b]		.....	...

[a] Platinum chloride double salt.

[b] These compounds were not isolated. It was merely shown that the calculated amount of hydrogen was taken up for their formation.

(1) *Ann.*, **247**, 5 (1888); (2) *Monatsh.*, **15**, 180 (1894); (3) *Ann.*, **276**, 182 (1893); (4) *Ber.*, **57**, 166 (1924); (5) *J. prakt. Chem.*, [2] **41**, 345 (1890); (6) *ibid.*, **43**, 287 (1891); (7) *ibid.*, **43**, 271 (1891); (8) *Monatsh.*, **15**, 668 (1894); *Arch. Pharm.*, **240**, 78 (1902); (9) *Ber.*, **12**, 1322 (1879); (10) *Jahresber.*, **1882**, 1109; (11) *Ann.*, **247**, 55 (1888); (12) *Ber.*, **23**, 2570 (1890); *Ann. chim. phys.*, [3] **38**, 76 (1853); (13) *Ber.*, **40**, 3930 (1907); (14) *Ber.*, **21**, 2279 (1888); (15) *Ber.*, **32**, 74 (1899); *J. Chem. Soc.*, **99**, 1927 (1911); (16) *Ber.*, **32**, 728 (1899); (17) *Ber.*, **31**, 2840 (1898); (18) *Ber.*, **14**, 1877 (1881); (19) *Ber.*, **14**, 1876 (1881); (20) *Ber.*, **27**, 1479 (1893).

Summary

It has been shown that pyridine hydrochloride, quinoline hydrochloride or the corresponding pyridonium and quinolonium salts are readily reduced by means of hydrogen and platinum-oxide platinum black to the hexahydro compounds in the case of pyridine and tetrahydro compounds in the case of quinoline. The reductions under various conditions are described.

URBANA, ILLINOIS

[CONTRIBUTIONPROM THE FURMAN CHEMICAL LABORATORY, VANDERBILT UNIVERSITY]

A SECOND NEW METHOD FOR THE COMPLETE RESOLUTION OF EXTERNALLY COMPENSATED ACIDS AND BASES

BY. A. W. INGERSOLL

RECEIVED MAY 17, 1928 PUBLISHED AUGUST 4, 1928

In a previous paper[1] the author has described a new method for the resolution of externally compensated acids and bases by which both active forms are obtained completely pure.[2] In its simplest form the method requires two main steps. First, for example, an inactive base (dl-B) is combined with an active acid, for example, d-A, and the resulting salts d-B-d-A and *l*-B-*d*-A are fractionally crystallized until the less soluble one, for example, 2-B-d-A, is pure. From this salt pure *l*-B is obtained by hydrolysis. From the mother liquors there will be obtained on hydrolysis a mixture of the two active bases with d-B in excess. For convenience this mixture may be regarded as dl-B + d-B.

In the second step this mixture is dissolved with an equivalent amount of the inactive form of the acid originally used (dl-A), or with any suitable externally compensated acid. Upon crystallization the ions now in solution may combine in one of two ways, depending on whether the inactive acid is resolved by the active base present in excess (Equation 1) or forms a half racemic salt with it (Equation 2).

$$(\text{dl-B} + \text{d-B}) + \text{dl-A} \longrightarrow \text{dl-B-dl-A} + \text{d-B-d-A} + \text{d-B-I-A} \qquad (1)$$

$$(\text{dl-B} + \text{d-B}) + \text{dl-A} \longrightarrow \text{dl-B-dl-A} + \text{d-B-dl-A} \qquad (2)$$

When the situation is represented by Equation 1 and when the d-B-I-A salt is the least soluble, the latter can be obtained pure by fractional crystallization. From the pure 2-B-d-A and d-B-I-A salts thus obtained in the two steps, both active forms of the base, and of the acid as well, may be obtained by hydrolysis. Two cases in which a complete resolution was effected in this way were described in the previous paper.

It is apparent, furthermore, that a complete resolution of the base (though not of the acid) is also possible when Equation 2 represents the second step of the process. Thus whenever the half racemic salt d-B-dl-A is less soluble than the inactive salt, the former, and its component base, can be obtained pure. The present paper contains a description of a complete resolution based upon this behavior. Thus inactive *iso*-diphenylhydroxy-ethylamine was partially resolved in the usual way with d-camphor-10-sulfonic acid,[3] the less soluble d-B-d-A salt being obtained

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[1] Ingersoll, THIS JOURNAL, 47, 1168 (1925).

[2] Some interesting modifications of the older methods have recently been described by Read and Reid, J. *Soc.* Chem. *Ind.*, 47, 8T (1928).

[3] The resolution of *iso*-diphenylhydroxy-ethylamine was first carried out by Erlenmeyer, Ber., 32, 2377 (1899); 36, 978 (1903); *Ann.*, 337, 307 (1904), using helicin or tartaric acid. The resolution with tartaric acid has recently been improved by Read

pure in the first step. The base recovered from the mother liquors (dl-B + *l*-B) was combined with inactive camphorsulfonic acid and the salts fractionally crystallized. The half racemic salt 2-B-dl-A was the first to separate and was readily purified. Alkaline hydrolysis of the pure d-B-d-A and *l*-B-*dl*-A salts thus obtained gave the pure isomeric bases in excellent yields. The pure *l*-B-*d*-A and dl-B-dl-A salts were also synthesized for comparison. All the salts of this series have one molecule of water of crystallization. The solubilities in water at 25° were in the order d-B-d-A < *l*-B-*dl*-A < l-B-d-A < dl-B-dl-A.

Generality of the Combined Methods

So far as the second step is concerned, both of the methods (depending on Equation 1 and Equation 2, respectively) appear to be new in principle and of rather general utility. Since the same reagents and procedure are used in both methods, these are mutually complementary and afford a double chance for successfully completing a resolution. They may be applied equally well to the resolution of an acid or a base. They should hold also for ester, amide, hydrazone, imine and similar combinations as well as for salts.

It is clear, however, that each method depends for its success on a favorable order of solubility of the isomeric compounds involved. This point has been discussed in the previous paper, for resolutions depending on Equation 1. While there seems to be no rule known at present from which it can be predicted that the order of solubility will always be favorable, it is remarkable that of the three cases thus far studied all have resulted in complete resolutions. A fourth case now being studied, that of the acid tartrates of iso-diphenylhydroxy-ethylamine, has also given preliminary results indicating a similar behavior. The uniformity of these results points to the probable existence of an underlying rule and the study is being continued in the hope of disclosing such a rule.

Experimental Part

Partial Resolution of the Base.—In one experiment a solution containing 42.6 g. of inactive iso-diphenylhydroxy-ethylamine, m. p. 130°, and 48.0 g. of d-camphor-10-sulfonic acid in 1 liter of water was decolorized and the solute fractionally crystallized. While the first crop of crystals showed a strongly positive rotation the following crops showed an alternation of low and high rotations. The further separation of these was therefore best carried out by combining similar fractions in fresh solvent and seeding with samples of the extreme fractions. Working in this way there was obtained 35.2 g. of the pure d-B-d-A salt in the less soluble

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and Steele, *J. Chem. Soc.*, 131, 910 (1927), who mentioned also the use of camphorsulfonic acid but gave no details.

fraction. In later experiments it was found that the separation could also be effected readily by using moist ethyl acetate (3% water) as solvent.

d-iso-**Diphenylhydroxy-ethylamine** d-Camphorsulfonate forms masses of small prisms from water or distinct crystals from moist ethyl acetate, both being hydrated. It is soluble in about 59 parts of water at 25°. The anhydrous salt melts indistinctly at 207–208' (corr.) but the melting points of this series of salts are not good indications of purity.

Anal. Subs., 1.8429: lost 0.0704 g. at 105°. Calcd. for $C_{24}H_{31}O_5NS \cdot H_2O$: H_2O, 3.88. Found: H_2O, 3.82.

Rotation (Hydrated salt). Subs., 0.8005: made up to 50 cc. in water gave $\alpha^{22}_{D} = +1.88°$ in a 2-dm. tube. Hence $[\alpha]^{22}_{D} = +58.7°$. (Anhydrous salt). Subs., 0.9442: made up to 50 cc. in water gave $\alpha^{22}_{D} = +2.31°$ in a 2-dm. tube. Hence $[\alpha]^{22}_{D} = +61.2°$; $[M]_D = +272°$. Assuming $+52°$ as the molecular rotation of the d-camphorsulfonate ion, $[M]_D$ for the base ion is $+220°$.

d-iso-**Diphenylhydroxy-ethylamine.**—A warm solution of the d-B-d-A salt was treated with excess ammonium hydroxide. The precipitated base after one crystallization from alcohol melted at 115.2" (corr.) and had $[\alpha]^{22}_{D} = +125.1°$ in absolute alcohol, values that confirm those of Read and Steele.[3]

l-iso-**Diphenylhydroxy-ethylamine *d*-Camphorsulfonate.**—The more soluble fractions obtained in the resolution were combined and recrystallized several times from water. The extreme specific rotation observed was –33.5'. In a later experiment the pure I-B-d-A salt was obtained by combining the pure 2-base (obtained as described in the next section) with *d*-**camphorsulfonic** acid. As its specific rotation was –36.1° the salt obtained in the resolution was still somewhat impure. The pure salt crystallizes from water in long, tetragonal prisms. It is soluble in about 32 parts of water at 25° and is hydrated. It is much more soluble in ethyl acetate than the d-B-d-A salt. The anhydrous salt melts at 205–206° (corr.).

Anal. Subs., 1.1226: lost 0.0434 g. at 105°. Calcd. for $C_{24}H_{31}O_5NS \cdot H_2O$: H_2O, 3.88. Found: H_2O, 3.87.

Rotation. (Hydrated salt). Subs., 0.8113: made up to 50 cc. in water gave $\alpha^{22}_{D} = -1.17'$ in a 2-dm. tube. Hence $[\alpha]^{22}_{D} = -36.1°$. (Anhydrous salt). Subs., 1.0792: made up to 50 cc. in water gave $\alpha^{22}_{D} = -1.62°$ in a 2-dm. tube. Hence $[\alpha]^{22}_{D} = -37.5°$: $[M]_D = -167°$; $[M]_D$ for the base ion –219".

Completion of the Resolution

A sample of the base (16.0 g.) recovered from the intermediate fractions of the original resolution ([a], = –58°; 46% excess I-base) was combined with inactive camphorsulfonic acid (18.0 g.) in sufficient water (450 cc.) so that about half of the total salt separated on cooling. The first crop (15.3 g.) had $[\alpha]_D = -43°$. By systematic crystallization there was finally obtained 12.7 g. of pure, hydrated *l*-B-*dl*-A salt in the less soluble fraction. In a further experiment 12.3 g. of base having [a], = –108° (87% excess I-base) was combined with 14.0 g. of inactive camphorsulfonic acid. There was easily obtained 20.3 g. of pure I-B-dl-A salt.

l-iso-**Diphenylhydroxy-ethylamine *dl*-Camphorsulfonate** crystallizes from water in small prisms or feathery clusters. It is soluble in about 42 parts of water at 25° and is hydrated. The anhydrous salt melts at 206–207° (corr.).

Anal. Subs., 3.3332: lost 0.1306 g. at 105". Calcd. for $C_{24}H_{31}O_5NS \cdot H_2O$: H_2O, 3.88. Found: H_2O, 3.92.

Rotation (Hydrated salt). Subs., 0.8397: made up to 50 cc. in water gave $\alpha^{22}_{D} = -1.62'$ in a 2-dm. tube. Hence $[\alpha]^{22}_{D} = -48.4'$. (Anhydrous salt). Subs., 0.8443:

made up to **50** cc. in water gave $\alpha_D^{22} = -1.72°$ in a 2-dm. tube. Hence $[\alpha]_D^{22} = -50.3°$; $[M]_D = -223°$.

l-iso-Diphenylhydroxy-ethylamine was obtained from the pure **I-B-dl-A** salt and purified as described for the d-base. It melted at 115.2° (corr.) and had $[\alpha]_D^{22} = -125.6'$ in absolute alcohol; values in agreement with those of the d-base.

d-iso-Diphenylhydroxy-ethylamine *dl*-Camphorsulfonate.—For comparison this salt was made from the pure components. It is similar in all respects to the enantiomorphous *l*-B-*dl*-A salt.

Rotation (Hydrated salt). Subs., **1.0242:** made up to 50 cc. in water gave $\alpha_D^{22} = +1.98°$ in a 2-dm. tube. Hence $[\alpha]_D^{22} = +48.2°$.

dl-iso-Diphenylhydroxy-ethylamine *dl*-Camphorsulfonate.—From the mother liquors from the separation of the *l*-B-*dl*-A salt there was obtained a much more soluble salt in masses of poorly formed prisms. It still showed **a** faint negative rotation. For comparison the pure salt was made from the pure components. It is soluble in about **26** parts of water at 25° and is hydrated. The anhydrous salt melts at 198–199° (corr.).

Anal. Subs., **3.6527:** lost **0.1392 g.** at 105°. Calcd. for $C_{24}H_{31}O_5NS{\cdot}H_2O$: H_2O, **3.88.** Found: H_2O, **3.81.**

The author is indebted to the University of Illinois for part of the chemicals used and for laboratory facilities during part of the work.

Summary

A second new method for the complete resolution of externally compensated compounds has been described in connection with a related method previously described. The method was applied to the resolution of inactive iso-diphenylhydroxy-ethylamine with d- and dl-camphorsulfonic acids.

NASHVILLE, TENNESSEE

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

THE MECHANISM OF CARBOHYDRATE OXIDATION. IX. THE ACTION OF COPPER ACETATE SOLUTIONS ON GLUCOSE, FRUCTOSE AND GALACTOSE[1]

BY W. L. EVANS, W. D. NICOLL, G. C. STROUSE AND C. E. WARING[2]

RECEIVED MAY 19, 1928 PUBLISHED AUGUST 4, 1928

The mechanisms proposed in some of the more recent literature dealing with the oxidation of carbohydrates in alkaline solutions rest on one or more of the following ideas: *(a)* that carbohydrates in alkaline solutions are converted into equilibrated systems consisting of a number of isomeric carbohydrates;[3] (b) that these carbohydrates give rise to a series of three

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[1] Presented to the Second National Symposium on Organic Chemistry, Columbus, Ohio, December **29, 1927.** References have been made in this communication to papers which have appeared subsequently.

[2] E. I. DuPont de Nemours Fellow, **1927.**

[3] (a) De Bruyn and van Ekenstein, Rec. *trav. chim.*, **14, 156, 203 (1895); (b) 15, 92 (1896);** (c) **16, 257, 262, 274 (1897);** (d) **19, 1 (1900);** (e) **27, 1 (1908);** (f) Wolfrom with Lewis, THIS JOURNAL, **50,842 (1928).**

enediols which form a restricted equilibrium;[4] (*c*) that the general equilibrium consisting of the components in (*a*) and (b) may be influenced by certain experimental factors, such as a change in both the temperature of the reaction and also the concentration of the alkali used.[5] Nef[6] states that these enediols do not exist in solutions of an alkalinity less than $N/30$, and that they begin to decompose in systems above an alkalinity of $N/20$. In view of the data obtained in this Laboratory with reference to the behavior of glucose, mannose and fructose toward aqueous solutions of potassium hydroxide, the question arises whether one or more of these enediols may not exist in alkaline solutions of even lower normality than $N/30$ and possibly in solutions of less PH value than 7; that is, would the molecular mechanism involved in the oxidation of these sugars in an acid solution be in harmony with the concept which postulates the presence of enediols as intermediate substances in reactions of this character?

Experimental Part

The following is an account of the experimental methods used by us in this investigation.

Oxidizing Agent.—Copper acetate was chosen as our oxidizing agent by reason of the following distinct advantages. (*a*) A saturated solution of this salt is acid. (*b*) Since the cupric ion is reduced to the cuprous condition during the progress of the reaction, the cuprous oxide thus formed becomes an accurate measure of the oxygen consumed in the oxidation. (c) Although preliminary experiments showed that the rate of oxidation of fructose with copper acetate is greater than that of either glucose or galactose under the same conditions, yet the reaction proceeds slowly enough for the purposes of measurement and it may be stopped at any desired time. (*d*) Certain compounds formed in the oxidation of carbohydrates in acid solutions may escape detection when the same sugars are oxidized in alkaline solutions by reason either of their very rapid rearrangement to other compounds or a further oxidation of the intermediates. (e) The unused copper ion is easily removed from solution with hydrogen sulfide.

Oxidation Procedure.—Nine-tenths g. of either glucose, fructose or galactose was placed in a 250-cc. Florence flask containing 25 cc. of **a** copper acetate solution pre-

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[4] (a) Nef, *Ann.*, 403, 208–213 and note on 239 (1915); (b) compare Powell, *J. Chem. Soc.*, 107, 1335 (1925), also Armstrong, "The Carbohydrates and the Glucosides," Longmans, Green and Co., 1924, p. 59; (c) Anderson, *Am. Chem. J.*, 42, 407 (1909); (d) Spoehr, *ibid.*, 43, 241 (1910); (e) Upson, *ibid.*, 45, 458 (1911); (f) Glattfeld, *ibid.*, 50, 135 (1913); (g) Jensen and Upson, THIS JOURNAL, 47, 3023 (1925); (h) Gustus with Lewis, *ibid.*, 49, 1512 (1927).

[5] Evans and co-workers, *ibid.*, 47, 3086 (1925); 48, 2666 (1926); 50, 1496 (1928); Amick, *J. Phys. Chem.*, 31, 1473 (1927).

[6] Nef, *Ann.*, 403, 224 (1915).

viously saturated at 50°. To this mixture an excess of copper acetate was added, the amount of it depending on the duration of the experiment. For all experiments of less than one hundred hours 10 g. was added, while 15 g. was sufficient for the longer periods. The flask was closed with a tightly fitting rubber stopper and was then shaken by means of a mechanical agitator in a thermostat kept at 50".

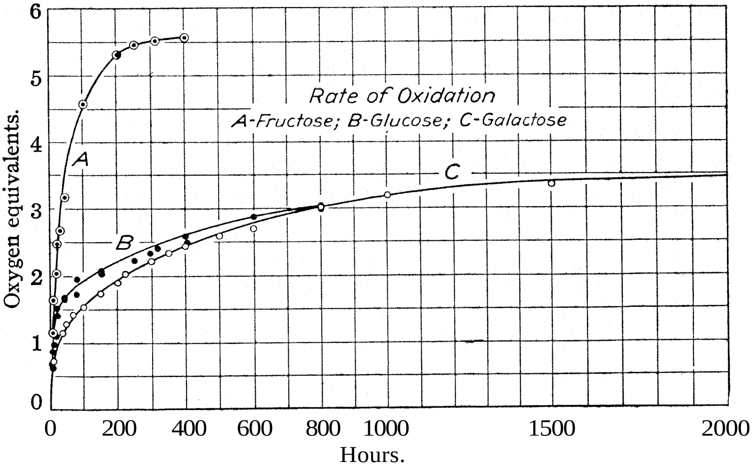

Fig. 1.—Rate of oxidation.

Determination of Consumed Oxygen.—When the sugar had been oxidized for the desired length of time, the flask was removed and cooled with tap water before taking out the stopper in order to avoid the loss of volatile products, for instance, formic acid. The cuprous oxide and unchanged copper acetate were collected in a weighed Gooch crucible, the excess of the acetate being removed by washing the residue with about 50 cc. of cold water. The crucible contents were dried in a vacuum oven at 70–80° without any appreciable oxidation of the cuprous oxide. The rate at which oxygen is used up by these carbohydrates in solutions of copper acetate at 50° is shown in Fig. 1. In Fig. 2, it is seen that the relation between the logarithm of the oxygen equivalents and that of the experimental period is a linear one.

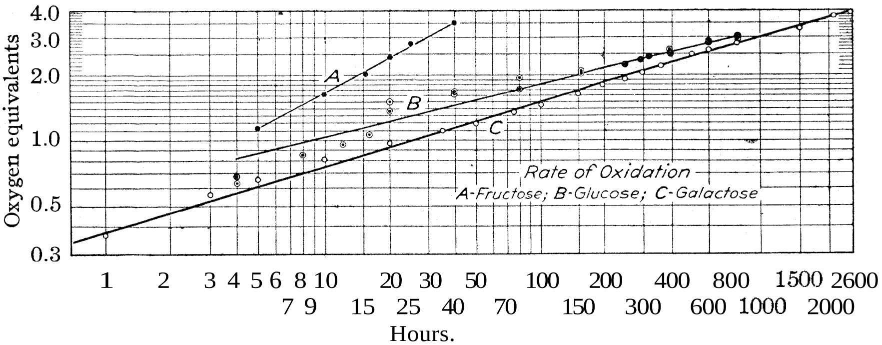

Fig. 2.—Rate of oxidation.

Reaction Products.—Our reaction mixtures were examined for oxalic, formic, glyoxylic and carbonic acids, and glucosone. The percentages of the hexose carbon converted into each of these compounds is expressed as a function of the time in Figs. **3,** 4 and **5.** The number of oxygen equivalents used per gram molecular weight of the hexose was calculated by dividing the weight of the cuprous oxide by the factor 0.716.

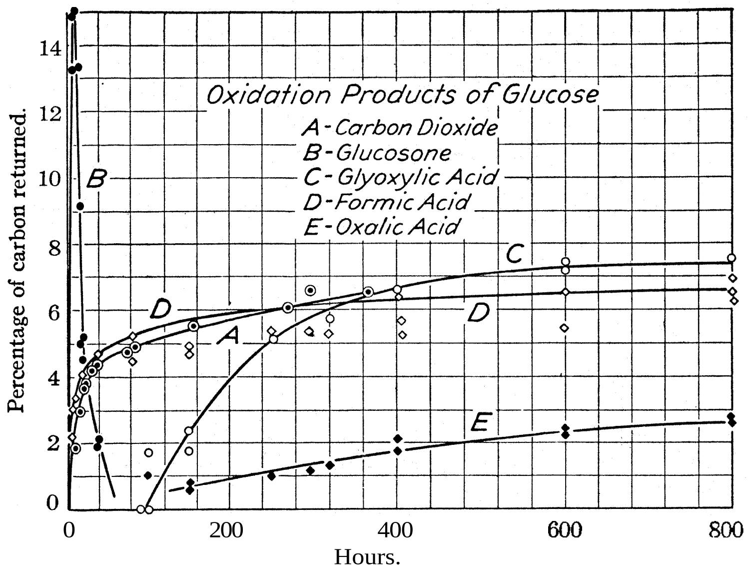

Fig. 3.—Oxidation products from glucose.

The percentages of the hexose carbon converted to the reaction products for which our mixtures were examined is expressed as a function of the oxygen equivalents in each case in Figs. 6, 7 and 8.

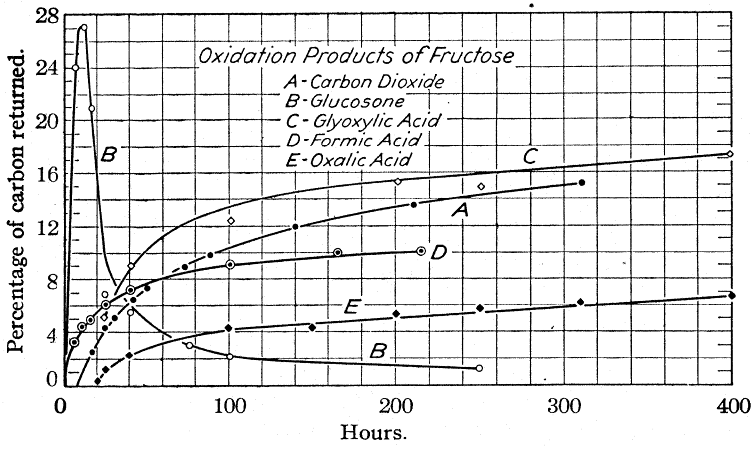

Fig. 4.—Oxidation products from fructose.

Oxalic Acid. (a) Qualitative Identification.—When the cuprous oxide and the unused solid copper acetate from the oxidations of longer duration had been filtered and washed with water, a greenish-white, scaly material was found associated with the residual cuprous oxide. From the work of McLeod[7] it was thought that this substance might be copper oxalate, although this investigator states that the cuprous oxide obtained by him contained no copper oxalate. Our suspected oxalate was soluble in dilute ammonium hydroxide solution. Its identity was established by its conversion to the calcium salt, the composition of which was determined by titrating with potassium permanganate in the presence of sulfuric acid, and also by converting a weighed portion dried in *vacuo* at 120° into the sulfate. This specimen of calcium oxalate contained 27.3% of calcium, while the monohydrate contains 27.43%. Furthermore, the oxalic acid present in the above ammoniacal solution was also converted into the highly insoluble phenylhydrazine oxalate.[8]

(b) Quantitative betermination.--The oxalic acid in these oxidations was determined quantitatively essentially as just described. The cuprous oxide residue was

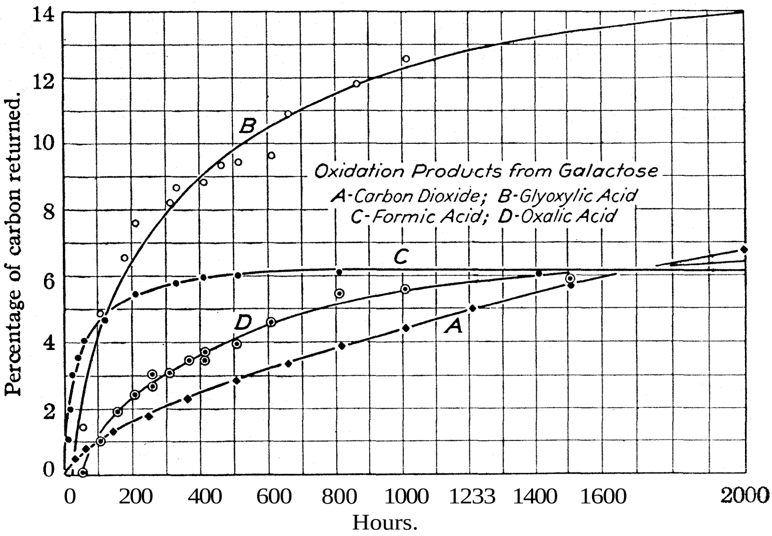

Fig. 5.—Oxidation products from galactose.

treated with 25 to 30 cc. of dilute ammonium hydroxide (1:19). By this procedure small amounts of the cuprous oxide as well as the cupric oxalate were dissolved. In all of the quantitative data throughout this report, the necessary corrections for the solubility of cuprous oxide have been made at the appropriate places. After acidifying the ammoniacal filtrate with acetic acid, the oxalic acid was precipitated as calcium oxalate, which was measured in the way described above.

The formula given by Schaefer[9] for cupric oxalate is $CuC_2O_4\cdot{}^1/_2H_2O$. This formula was used in determining the correction to be applied to the weight of the cuprous oxide obtained in our oxidation curves. The solubility of the oxalate, as determined by Schaefer by conductivity methods at 25°, is 0.02364 g. per liter. It was conclusively proved that all of the oxalic acid obtained in these oxidations was present as the in-

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[7] McLeod, *Am. Chem. J.*, **37**, 20 (1907).

[8] Fischer, *Ann.*, 190, 85 (1878). See Evans, Mong and Sinks, THIS JOURNAL, **39**, 1724 (1917).

[9] Schaefer, *Z.* anorg. *Chem.*, *45*, 310 (1905).

soluble oxalate, since the original filtrates showed no evidence of the presence of this acid.

Formic Acid.—The original filtrate obtained in the procedure described above under "Determination of Consumed Oxygen" was made copper ion-free in the cold by means of hydrogen sulfide. The addition of 1 g. of sodium chloride to this filtrate was found to be fairly effective in preventing the formation of colloidal cupric sulfide. After removing the copper sulfide by suction and washing with water, the filtrate usually had a volume of approximately 150 cc. The presence of formic acid was established by distilling a portion of this copper ion-free filtrate in a vacuum apparatus through which a small amount of natural gas instead of air was allowed to pass. This distillate was examined for formic acid by Fincke's method.[10] It was also found to decolorize dilute alkaline potassium permanganate solutions in the cold. Formic acid was determined quantitatively by using a modification of Jones' well-known method.[11]

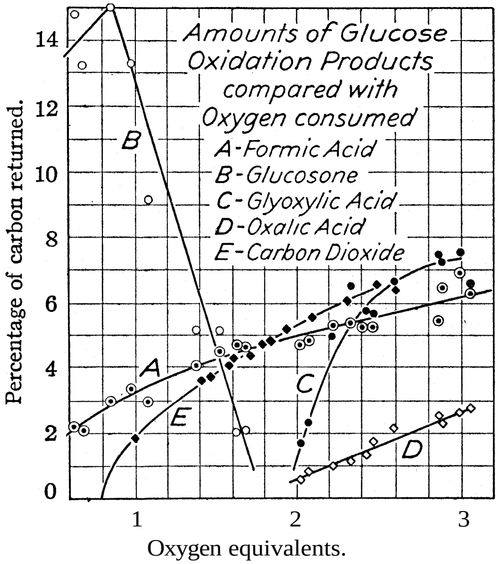

Fig. **6.**

Glyoxylic Acid. Qualitative Identification.—(a) The solution obtained by the removal of the copper ions from the filtrate from the cuprous oxide, unused solid copper acetate and the copper **oxalate** resulting from the oxidation of 0.90 g. of fructose for 165 hours was evaporated to dryness, thus removing formic and acetic acids. On theoretical grounds, we had reason to think that glyoxylic acid should be one of the reaction products in these oxidations. The solution obtained by dissolving the residue resulting from this evaporation in 100 cc. of water was treated with a calcium acetate solution in the hope that calcium glyoxalate would precipitate. By reason of the known insolubility of copper oxalate, we were much surprised to learn that our fine, white precipitate was calcium oxalate. In the filtrate from this precipitate, there began a deposition of comparatively large crystals which were shown by microscopic examination to be different from calcium oxalate. A solution obtained by the same procedure from an experiment with 0.90 g. of fructose for 215 hours yielded almost 0.30 g. of these same crystals. When 0.2806 g. of the crystals, previously dried in a desiccator, was fumed with sulfuric acid, 0.1775 g. of calcium sulfate was obtained. This corresponds to 18.62% of calcium, while calcium glyoxalate dihydrate ($Ca(C_2HO_3)_2 \cdot 2H_2O$) contains 18.02% of calcium. In a similar procedure, 0.90 g. of these crystals was obtained from the 200, 300 and 400 hour experiments with galactose. On analysis these were found to contain 18.35% of calcium. When the solution from a 200-hour experiment with galactose was treated with barium acetate instead of calcium acetate, a white and fairly crystalline compound

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[10] Fincke, *Z. Nahr. Genussm.*, **21,** 1 (1911); **22,** 88 (1911); see Bender, Bur. of Chem. ***Bull.,*** 162, 78 (1912).

[11] Jones, *Am. Chem.* **J., 17, 539** (1887); see Evans, Edgar and Hoff, THIS JOURNAL, 48, 2667 (1926).

was obtained after twenty-four hours' standing. When filtered immediately after precipitation and dried at 100°, this substance had a barium content of 49.9% when fumed with sulfuric acid. An air-dried specimen obtained by slow precipitation was found to contain 47.06% of barium. Anhydrous barium glyoxalate contains 48.48% of barium, the monohydrate 45.59%, and the oxalate monohydrate 56.54%. (b) Positive identification of glyoxylic acid was made as follows. After the original filtrates from a 200-hour experiment with fructose and a 300-hour experiment with galactose had been made copper ion-free, they were treated without previous distillation with 3 cc. of phenylhydrazine. If the slow-forming precipitate contained glyoxylic acid phenylhydrazone, then according to Fischer's[12] observations, the latter should be soluble in alkali and be reprecipitated on treatment with hydrochloric acid. When so treated the lemon-yellow colored precipitate was found to melt at 143° (uncorr.). Fischer gave 138°, Pechmann[13] found 143–145°.

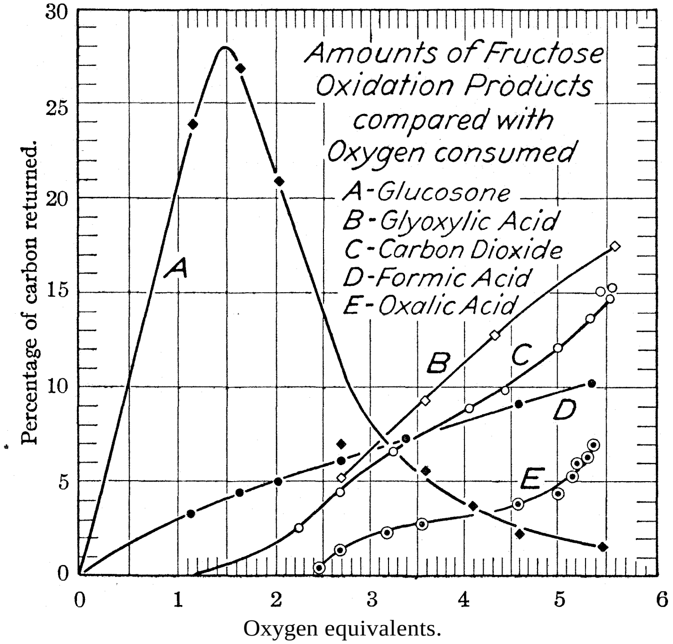

Fig. 7.

Qualitative Identification of **Glucosone.**—When the original filtrates from the glucose and fructose oxidations of five to ten hours' duration were made copper ion-free and were then treated with phenylhydrazine in the cold, glucosazone was immediately precipitated. This behavior corresponds with that of glucosone, which is known to form the osazone in the cold immediately. A control test on glucose and fructose under similar conditions showed that it took several hours for the osazone to precipitate. No galactosone was found in our experiments.

Presence of Unchanged Glucose and Fructose.—If the glucosazone formed on standing at room temperature for about an hour is filtered, and the resulting filtrate is

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[12] Fischer, *Ber.*, 17, 577 (1884).

[13] Pechmann, *Ber.*, 29, 2163 (1896).

heated at 100° for an hour, the amount of precipitated glucosazone is so large that it can hardly be accounted for on the ground that it resulted only from the osone still remaining in the solution.

Determination of **Glyoxylic** Acid, Glucosone and Unchanged Carbohydrate.—The following method was adopted for the estimation of glyoxylic acid, glucosone and unchanged carbohydrate. The solution which had been made copper ion-free was made up to 100 cc. and then treated with 3 cc. of phenylhydrazine. The mixture was allowed to stand at room temperature for three hours. Parallel experiments with fructose and glucose showed no reaction during this time.[14] At the end of this period, the osazone was filtered, allowed to remain in contact with 25 cc. of a saturated sodium carbonate solution for two or three hours, again filtered, washed with water, dried *in vacuo* at 60° and weighed About 25 cc. of cold benzene was allowed to percolate through the glucosazone in the crucible, which was again dried and weighed. This weight was considered as that of the osazone of glucosone. The sodium carbonate extract was now acidified with hydrochloric acid, which caused a precipitation of any glyoxylic acid phenylhydrazone which might have been present. This yellow-colored precipitate was transferred to a Gooch crucible, dried in a vacuum oven and weighed. From this weight the amount of glyoxylic acid formed in these oxidations was calculated. Fischer[15] states that phenylhydrazine will detect one part of glyoxylic acid in 300 parts of water.

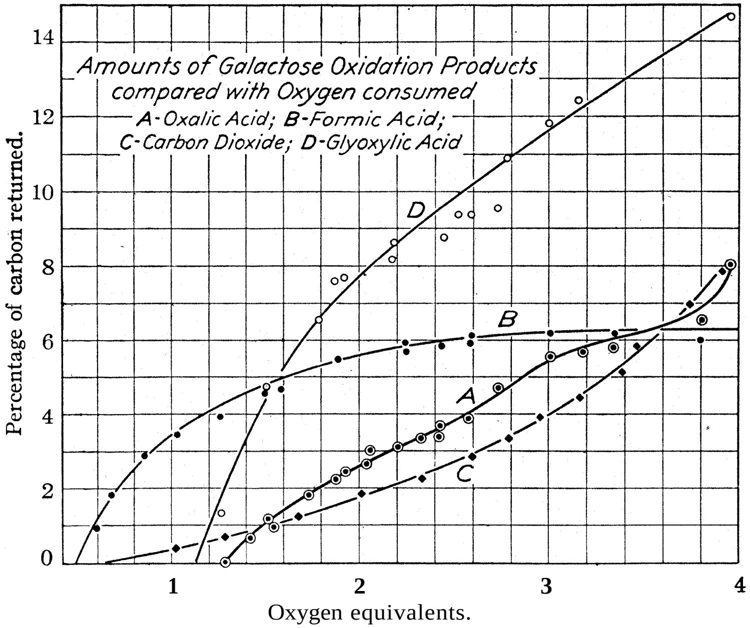

Fig. 8.

The filtrate from the above osazone was now heated on a boiling water-bath for an hour, after which it was cooled in an ice-bath and filtered. After treatment with sodium carbonate, the residue was washed, dried and weighed as described above, in order to determine the osazone of the unchanged sugar. In all but one case it was found that all

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[14] See Morrell and Crofts, *J. Chem. Soc.*, 75, 787 (1899).

[15] Fischer, *Ber.*, 17,577 (1884).

of the glyoxylic acid phenylhydrazone was completely removed in the first precipitation with phenylhydrazine. The osazone thus obtained was regarded as that of the unoxidized carbohydrate. The first melting points of the osazones prepared in this way were usually low, 185–190°, but percolation of the crucible contents with two crucible volumes of cold benzene to remove traces of tar resulted in obtaining a pure product, m. p. 206–208°. Previous tests on pure glucosazone had shown that the loss in weight on treatment with cold benzene was well within the limits of error of our method.

With reference to the accuracy of the separation of glucosone and unchanged sugar, our method leaves much to be desired, but every attempt was made to make it relatively accurate. Morrell and Crofts[14,16] found that both glucose and glucosone were precipitated only very incompletely by phenylhydrazine. From this it is to be concluded that our glucosone was not completely precipitated in the cold and that the remainder would be found with the osazone of the unchanged sugar. However, the formation and the partial estimation of the glucosone present as a reaction product, together with the very accurate measure of the oxygen consumed, have aided us very greatly in the interpretation of the mechanism involved in the oxidation of these carbohydrates with copper acetate solutions. Mr. E. F. Schroeder, of this Laboratory, is at present studying the properties of glucosone.

Carbon Dioxide.—During these oxidations gas pressure developed within the reaction flasks. The gas was found to be carbon dioxide. In some cases, especially that of fructose, the pressure became so great that the stoppers were blown from the flasks with considerable force. The apparatus used for the quantitative determination of carbon dioxide consisted of a sufficiently large flask (500–1000 cc.), closed with a stopper fitted with an inlet tube for the admission of carbon dioxide-free natural gas, an outlet tube attached to a small Liebig condenser inclined at an angle of 45° and a mercury seal through which a mechanical stirrer passed. The condenser was connected to two ordinary gas washing bottles arranged in series. These contained barium hydroxide solution. To the outlet of the last wash bottle a soda lime tube was attached. The natural gas used to sweep the carbon dioxide to the absorption train was passed very slowly through a large soda lime tower attached to the inlet tube of the reaction flask. All stoppers were coated with shellac. The reaction flask was immersed in the thermostat. The following oxidation charges were used lor the carbon dioxide determinations in these experiments. (a) Eighteen grams of glucose was dissolved in 500 cc. of copper acetate solution saturated at 50°. To this solution, 300 g. of solid copper acetate was added, the total reaction mixture being contained in a 1000-cc. Pyrex flask. *(b)* Nine grams of fructose and 27 g. of galactose were used, the other agents and size of reaction flask being in the same ratio as that given for glucose. The barium carbonate formed in the absorption train was removed by filtration through a porous Alundum crucible, then thoroughly washed with recently boiled water, dried in a vacuum oven and weighed. The crucible was freed from the barium carbonate with dilute acetic acid, carefully washed with water, dried and weighed. The difference between the two weights was regarded as that of barium carbonate.

Hydrogen Ion Concentration.—Preliminary work had shown that the hydrogen electrode could not be used for this work because the platinized platinum electrode soon became coated with copper. However, the quinhydrone electrode gave satisfactory results if the temperature was not too high.[17] We used two general methods in actual practice. *(a)* In one, **3.6** g. of glucose was dissolved in saturated copper acetate

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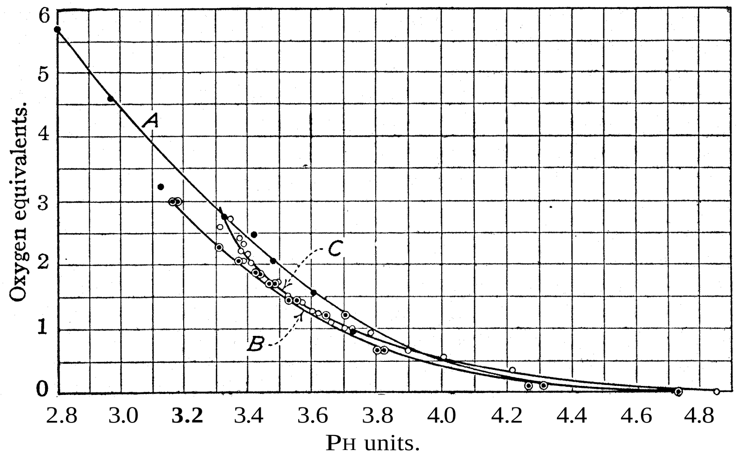
[16] See Fischer, Ber., 21, 2632 (1888).

[17] (a) Mathews, Trans. Faraday *Soc.*, July 6 (1925); (b) Eucken, Jette and LaMer, "Fundamentals of Physical Chemistry," McGraw-Hill Book Company, New York, 1925, p. **396.**

solution. The reaction mixture was kept under exactly the same conditions as described for the oxidation procedure. At suitable intervals 5cc. samples were withdrawn and the voltages measured with the saturated calomel electrode and the quinhydrone electrode, using the standard potentiometric method. *(b)* Our second method, employed with fructose and galactose, consisted in using individual reaction mixtures for each reading. In both cases the PH values were calculated from the equation PH = $7.68-(E/0.059)$, in which E is the observed voltage.[18] The change in the hydrogen ion concentration throughout these oxidations is shown in Fig. 9.



A, fructose; B, glucose; C, galactose.

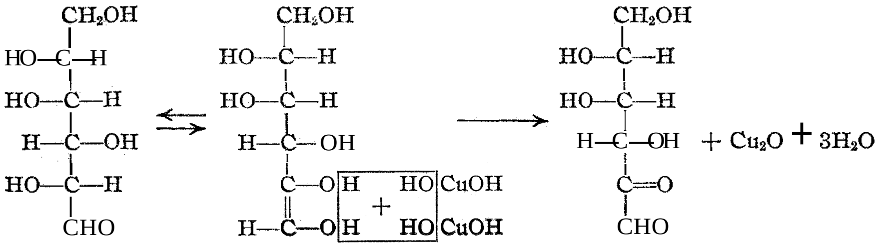
Fig. 9.—Change of hydrogen ion concentration.

Theoretical Part

Glucosone.—It has been pointed out above that one of the main objectives in these experiments was to determine whether the general principles underlying the mechanism of carbohydrate oxidation in alkaline solutions were sufficient to explain the course of such oxidations in acid solutions. Our experimental data show that 13.25% of the glucose carbon and 23.83% of that of fructose were recovered from the reaction mixture of each carbohydrate as glucosone at the end of the first five-hour period. These facts and the relative rate of formation of the hexosone from these two sources are shown in Fig. 10. Galactosone was not detected in the reaction mixtures of galactose. Its absence may have been due to its being oxidized at a greater velocity than that at which it was formed.[19] The presence of glucosone in these reactions is easily understood on the assumption that the common 1–2 hexose enediol of glucose and fructose is present in these acidic solutions, and that this enediol is oxidized in accordance with the following reactions.

[18] LaMer and Rideal, THIS JOURNAL, 46, 224 (1924).

[19] See Morrell and Crofts, J. Chem. *Soc.*, 77, 1220 (1900).



Glucose Glucose 1–2 enediol Glucosone

Such an explanation would regard the enediol as being an acid. In addition to the well-known behavior of these hexoses in alkaline solutions of varying concentrations, the following evidence seems to support this point of view. (*a*) Michael and Rona[20] determined the dissociation constants of some very weak acids, particularly the carbohydrates, and found that the value for fructose was 8.8 X 10^{-13}, for glucose 6.6 X 10^{-13} and for galactose **5.3** X 10^{-13}. (*b*) Powell[21] has shown both by conductivity methods and also by the change of rate in the hydrolysis of ethyl acetate in the presence of fructose and glucose that these carbohydrates form definite compounds with the base, and in the case of sodium hydroxide the reaction takes place in the ratio of one molecule of each. (*c*) Kling[22] found that

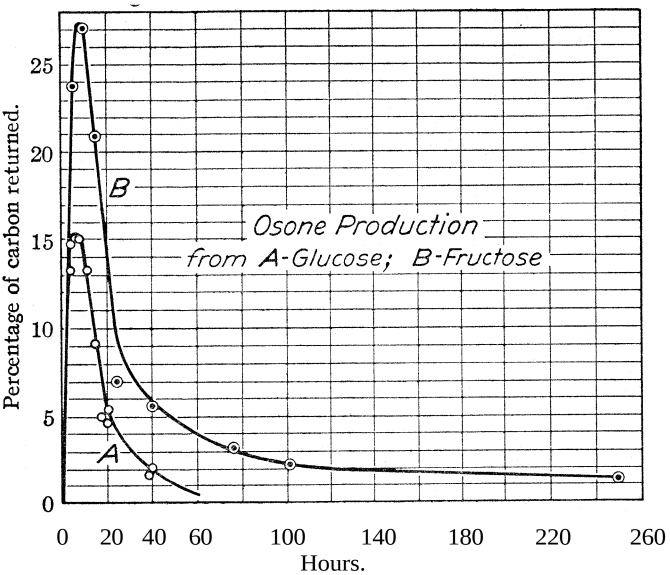


Fig. 10.—Osone production.

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[20] Michael and Rona, *Biochem. Z.*, 49,232–248 (1913); C. A., 7,2715 (1913).

[21] Powell, J. *Chem. Soc.*, **107**, 1335 (1915).

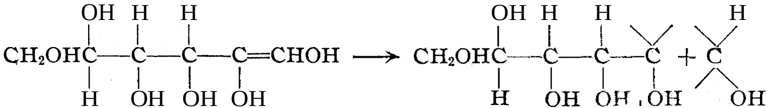
[22] Kling, *Compt. rend.*, **140**, 1256 (1905); see Evans and Hoover, THIS JOURNAL, 44, 1739 (1922).

acetol gives an acid reaction when dissolved in water and that the acidity returns even after neutralization. Acetol may undergo the following reaction

$$CH_3COCH_2OH \rightleftarrows CH_3C(OH){=}CHOH$$

This observation of Kling with reference to the behavior of acetol toward aqueous solutions of alkalies suggests an analogous behavior in the carbohydrates, especially fructose. (d) Wolfrom and Lewis[23] have shown recently that the P_H value of one liter of lime water to which had been added one mole of d-glucose is changed from 12.6 to 10.6. In a separate experiment it was established that gluconic acid is not oxidized with copper acetate under the same experimental conditions as those employed with fructose, glucose and galactose. The same observation was made with galactonic acid lactone. Therefore, it is clear that these oxidations proceed by some mechanism other than through the formation of these acids.

Existence of Hydroxymethylene. Formic Acid.—If the hexose-1,2-enediol of these carbohydrates exists in these solutions, the presence of formic acid as an oxidation product shows that the common 1,2-enediol of fructose and glucose and that of galactose are suffering decomposition according to the following equation.



$$CH_2OH\overset{OH}{\underset{H}{C}}-\overset{H}{\underset{OH}{C}}-\overset{H}{\underset{OH}{C}}-\underset{OH}{C}{=}CHOH \longrightarrow CH_2OH\overset{OH}{\underset{H}{C}}-\overset{H}{\underset{OH}{C}}-\overset{H}{\underset{OH}{C}}-\underset{OH}{C} + \overset{H}{\underset{OH}{C}}$$

(Galactose-1,2-enediol) (Lyxose—active form) + (Hydroxymethylene)

The active form of the pentose and that of formaldehyde may be oxidized to the pentonic and formic acids, respectively. This interpretation is

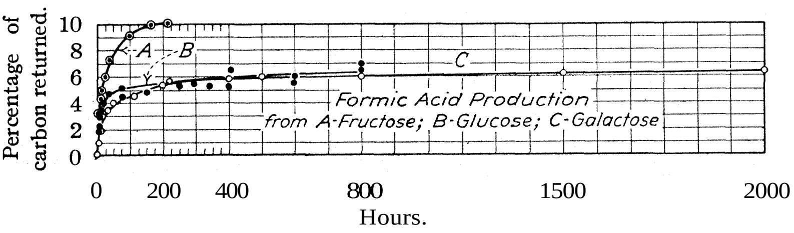


Fig. 11.—Formic acid production.

strongly supported by the recent convincing experiments of Gustus and Lewis on the oxidation of 2,3,4,6-tetramethyl glucose.[4h] The percentages of the hexose carbon converted to formic acid through oxidation with copper acetate is expressed as a function of the time in Fig. 11.

The postulated existence of hydroxymethylene as an intermediate product in these carbohydrate oxidations made it necessary to ascertain

[23] Wolfrom with Lewis, THIS JOURNAL, 50, 842 (1928).

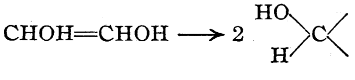
whether, if formed, it could be oxidized with copper acetate directly to formic acid. In order to obtain information on this very important point, we carried out the following experiments.

(a) **Hydroxypyruvic** Acid and Copper Acetate.—The action of hydroxypyruvic acid toward copper acetate was first studied. It was prepared by the following modification of Wills'[24] method. A solution of 40 g. of collodion in 160 g. of ether added to 500 cc. of 10% sodium hydroxide solution was allowed to stand for thirty-six hours. The solution obtained by acidifying the final lower layer of this mixture was evaporated to 200 cc., boiled with animal charcoal, made just alkaline with ammonium hydroxide and then treated with lead acetate. After filtration, the thick, white precipitate was suspended for an hour in water through which a current of air was passing to remove any free ammonia. A portion of the light yellow filtrate obtained after decomposing the suspended white precipitate with hydrogen sulfide gave an osazone which melted at 200–201° without purification. Wills found 205° for the pure substance. Aliquot portions (25 cc.) of a 200cc. solution containing 0.1544 g. of hydroxypyruvic acid were treated with 2 g. of solid copper acetate in the thermostat at 50° for 360 hours. The mixtures gave positive reactions when examined qualitatively for formic acid by the methods of Fincke and Bender. Another reaction mixture containing 0.193 g. of hydroxypyruvic acid was found to contain 0.0482 g. of cuprous oxide (1.81 oxygen equivalents per one g.m.w. of hydroxypyruvic acid), and 0.0162 g. of formic acid (6.66 cc. of 0.1 N $KMnO_4$). The carbon dioxide evolved in one sample gave 0.0365 g. of barium carbonate (0.008 g. of CO_2). If hydroxypyruvic acid should undergo the following reaction in the presence of copper acetate

$$CH_2OHCOCOOH \longrightarrow CH_2OHCHO + CO_2$$

the glycol aldehyde thus formed should in turn undergo an enolization to ethenediol and this tautomer then subsequently decompose according to the following equations

$$CH_2OHCHO \rightleftarrows CHOH{=}CHOH$$



$$CHOH{=}CHOH \longrightarrow 2\ \begin{matrix}HO\\H\end{matrix}\!\!>C<$$

two molecules of formic acid and one molecule of carbon dioxide should be found in the reaction products. Our experimental data are compared with the demands of these assumptions in the following table.

	$CH_2OHCOCOOH$ used, g.	Oxygen equivalents	CO_2	HCOOH
Found	0.193	1.81(90.5%)	0.008	0.0162(95%)
Theoretical	.193	2.00	.008	.0171

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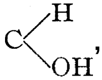
[24] Wills, Ber., 24, 401 (1891).

(b) Glycol Aldehyde and Copper Acetate.—Dihydroxymaleic acid (3.4 g.) was converted into glycol aldehyde according to the directions of Nef,[25] a procedure which should yield 1.2 g. of the desired compound. In this experiment we removed the carbon dioxide with carbon dioxide-free natural gas instead of air. On treating 25 cc. of a 200cc. aqueous solution of this product with *p*-nitrophenylhydrazine hydrochloride and sodium acetate, 0.5058 g. of the hydrazone was obtained,[26] thus showing that our solution contained 0.736 g. of the aldehyde instead of 1.2 g. Since the hydrazone is somewhat soluble, this figure may be a little too low. Six 25cc. portions of our standard solution were treated with 2 g. of solid copper acetate and agitated on the thermostat at 50°. Their distillates, prepared as described above, were examined for formic acid. Cold alkaline potassium permanganate and Fincke's test gave positive reactions. Denigès' test for hydroxy acids gave only a faint response. A quantitative determination showed that 25% of the aldehyde had been converted into formic acid. Neither of the final reaction mixtures in (a) and (b) reduced Fehling's solution nor did they affect Schiff's reagent. (c) In this connection we confirmed the observations of McLeod with reference to the fact that aqueous solutions of formaldehyde do not reduce copper acetate.[27] This investigator used a temperature of 100°, while ours was 50°.

From these experimental results it is clear that the active form of formaldehyde must be hydroxymethylene. Baly[28] in his lecture on "Photosynthesis" said, "In view of the remarkable reactivity of activated formaldehyde it seems to me that it is necessary to picture a different formula from that given to ordinary formaldehyde. This abnormal activity is well expressed by the Nef formula,  $\mathrm{C}\begin{smallmatrix}\diagup\mathrm{H}\\ \diagdown\mathrm{OH}\end{smallmatrix}$, with the carbon atom bivalent." Nef himself had given expression previously to a similar opinion in the statement,[29] "Die physiologischen Wirkungen des Formaldehyds beruhen zweifellos auf einer Dissociation desselben in Oxymethylen." ("The physiological activities of formaldehyde doubtless depend upon a dissociation of it into oxymethylene.")

We feel that our experimental results given above in (a), (b) and (c) are convincing evidence for this general point of view, and that the hydroxymethylene obtained from these sugars must be oxidized to formic acid under the conditions of our experiments.

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[25] Nef, *Ann.*, 376, 40 (1910). The recent experiment of Fischer, Taube and Baer, *Ber.*, 60, 479 (1927), appeared after our work was completed. (W. L. E.)

[26] Wohl and Neuberg, *Ber.*, 33, 3108 (1900).

[27] McLeod, *Am. Chem. J.*, 37, 50 (1907); see Zimmerli, *Ind. Eng. Chem.*, 19, 524 (1927).

[28] Baly, The *Rice Institute Pamphlet*, 12, 93 (1925).

[29] Nef, Ann., 298, 303, reference 147 (1896).

Carbon Dioxide.—Carbon dioxide was being evolved from galactose in decreasingly smaller amounts at the end of 2000 hours and in similar amounts from glucose and fructose at the end of 366 hours and 315 hours, respectively. Our quantitative data show that this gas begins to appear as one of the reaction products of fructose and glucose at about the same time that the glucosone production has reached a maximum. In view of this fact, we concluded that a-ketogluconic acid was being formed by the direct oxidation of the osone, and that this compound was undergoing decomposition into carbon dioxide and arabinose. Since α-ketogluconic acid is unknown as a stable substance,[30] hydroxypyruvic acid was chosen for our study as being representative of hydroxy-α-keto acids. This acid under the same experimental conditions decomposes with an evolution of carbon dioxide, as pointed out above. As the time of oxidation of these carbohydrates is increased, it is seen from Figs. **3,** 4 and 5 that the glucosone gradually is being used up. The percentage of the hexose carbon being converted to carbon dioxide is expressed as a function of the time in Fig. 12. It is seen that fructose is the most sensitive of the three sugars to copper acetate. Ruff found that gluconic acid on being oxidized with bromine was converted into a-ketogluconic acid. In our experiments with fructose and glucose we found no derivative of a-ketogluconic acid. By the following special experiments it was conclusively proven that carbon dioxide was not a decomposition product of the following compounds.

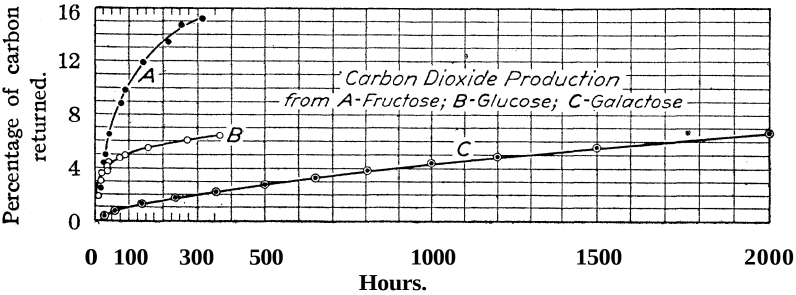

Fig. 12.—Carbon dioxide production.

(a) Galactonic and Gluconic Acids.—One gram of gluconic acid and of galactonic acid lactone were each treated for one week at 50° with copper acetate. Only a trace of cuprous oxide was formed. This was probably due to some slight impurity. The solid copper acetate disappeared and the solution took on the well-known dark blue color.

(b) **Glyoxal.**—No trace of cuprous oxide was found when glyoxal was treated with copper acetate.

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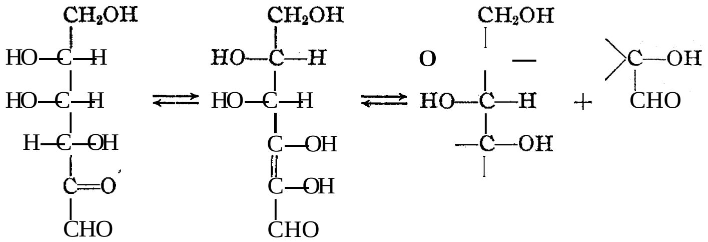
[30] Ruff, *Ber.*, **32**,2269 (1899).

(c) Glycolic Acid.—This acid gave the merest trace of reduction.

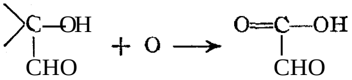
(d) McLeod made the same kind of observations with formic acid, formaldehyde, glycolic acid and oxalic acid,

Hexosone-2,3-enediol. Glyoxylic, Oxalic and Glycolic Acids.—(a) The hexosones formed in these oxidations may also undergo an enolization. The hexosone-2,3-enediol thus formed may then split at the double bond, thus giving rise to a tetrose and glyoxal. These changes may be represented by the following reactions.



Glucosone Glucosone-2,3-enediol Active form of erythrose Half active form of glyoxal

Although Fischer[31] does not record the nature of the insoluble lead compound of glucosone which he prepared by the interaction of lead hydroxide and the hexosone, it is quite probable that it is a lead salt of the hexosone-2,3-enediol. No compounds were formed in our reaction products which indicated that the hexosone-2,3-enediol itself had undergone oxidation with copper acetate. *(b)* In quite the same manner as hydroxymethylene is oxidized to formic acid, so also is the half active form of glyoxal converted to glyoxylic acid according to the following reaction.



In connection with this point of view concerning the half active form of glyoxal, it is of importance to emphasize that glyoxal itself is unacted upon by copper acetate under the experimental conditions of this work. The oxalic and glycolic acids obtained in these experiments are undoubtedly derived from the glyoxylic acid, a compound which Debus[32] observed would rearrange into these two acids. He also noticed that its calcium salt was converted into calcium oxalate and glycolate in the presence of lime water. Debus furthermore observed that glyoxylic acid does not reduce copper acetate. In solutions of copper acetate containing this acid, we found that copper oxalate was being formed without the formation of any cuprous oxide. With reference to the decomposition of the hexosone-2,3-enediol, it is of much interest to note that Morrell and Crofts[33]

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[31] Fischer, *Ber.*, 21,2631 (1888); **22,** 87 (1889).

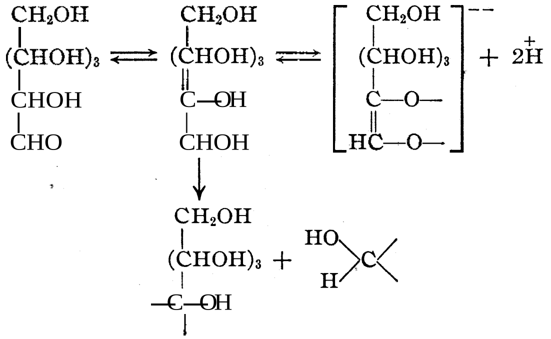
[32] Debus, Ann., 338,336 (1905).

[33] Morrell and Crofts, J. Chem. *Soc.*, 81, 67 (1902).

oxidized glucosone with bromine and isolated the erythronic acid so formed as the calcium salt.

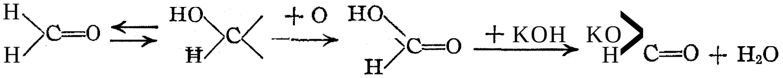
Hydrogen Ion Concentration.—It has been pointed out previously that an increase in the alkali normality of aqueous solutions of the hexoses and potassium hydroxide causes a shifting in the equilibrium existing between the three isomeric enediols in the direction of the 3,4-form. The relation existing between the amounts of lactic acid formed from these sugars and the alkali normality favors this point of view, as do also the character and amounts of oxidation products obtained when these aldohexoses are oxidized with alkaline potassium permanganate. The observations of Amick concerning the influence of alkalinity on the copper number of glucose is especially significant in this connection. Therefore, it is clear that an increase in the hydrogen ion concentration of the oxidizing mixtures containing copper acetate should have the opposite tendency and that the degree of ionization of these enediols should be diminished through the mass action effect of the common ion. The recent work of Wolfrom with Lewis on the de-enolization of an equilibrated mixture obtained from 2,3,4,6-tetramethyl glucose supports this point of view.

The equilibrium represented by the following equation would be shifted to the left by an increase in the hydrogen ion concentration.



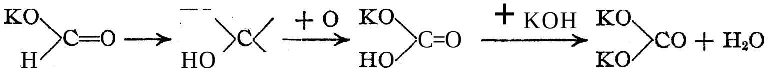
Since this would tend to diminish the concentration of the hexose-1,2-enediol, it follows that the amount of hydroxymethylene would diminish accordingly. This would result in the yield of formic acid being a decreasing function of the time. That this is so is seen in Fig. 11. That the oxidation of the hexose to a hexosone still continues after the cessation of formic acid is evidenced by the fact that glyoxylic and carbonic acids are still forming. In this connection it is of interest to point out that the oxidation of these hexoses with aqueous solutions of copper sulfate proceeds very much more slowly than with copper acetate. Furthermore, when copper acetate solutions are treated with highly ionized acids, the oxidation of the sugars practically stops. We found no evidence for the oxidation of the hexosone-2,3-enediol, since phenylhydrazine did not yield a trihydrazone.

Applying this point of view to the following equation it is seen that alkaline oxidizing agents should yield alkali metal formates.



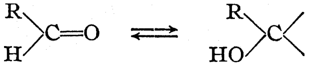
$$\begin{matrix}\text{H}\\\text{H}\end{matrix}\!>\!\text{C{=}O} \rightleftarrows \begin{matrix}\text{HO}\\\text{H}\end{matrix}\!>\!\text{C}\!< \xrightarrow{+\text{O}} \begin{matrix}\text{HO}\\\text{H}\end{matrix}\!>\!\text{C{=}O} \xrightarrow{+\text{KOH}} \begin{matrix}\text{KO}\\\text{H}\end{matrix}\!>\!\text{C{=}O} + \text{H}_2\text{O}$$

The conversion of formates into carbonates in alkaline potassium permanganate oxidations must be preceded by a further enolization before oxidation takes place. These changes may be represented by the following equation.



$$\begin{matrix}\text{KO}\\\text{H}\end{matrix}\!>\!\text{C{=}O} \longrightarrow \begin{matrix}\text{--}\\\text{HO}\end{matrix}\!>\!\text{C}\!< \xrightarrow{+\text{O}} \begin{matrix}\text{KO}\\\text{HO}\end{matrix}\!>\!\text{C{=}O} \xrightarrow{+\text{KOH}} \begin{matrix}\text{KO}\\\text{KO}\end{matrix}\!>\!\text{CO} + \text{H}_2\text{O}$$

In this general interpretation it is obvious that the ionization of hydroxymethylene after the same manner as the sugar enols might be considered, but we have assumed that the monose is probably oxidized instantly to formic acid. From this discussion one must conclude that the direct oxidation of aldehydes in general seems to involve an equilibrium condition in which a certain portion of the aldehyde molecules is in the activated condition. This may be expressed by the following equation



$$\begin{matrix}\text{R}\\\text{H}\end{matrix}\!>\!\text{C{=}O} \rightleftarrows \begin{matrix}\text{R}\\\text{HO}\end{matrix}\!>\!\text{C}\!<$$

Inactive to oxidation Active to oxidation

In harmony with this point of view with reference to the experiment of Upson and Jensen in which these investigators obtained only 0.5 g. of gluconic acid from 200 g. of glucose is the observation of Amick to the effect that "enolization must occur before oxidation."

Summary

1. Aqueous solutions of fructose, glucose and galactose have been oxidized with copper acetate at 50° for the purpose of ascertaining whether the general principles underlying the mechanism of carbohydrate oxidation in alkaline solutions are sufficient to explain the course of such oxidations in acid solutions. The advantages in the use of copper acetate are outlined.

2. The reaction mixtures were examined for glucosone, formic, carbonic, glyoxylic and oxalic acids. The presence of glycolic acid was proved qualitatively but it was not measured quantitatively. The quantities of these are expressed both as functions of the time and the oxygen consumed. The oxygen consumed by each sugar is expressed as a function of the time. The hydrogen ion concentration is expressed as a function of the oxygen consumed.

3. The hexose-1,2-enediols are regarded as being oxidized to the

hexosones. The glucosone is obtained as the osazone. The galactosone was not obtained as a reaction product. It is probably used up as rapidly as it forms.

4. The formic acid arises from the oxidation of the hydroxymethylene obtained by the decomposition of the hexose-1,2-enediols. That hydroxymethylene will undergo this change was shown by a study of the behavior of copper acetate toward glycol aldehyde and hydroxypyruvic acid.

5. It is thought that carbon dioxide arises from the decomposition of the unstable α-ketohexonic acids. Hydroxypyruvic acid loses a molecule of carbon dioxide when oxidized with copper acetate.

6. The hexosones may form hexosone-2,3-enediols, which are thought to decompose into the active form of the tetrose (tetrose methylenol) and glyoxal (half active form). The latter is oxidized to glyoxylic acid, which in part is converted into oxalic and glycolic acids. Glyoxal does not reduce copper acetate solutions, hence it is thought that the glyoxylic acid comes from an activated form (glyoxal-half-methylenol).

7. The increase in the hydrogen ion concentration tends to reverse the equilibrium between the enediols in the direction of suppressing enediol formation. This would lead to a reduction in the formic acid yields with increasing time. The increase in the hydrogen ion concentration would tend to suppress the enolization of the hexosone-2,3-enediol. This harmonizes with the fact that no derivatives were found of 2,3-diketohexoses when the reaction mixtures were treated with phenylhydrazine.

8. The view is expressed that aldehydes exist in two forms, those active toward oxidizing agents and those not. The former are derivatives of methylenols; that is, the hydrogen is bound to oxygen and the carbon is bivalent. In the inactive molecules the carbon is tetravalent. An equilibrium exists between these two forms which may be shifted by a change in the hydrogen ion concentration. The conversion of aldehydes to carbonates in alkaline solutions is explained on this basis.

COLUMBUS, **OHIO**

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA]

4-AMINO-5-BROMO-1,3-DIMETHYLBENZENE

BY ALVIN S. WHEELER AND R. E. THOMAS[1]

RECEIVED MAY 28, 1928 PUBLISHED AUGUST 4, 1928

5-Bromo-m-xylidine (old nomenclature) has been prepared by bromination of m-4-xylidine in hydrochloric acid solution[2] and also in glacial acetic acid,[3] the latter method being adopted in this investigation. Bromination of the free base produces the 5-bromo isomer, while the acetate gives the 6-bromo with a small amount of the 2-bromo form. The hydrochloride, benzoate, xylenol,[4] methyl and ethyl ethers and two dyes were also prepared.

Experimental Part

4-Amino-5-bromo-1,3-dimethylbenzene.—The method of preparation given by Noelting, Braun and Thesmar[3] was followed. However, in order to avoid the formation of an oil, the bromination product, instead of being poured into water, was filtered off, washed with glacial acetic acid and dried. The base was set free with sodium carbonate solution and recrystallized from dilute methyl alcohol; m. p. 46°.

Hydrochloride.—The hydrochloride consists of white crystals which are quite stable, not changing in a year. It readily sublimes without decomposition.

Anal. Calcd. for $C_8H_{10}NBr\cdot HCl$: HCl, 15.25. Found: 15.28.

Benzoate.—The benzoate was prepared by the Schotten-Baumann reaction. The product, obtained in nearly quantitative yield, was recrystallized from dilute alcohol. It forms prismatic needles melting at 186°.

Anal. Calcd. for $C_{15}H_{14}ONBr$: Br, 26.29. Found: 26.20.

Methyl Ether of 4-Hydroxy-5-bromo-1,3-dimethylbenzene, $C_6H_2(CH_3)_2BrOCH_3$.—The bromoxylidine was diazotized in the presence of sulfuric acid and converted into the xylenol (b. p. 228–230°) by boiling the solution; 3.1 g. of the xylenol was mixed with 1.2 cc. of methyl iodide and 0.36 g. of sodium in 10 cc. of methanol. After heating for two hours over steam, the volatile portion was boiled off, water added to the residue and the mixture extracted with ether. The oil obtained boiled chiefly at 232°; sp. gr. 1.362 (25°/25°); yield, high.

Anal. Calcd. for $C_9H_{11}OBr$: Br, 37.1. Found: 37.7.

Ethyl Ether.—Yield, high; boils chiefly at 246°; sp. gr. 1.290 (25°/25°).

Anal. Calcd. for $C_{10}H_{13}OBr$: Br, 34.9. Found: 34.9.

4-Chloro-5-bromo-1,3-dimethylbenzene, $C_6H_2(CH_3)_2ClBr$.—The bromoxylidine was diazotized in the presence of hydrochloric acid and copper paste was added. The product from the distillation with steam was extracted with ether. The oil recovered from the ether boiled over a wide range. The portion boiling a little below to a little above 250° was analyzed.

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[1] This paper is an abstract of a Master's Thesis presented to the Faculty of the University of North Carolina by R. E. Thomas in June, 1928.

[2] Fischer and Windaus, *Ber.*, 33, 1971 (1900).

[3] Noelting, Braun and Thesmar, *Ber.*, 34, 2255 (1901).

[4] Stoermer and Göhl, *Ber.*, 36, 2875 (1903).

Anal. Calcd. for C_8H_8ClBr: Cl, 16.16. Found: 16.00.

1,3-Xylyl-5-bromo-4-nitrile, $C_6H_2(CH_3)_2BrCN$.—The bromoxylidine was converted into the nitrile by the Gattermann-Sandmeyer reaction. In the distillation with steam the nitrile crystallized in the condenser, from which it was removed with hot alcohol. It crystallized in needles which melted at 86–87°. A by-product appeared in the receiver. It boiled at 205° and was therefore regarded as 5-bromo-13-dimethylbenzene.

Anal. Calcd. for C_9H_8BrN: Br, 38.05. Found: 38.00.

1-(5-Bromo-1,3-xylyl-4-azo)-2-naphthol, $C_6H_2(CH_3)_2BrN_2C_{12}H_6OH$.—The bromoxylidine was diazotized and coupled with 2-naphthol in the presence of sodium hydroxide. The crude red precipitate melted at 132°. Recrystallization from a mixture of alcohol and petroleum ether gave rich red needles melting at 136°.

Anal. Calcd. for $C_{18}H_{15}ON_2Br$: Br, 23.50. Found: 23.15.

1-(5-Bromo-1,3-xylyl-4-azo)-4-phenol, $C_6H_2(CH_3)_2BrN_2C_6H_4OH$.—On coupling phenol with diazotized bromoxylidine a dark yellow precipitate formed, weight 3 g. from 2 g. of the xylidine. It was recrystallized from 90% acetic acid, or from a mixture of 3 parts of benzene and 7 parts of alcohol, to give small orange-colored crystals which melt at 166°.

Anal. Calcd. for $C_{14}H_{13}ON_2Br$: Br, 26.20. Found: 26.14.

Summary

1. The preparation of 4-amino-5-bromo-1,3-dimethylbenzene was improved upon.
2. Its hydrochloride and benzoate are described.
3. The methyl and ethyl ethers of the bromoxylenol were prepared.
4. The amino group was replaced by Cl and by CN.
5. Two azo dyes were made by coupling the diazotized bromoxylidine with phenol and with 2-naphthol.

CHAPEL HILL, NORTH CAROLINA

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

SYNTHETIC HOMOLOGS OF *d,l*-EPHEDRINE

BY J. F. HYDE,[1] E. BROWNING[1] AND ROGER ADAMS

RECEIVED MAY 31, 1928 PUBLISHED AUGUST 4, 1928

The interesting and important drug, ephedrine (I) has in recent years been brought to the attention of the medical profession and has become widely used chiefly through the brilliant investigations of Dr. K. K. Chen.[2] Although a careful comparison of the pharmacological action of *l*-ephedrine with *d,l*-ephedrine and pseudo-ephedrine has been completed, no study has as yet been made of the comparative values of 1-ephedrine or *d,l*-ephedrine with a series of homologs, particularly those in which an

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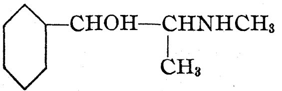
[1] Portions of theses of J. F. Hyde and E. Browning submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.

[2] Chen and Kao, *J. Am. Pharm. Assocn.*, **15**, 625 (1926). At the end of this article is given a bibliography of chemical, pharmacological and medical articles on ephedrine.

alkyl group other than methyl is found on the nitrogen or on the β-carbon atom from the benzene ring.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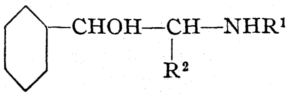
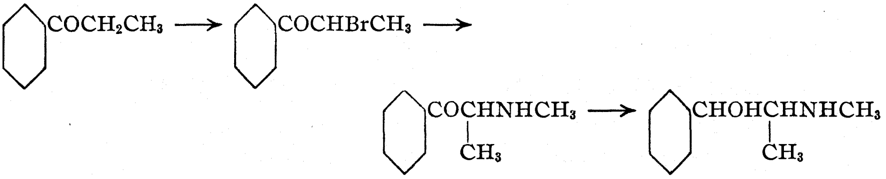

II

In this investigation a series of racemic compounds of the general formula (II) has been prepared where R^1 is methyl, ethyl, n-propyl, *iso*-propyl, n-butyl or n-amyl, and where R^2 is hydrogen, methyl, ethyl or n-propyl. In addition, one or two compounds were made in which both hydrogens of the nitrogen were replaced by alkyl groups. The methods of synthesis of *d,l*-ephedrine have been reviewed in the article of Chen previously referred to and so need not be repeated here. It is sufficient to say that for this work no attempt was made to find the process which might prove the most advantageous from a commercial standpoint, but merely the one which could be used most conveniently in the laboratory for obtaining small quantities of material. The one selected for the preparation of *d,l*-ephedrine and then applied to the preparation of its homologs was first described by Eberhard[3] and later repeated by Fourneau and Kanao[4] and Fourneau and Torres.[5] This consists in the bromination of propiophenone to a bromopropiophenone, condensation with methylamine to form the a-methylaminopropihphenone, and finally reduction to the corresponding amino alcohol. It is reported that if sodium amalgam was used as a reducing agent in the last step, a mixture of *d,l*-ephedrine and pseudo-ephedrine was usually formed. With palladium and hydrogen, however, Eberhard obtained *d,l*-ephedrine.



In this investigation *d,l*-ephedrine was first synthesized and the work carried out by H. A. Graffis. No particular comments are necesssary on the bromination. In the second step, however, the method of purification of the α-methylaminopropiophenone is worthy of mention, since the purity is important for the success of the subsequent reduction. The reaction mixture containing α-methylaminopropiophenone hydrochloride and excess methylamine hydrochloride was evaporated to dryness in a vacuum. The crude mixture obtained was extracted several times with chloroform, which left methylamine hydrochloride insoluble and dissolved

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[3] Eberhard, Arch. *Phurm.*, **253,** 62 **(1916).**

[4] Fourneau and Kanao, *Bull. soc. chim.*, [4] **35,614 (1924).**

[5] Fourneau **and** Torres, *Anales soc. españ. fís. quím.*, **23,450 (1925).**

the amino ketone hydrochloride. The latter was recrystallized and reduced by means of hydrogen and platinum-oxide platinum black to the amino alcohol.

This method of catalytic reduction proved to be an excellent procedure, not only on account of its convenience for the production of amino alcohol but also because apparently just one of the two possible isomeric amino alcohols resulted. The product isolated proved to be exclusively *d,l*-ephedrine, which was essentially pure after one crystallization.

The various homologs in which the alkyl group attached to the β-carbon atom was varied in size were made in the same general manner as that used for ephedrine, except that acetophenone, butyrophenone, valerophenone, etc., were halogenated in place of propiophenone and the subsequent steps carried out with these halogenated products.

In the series in which merely the alkyl group on the nitrogen was varied, the method of isolation of the amino ketones had to be modified because the excess alkylamine hydrochloride was soluble in chloroform. In this case the mixture of the amino ketone and excess of alkyl amine was isolated and the excess of the amine removed by distillation in *vacuo* at room temperature.

Dr. E. C. Kendall of the Mayo Clinic has kindly made tests on the amino ketones and amino alcohols to determine the effect of the compounds on blood sugar. His detailed results will be published elsewhere but it is sufficient to remark here that in the series where the methylamino group remains constant' and the alkyl group on the β-carbon atom is varied in size (in formula II, R^1 is methyl and R^2 varies from hydrogen to n-propyl) the molecule where the $R^2 = H$ is the most effective, and the increase in blood sugar becomes less as the group is varied from methyl to propyl. On the other hand, if the alkyl group on the β-carbon atom remains a methyl and the alkyl group on the nitrogen is varied in size (in formula II, R^2 is methyl and R^1 varies from methyl to n-amyl) the blood sugar steps up with the increase in the number of carbon atoms in the alkyl group. The butyl and amyl derivative cause convulsions and respiratory paralysis following the injection. Those substances in which two hydrogens of the nitrogen were replaced by alkyl groups showed no physiological effect.

The ketones corresponding to the effective alcohols gave essentially the same results as the alcohols in the effect on blood sugar.

The amount of blood sugar increase was dependent to a certain extent on the size of the dose.

The effect of these products on blood pressure was ascertained by Mr. C. Nielsen and assistants of the Abbott Laboratories, North Chicago, Illinois. They report that of the various homologs only one caused any marked rise in blood pressure. It was the homolog of ephedrine in which the methyl group of the β-carbon atom was replaced by hydrogen. Practically all of the others either caused merely a very slight rise in blood pressure preceded usually by a fall, or else caused a direct fall in blood pressure. The results were not of sufficient regularity to warrant drawing quantitative conclusions concerning this physiological effect.

These compounds are now being studied by Dr. K. K. Chen in order to determine their possible medical value as compared with 1-ephedrine.

Experimental

Brominated Ketones.—The procedure for the preparation was that of Schmidt,[6] according to which the ketone is brominated in glacial acetic acid.

α-Bromo-*n*-valerophenone.—As this substance has not previously been described in the literature, it may be mentioned that it is a straw-colored liquid boiling at 150° at 2.5 mm.; n_D^{20}, 1.5600; d_4^{20}, 1.3993.

Reaction of the Bromo Ketones with Methylamine.—One-tenth of a mole of the bromo ketone was added drop-wise with vigorous stirring to 0.25 mole of methylamine (in the form of a 30% solution in absolute alcohol) over the required period of time (one hour for bromopropiophenone, seventeen to eighteen hours for a-bromobutyrophenone, twenty-four hours for a-bromovalerophenone). The reaction flask was immersed in ice water during the reaction and stirring was continued for one-half to three-quarters of an hour after the addition of the bromo compound. Cold, concd. hydrochloric acid was then added very slowly along with some finely cracked ice until the mixture was acidic. If it became warm the product turned very dark in color and a larger proportion of tar was produced. At this point the reaction mixture was orange or red due to the presence of some bromo ketone that had not reacted and to the formation of certain tarry by-products. These were extracted with ether from the water layer and the bromo ketone recovered. The water layer was evaporated to dryness in *vacuo*, treated with a little chloroform and evaporated to dryness again to assist in removing the moisture from the rather hard mass. After standing in a vacuum desiccator for a day, the residue was extracted several times with fresh portions of chloroform and each time the insoluble crystals of methylamine hydrochloride were filtered. The chloroform solution was then evaporated until it was very concentrated, and acetone was added to cause the crystallization of the amino ketone hydrochloride. Recrystallization was carried out by dissolving in a small amount of alcohol, filtering, and adding about twice the volume of acetone in small portions.

In the condensation of chloro-acetophenone with methylamine, the reaction was carried out in essentially the same way as the one just described for the bromo ketones except that the chloro-acetophenone was added in the form of a powder and allowed to react with the alcoholic methylamine for a period of five to six hours.

For the preparation of the alkylamino ketones in which a group larger than methyl was attached to the nitrogen, a slightly different procedure was used. A 50% aqueous solution of the amine was cooled down carefully to 5–10° in an ice-bath and previously cooled bromo ketone was added slowly with mechanical stirring in the ratio of 1 mole of bromo ketone to 2 moles of amine. The reaction product was allowed to stand and to come to room temperature and the stirring continued until no layer of unreacted bromo ketone separated upon standing. The reaction mixture was then cooled and an excess of concd, potassium hydroxide solution was added slowly with stirring, the temperature not being permitted to rise above 15–20". The amino ketone and excess alkylamine separated and were extracted with ether and the ether solution was washed with water.

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[6] Schmidt, Ber., 22,3251 (1889).

Upon evaporation of the ether and then warming the residue in *vacuo* to a temperature not over 40°, the excess alkylamine was removed. The residual amino ketone was dried with solid potassium hydroxide, taken up in dry ether, cooled thoroughly and dry hydrogen chloride passed in with stirring. In the course of a few minutes the hydrochloride of the amino ketone began to crystallize.

These hytlrochlorides were purified by first digesting with hot acetone and filtering. This helped to remove the color. The hydrochlorides were crystallized from ethyl acetate containing a small amount of ethyl alcohol (3–10%, depending upon the product being prepared), or from alcohol by addition of some acetone as described under the crystallization of the amino ketone hydrochlorides.

In the condensation of chloro-acetophenone with *n*-butylamine, the powdered chloro compound was added to 2.5 times the quantity of anhydrous n-butylamine over a period of seven hours and stirring continued ior three hours more. The reaction flask was cooled well during this time. The reaction product was worked up in the same manner as previously described for the condensation of various amines other than methylamine with the halogenated ketones.

If any decomposition occurred during the formation of the amino ketones, the hydrochlorides invariably separated as oils which crystallized only with great difficulty. In one or two instances it was found possible to vacuum distil the amino ketone base in an atmosphere of nitrogen, but ordinarily this procedure is not to be recommended because some decomposition always takes place.

In condensing bromobutyrophenone with di-*n*-butylamine, the reaction was carried out by adding the bromo ketone to the amine in the proportion of 1 to 3 moles, respectively. Stirring was continued and no attempt was made to cool the reaction mixture. The crystals of di-*n*-butylamine hydrobromide were filtered and washed with ether. The ether solution was worked up as previously described. The hydrochloride separated as a red, sirupy mass. After drying it in a vacuum desiccator, it was dissolved in a little dry acetone and by adding small amounts of ether a solid product was obtained and purified.

TABLE I

SUBSTITUTED α-AMINO PROPIOPHENONES

 $C_6H_5CO\overset{R}{C}HNHCH_3$ R =	M. p., °C. HCl salt	Yield, %	Analyses, % Cl Calcd.	Found
H^7	219	23	...	...
$CH_3{}^2$	176–177	57	...	...
C_2H_5	190–192	33	16.63	16.86
n-C_3H_7	183.5–184 5	39	15.60	15.64
$C_6H_5COCH_2NHC_4H_9(n)$	214–215	35	15.58	15.60
$C_6H_5COCHN(C_4H_9(n))_2CH_2CH_3$	138–140	30	11.32	11.26
$C_6H_5COCH(CH_3)NHR$ R =				
C_2H_5	183	30	16.60	16.60
C_3H_7	180	35	15.59	15.04
iso-$C_3H_7{}^{8a}$	213–213 5	51	15 59	15 52
n-$C_4H_9{}^{8b}$	158–159	39	14.68	14.60
n-C_5H_{11}	150	41	13 89	13.64
$C_6H_5COCH(CH_3)N(C_2H_5)_2$	167–168	25	14 68	14.45

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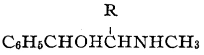
[7] Almström, Ann., 409,300 (1915); Gabriel, *Ber.*, 47, 1337 (1914).

[8] (a) B. p. of free base 105–110° at 3 mm.; (b) b. p. of free base 140–142° at 8 mm. with some decomposition.

Reduction of Amino Ketones to Amino Alcohols.—The amino ketones were dissolved in ordinary ethyl alcohol in the proportion of 0.1 mole of ketone to 50–100 cc. of solvent and 0.1 g. of platinum oxide[9] was added. The reductions were carried out under a pressure of 30–40 pounds and the calculated amount of hydrogen was always absorbed. The rate of reduction depended upon the purity of the amino ketone hydrochlorides. In general the time ran from twenty minutes to six hours in the compounds studied. The products were removed from the reaction mixture merely by filtration of the catalyst and evaporation to a concd. solution. They were recrystallized either by dissolving in absolute alcohol and adding acetone to the hot solution to the point where precipitation just started, or from ethyl acetate containing a few per cent. of ethyl alcohol. The products were generally pure after one crystallization and the yields amounted to about 90%.

Table II

α-Phenyl β-Methylamino Alkanols

 $C_6H_5CHOH\overset{R}{C}HNHCH_3$ R =	M. p., °C. HCl salt	M. p., °C. Base	Analyses, % Cl	
			Calcd.	Found
H[10]	105–106	75–76	18.90	18.79
CH_3[2]	189–190	76–77	...	...
C_2H_5	201–202	89–90	16.46	16.31
$n\text{-}C_3H_7$	224–225	76–77	15.46	15.46
$C_6H_5CHOHCH_2NHC_4H_9(n)$	218–220	58–59	15.46	15.41
$C_6H_5CHOHCHN(C_4H_9(n))_2C_2H_5$	114–116	...	11.32	11.88
$C_6H_5CHOHCH(CH_3)NHR$ R =				
C_2H_5	190–191		16.47	16.26
C_3H_7	218		15.51	15.38
$iso\text{-}C_3H_7$	193		15.51	15.79
$n\text{-}C_4H_9$	220–221		14.55	14.43
$n\text{-}C_5H_{11}$	219		13.79	13.91
$C_6H_5CHOHCH(CH_3)N(C_2H_5)_2$	205–206		14.55	14.46

Summary

A series of homologs of *d,l*-ephedrine has been prepared in which the alkyl group on the nitrogen has been varied from methyl to n-amyl; a series in which the alkyl group on the β-carbon has been replaced by H, ethyl and n-propyl and two compounds in which the alkyl groups are present on the nitrogen.

Blood sugar is increased as the alkyl group on the nitrogen is made larger; blood sugar is decreased as the alkyl group on the @-carbonis increased in size; the ketones showed a similar action; the dialkylamino compounds produced no physiological action.

The only homolog which gave a dependable increase in blood pressure was the a-phenyl β-methylamino-ethanol.

Urbana, Illinois

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[9] Adams and Shriner, This Journal, 45, 2171 (1923). See "Organic Syntheses," Vol. VIII, John Wiley and Sons, New York, 1928, for complete details of apparatus and catalyst.

[10] Barger and Dale, *J. Physiol.*, 41, 19 (1910).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF KANSAS]

THE REPLACEABILITY OF CERTAIN METHYLENE GROUPS AND THE RELATION OF CONSTITUTION TO THE STABILITY OF A C=C LINKAGE

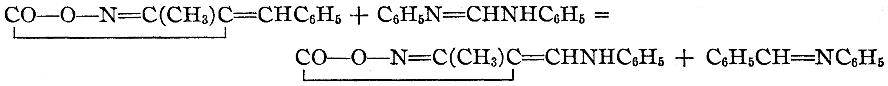
H. V. MOYER[1] AND F. B. DAINS

RECEIVED JUNE 4, 1928 PUBLISHED AUGUST 4, 1928

In a previous series of papers,[2] it has been shown that the methylene hydrogen in many compounds when heated with the substituted formamidines could be readily replaced by the anilidomethylene grouping, thus synthesizing a C=C bonding.

$$>CH_2 + RN{=}CHNHR = >C{=}CHNHR + RNH_2$$

An exception was noted in the case of methylisoxazolone, which gave only tarry products with diphenylformamidine. Further experiments showed, however, that the benzal derivative reacted easily and smoothly with the formamidine, yielding the anilidomethylenemethylisoxazolone, as follows:



$$CO{-}O{-}N{=}C(CH_3)C{=}CHC_6H_5 + C_6H_5N{=}CHNHC_6H_5 = CO{-}O{-}N{=}C(CH_3)C{=}CHNHC_6H_5 + C_6H_5CH{=}NC_6H_5$$

The reaction was unusual since it involved the separation of carbon from carbon and the formation of another C=C linking. It seemed worth while to investigate this further and the following paper is a preliminary study of the types of compounds which lend themselves to such an interchange.

$$R_2C{=}CHC_6H_5 + R'N{=}CHNHR = R_2C{=}CHNHR + R'N{=}CHR'$$

Thus far the replacement has been successful only in the case of the aldehyde (RCH=) derivatives of certain heterocyclic rings, namely: isoxazolone, pyrazolone and rhodanine (thiazolidone) and is probably confined to those compounds in which the benzal group can be removed easily by hydrolysis with dilute acids or heating with phenylhydrazine.

$$R_2C{=}CHR' + HOH = R_2CH_2 + RCHO$$
$$R_2C{=}CHR' + C_6H_5NHNH_2 = R_2CH_2 + C_6H_5NHN{=}CHR'$$

With open chain derivatives such as benzalphenyl cyanide or nitrobenzalacetylacetone it was found impossible to break the double bonding and introduce an aminomethylene grouping.

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[1] From a dissertation presented by H. V. Moyer to the Faculty of the Graduate School of the University of Kansas in partial fulfilment of the requirement for the degree of Doctor of Philosophy.

[2] (a) Dains, Ber., 35, 2509 (1902); (b) Dains and Griffin, THIS JOURNAL, 35, 962 (1913); (c) Dains and Brown, *ibid.*, 31, 1148 (1909); (d) Dains and Stephenson, *ibid.*, **38**, 1841 (1916); (e) Dains and Harger, *ibid.*, 40, 562 (1918); (f) Dains, Thompson and Asendorf, *ibid.*, 44, 2310 (1922).

Experimental

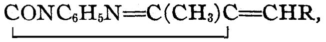
The Aldehyde Derivatives of 3-Phenylisoxazolone and Diphenyl Formamidine

4-Benzal-3-phenylisoxazolone was readily formed when molar quantities of benzaldehyde and the isoxazolone were heated for a few minutes at the melting point of the mixture. The benzal derivative (**5** g.) and diphenylformamidine (**4** g.) were heated at 145° until the mixture melted and then at 120° for forty-five minutes. From the reaction product was isolated **2.5** g. of the 4-anilidomethylene-3-phenylisoxazolone,[2b] which was identified by a mixed melting point and analysis.

Anal. Calcd. for $C_{16}H_{12}O_2N_2$: N, **10.61.** Found: N, **10.88.**

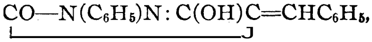
In order to ascertain the effect of other aromatic aldehyde groupings, the piperonal-, anisal-, m-nitrobenzal- and cinnamylidenephenylisoxazolones were heated with diphenylformamidine under similar conditions. In all cases the aldehyde grouping was replaced by the anilidomethylene radical. It should be noted that this is the only instance in which the unsaturated cinnamylidene group has been replaced. Later experiments with the cinnamic aldehyde[3] condensation products of other ring compounds gave only tarry products. Negative results were obtained with the furfuralphenylisoxazolone.

Diphenylformamidine with the Aldehyde Derivatives of Various Pyrazolones

The experimental work has shown that the methylene hydrogen as well as the benzal groups in the substituted pyrazolones can be replaced, though the ease is determined somewhat by the nature of the substituents in the ring. Thus from the benzal and piperonal derivative of 1-phenyl-3-methylpyrazolone,  $CONC_6H_5N{=}C(CH_3)C{=}CHR$, at 140°, the 4-anilidomethylenepyrazolone (m. p. 154°)[4] was obtained. The ease with which the aldehyde bonding can be broken was shown by the fact that when the piperonalpyrazolone was heated in alcohol solution with phenylhydrazine, piperonalphenylhydrazone and methylphenylpyrazolone were isolated and identified.

1,3-Diphenylbenzalpyrazolone gave at **160°** the anilinomethylene derivative (m. p. **140°**) alone. This is of advantage since the diphenylpyrazolone with diphenylformamidine yielded both the **140°** compound and *bis*-diphenylpyrazolone (m. p. **247°**).[4,5]

Anal. Calcd. for $C_{31}H_{22}O_2N_4$: N, **11.62.** Found: N, **11.87.**

3-Hydroxy-1-phenyl-4-benzalpyrazolone,[6]  $CO{-}N(C_6H_5)N:C(OH)C{=}CHC_6H_5$, was prepared by heating benzaldehyde and the pyrazolone at 130° or, better, by simply refluxing the components in alcohol solution for an hour. The dark red needles melted at 275°.

Anal. Calcd. for $C_{16}H_{12}N_2O_2$: N, **10.60.** Found: N, **10.87.**

It was heated with diphenylformamidine first at **210**" and then at 180° for thirty minutes. From the reaction product was isolated the 1-phenyl-3-hydroxy-4-anilinomethylenepyrazolone, which separated from boiling acetic acid in yellow needles melting at 272–273°. It was soluble in dilute potassium hydroxide and was precipitated unchanged by acids.

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[3] Giua, *Gazz. chim. ital.*, **55,567–576 (1925).**

[4] Ref. 2c, p. **1154.**

[5] Betti and Mundici, *Gazz. chim. ital.*, [1] **36, 184 (1906).**

[6] Michaelis and Burmeister, **Ber.,** 25, **1509 (1892).**

Anal. Calcd. for $C_{16}H_{13}O_2N_3$: N, 15.05. Found: N, 15.34, 14.85.

Corresponding results were obtained on heating the anisalpyrazolone (m. p. 250°)[7] with the formamidine. As a check the same anilinomethylene compound, m. p. 272–273°, was synthesized from the hydroxyphenylpyrazolone by heating with the formamidine at 160°.

3-Phenyl- **and 3-Methyl-4-benzalpyrazolone,** $CONHNC(R)C{=}CHC_6H_5$.—These pyrazolones differ from the preceding in having the N in position 1 unsubstituted. Both were unchanged after heating with the diphenylformamidine, a result which would seem to show that the double bond becomes more stable as the positive nature of the ring is increased.

3-Methyl-4-anilinomethylenepyrazolone, $CONHN{=}C(CH_3)C{=}CHNHC_6H_5$.—The 3-methylpyrazolone with a free CH_2 grouping reacted only with difficulty. Finally, heating at 200° with a large excess of the formamidine produced a yellow compound melting at 204° which corresponded to the above.

Anal. Calcd. for $C_{11}H_{11}N_3O$: N, 20.9. Found: N, 21.68.

Benzalthiazolidone Derivatives

3-Phenylrhodanine, which illustrates another type of heterocyclic ring, the thiazole, possesses a reactive methylene grouping. Its benzal derivative, $S{-}CSNC_6H_5COC{=}CH{-}C_6H_5$ (m. p., 192°)[8] reacted in like manner with the formamidine at 200° in a sealed tube, yielding the 5-anilinomethylene compound (m. p. 247°).[9]

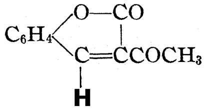
The cinnamylidenephenylrhodanine (m. p. 223°)[10] was unaffected at temperatures below 200°. Above this point, only decomposition products were obtained.

Anal. Calcd. for $C_{18}H_{13}NOS_2$: N, 4.33. Found: N, 4.36.

Benzaldi-o-Tolylthiazolidone, $SC(NHC_7H_7)NC_7H_7COC{=}CHC_6H_5$.—The only essential difference between the rhodanine and this compound is in having the S at position 2 replaced by a tolylimino grouping. The change has, however, increased the positive character of the molecule so that the heating at 220° for five hours with the formamidine gave only negative results.

Benzylidene Derivatives in Which the Methylene Carbon Is Not Part of a Ring

To illustrate this type, there were chosen benzalbenzylcyanide, *m*-nitrobenzalacetylacetone and cinnamylidene-acetylacetone. In no case did heating with the formamidine afford any evidence of breaking the C=C linking, although the free methylene compounds reacted readily with the amidine. The same negative result was obtained with acetylcoumarine,



which contains a C=C bonding due to aldehyde condensation with acetoacetic ester.

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[7] Asher, *Ber.*, 30, 1018 (1897).

[8] Andreash and Zipser reported 186°, *Monatsh.*, 24, 506 (1903).

[9] Dains and Davis, *Kansas Univ. Sci. Bull.*, 15, 265–270 (1924); *C. A.* 20, 600 (1926).

[10] Andreash and Zipser found 217°, *Monatsh.*, 24, 513 (1903).

Benzalacetophenone (Anil Formation with the Ketone Oxygen).—The experiments with benzalacetophenone, while they showed the stability of the double bonding, led to another interesting result. Molar quantities of the ketone and formamidine were heated at temperatures ranging from 130–150°. From the reaction product was isolated in not over 5% yield a compound which crystallized from alcohol in white needles and melted at 168°. Had the reaction involved the substitution of the benzal group, the compound $C_6H_5COCH{=}CHNHC_6H_5$ (m. p. 141°) should have resulted.[11] The 168° product gave the following results on analysis.

Anal. Calcd. for $C_{21}H_{17}N$: C, 89.1, H, 6.00, N, 4.9; mol. wt., 283. Found: C, 88.94, 89.0; H, 6.31, 6.15; N, 4.92, 4.93; mol. wt. 270, 286.

This corresponded, as was proved, to the anil of benzalacetophenone, $C_6H_5CH{=}CHC(NC_6H_5)C_6H_5$. The compound was unsaturated and gave on hydrolysis with dilute sulfuric acid, aniline, acetophenone and benzaldehyde, which indicated that the benzal group had not been removed. The mechanism of the reaction is doubtless the following

$$C_6H_5CH{=}CHCOC_6H_5\ 4\ RN{=}CHNHR \longrightarrow C_6H_5CH{=}CHC(NR)C_6H_5 + HCONHR$$

The isolation of p-bromoformanilide in one case where di-*p*-bromodiphenylformamidine was used points to this interpretation.

Direct Synthesis of the **Phenylimide.**—A 10% yield followed when the ketone and freshly distilled aniline were heated at 175° for four hours, but the yield was raised to 80% by using a dehydrating agent.

Thus benzalacetophenone (20 g.), aniline (8.8 g.) and anhydrous sodium acetate (20 g.) were thoroughly mixed and heated at 175° for three hours. The molten mass was poured into a large volume of water and the oily liquid which separated crystallized from alcohol and then from benzene.

As an additional confirmation of this synthesis, p-chloro-aniline and p-toluidine were used in place of aniline with equal success.

***p*-Chlorophenylimide** of Benzalacetophenone, $C_6H_5CH{=}CHCN(C_6H_4Cl)C_6H_5$, separates from alcohol in white needles which melt at 167°.

Anal. Calcd. for $C_{21}H_{16}ClN$: Cl, 11.16, N, 4.41. Found: Cl, 11.07; N, 4.30.

p-Tolyliminobenzalacetophenonehas a melting point of 170°.

Anal. Calcd. for $C_{22}H_{19}N$: N, 4.71. Found: N, 4.78, 4.81.

Action of Bromine on the **Phenyl Imino** Derivative.—Bromine added to the anil in carbon bisulfide on chloroform solution yielded a precipitate that blackened at 160° and decomposed at 240°.

Analysis showed it to be a mixture, but that addition had mainly taken place on the nitrogen was proved by the fact that one of the hydrolysis products was p-bromoaniline. This is in accord with the fact that in a grouping $C{=}NC_6H_5$, bromine adds to the nitrogen and then rearranges to the p-bromo derivative.

Summary

1. An aromatic aldehyde condensed with the methylene hydrogen of an isoxazolone was readily replaced by an anilinomethylene group, yielding a new C=C bonding.

2. The same reaction occurred with the benzalpyrazolones with a phenyl group in the 1-position, but not when this position was unsubstituted.

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[11] Claisen and Pischer, Ber., 20,2192 (1887).

3. Benzyl cyanide and the benzalacetylacetone were found not to react with the formamidine, though the free CH_2 derivatives did.

4. With benzalacetophenone and the formamidine the anil resulted—a product that was obtained in 80% yield on heating the ketone with aniline and sodium acetate.

LAWRENCE, KANSAS

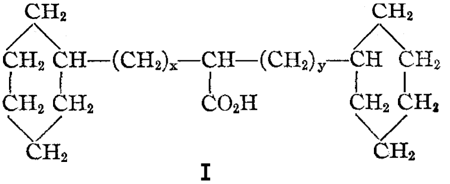
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ILLINOIS]

DI-(CYCLOHEXYLALKYL) ACETIC ACIDS. XIV[1]

BY LETHA A. DAVIES[2] AND ROGER ADAMS

RECEIVED JUNE 4, 1928 PUBLISHED AUGUST 4, 1928

In previous papers it has been demonstrated that when a cyclohexyl group is substituted at the end of a straight-chained aliphatic acid of certain molecular weight, the product is an effective bactericide *in vitro* toward *B. leprae*, whereas the corresponding straight-chained acid with the same number of carbon atoms is ineffective. It has been shown further that if the carboxyl group is removed from the end of the chain to a position nearer to the ring, the effectiveness of the isomeric acid is increased. As a consequence it seemed advisable to prepare a few di-(cyclohexylalkyl) acetic acids for testing, in which the carboxyl group is in the favored position. It is thus possible to determine whether a second ring structure would enhance the bactericidal properties. The compounds prepared are of the general formula represented by I where "x" is 1, 2, 3 or 4 and where "y" is 0, 1, 2 or 3. They were made in the usual way by introducing first one cyclohexylalkyl group into malonic ester and then a second, followed by saponification and heating of the malonic acid.



I

The bacteriological results in Table I indicate that no particular ad-

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[1] For previous articles in this field see (a) Shriner and Adams, THIS JOURNAL, 47, 2727 (1925); (b) Noller with Adams, *ibid.*, 48, 1080 (1926); (c) Hiers with Adams, *ibid.*, 48, 1089 (1926); (d) *ibid.*, 48, 2385 (1926); (e) Van Dyke and Adams, *ibid.*, 48, 2393 (1926); (f) Sacks with Adams, *ibid.*, 48, 2395 (1926); (g) Noller and Adams, *ibid.*, 48, 2444 (1926); (h) Adams, Stanley, Ford and Peterson, *ibid.*, 49, 2934 (1927); (i) Arvin with Adams, *ibid.*, 49, 2940 (1927); (j) Adams, Stanley and Stearns, *ibid.*, 50, 1475 (1928); (k) Yohe and Adams, *ibid.*, 50, 1503 (1928); (l) Arvin and Adams, *ibid.*, 50, 1983 (1928).

[2] This communication is an abstract of a portion of a thesis submitted by Letha A. Davies in partial fulfilment of the requirements for the Degree of Doctor of Philosophy in Chemistry at the University of Illinois.

vantage is gained by the introduction of the second ring. In fact, the two compounds which have 20 carbon atoms are, like most of the other molecules studied which contain that number of carbon atoms, comparatively inactive.

TABLE I

BACTERIOLOGICAL ACTION OF THE ACIDS

$C_6H_{11}(CH_2)_x—\underset{CO_2H}{CH}—(CH_2)_yC_6H_{11}$			Dilution of sodium salts in thousands 25	53	62	74	85	100	125	155	180	230
1	x = 0	y = 2	−	−	+	+	+	+	+	+	+	+
2	x = 1	y = 2	−	−	−	−	−	−	±	+	+	+
3	x = 2	y = 2	−	−	−	−	−	−	−	−	−	+
4	x = 2	y = 3	−	−	−	±	−	−	−	−	−	±
5	x = 3	y = 3	−	+	+	+	+	+	+	+	+	+
6	x = 2	y = 4	−	+	+	+	+	+	+	+	+	+

Experimental Part

The general procedures for the preparation of all of the intermediate and final compounds have been given in previous articles in this series.[1d,h]

TABLE II

DIETHYL-DI-(ω-CYCLOHEXYLALKYL) MALONATES

$C_6H_{11}(CH_2)_x—C(CO_2C_2H_5)_2—(CH_2)_yC_6H_{11}$	B. p., °C.	n^{20}_D	d^{20}_4	Analysis Calcd. C	H	Found C	H
1 x = 0 y = 2	**192 (4.5 mm.)**	1.4747	1.016	71.53	10.30	71.14	10.20
2 x = 1 y = 2	186–188 (3 mm.)	1.4725	1.003	72.06	10.46	71.96	10.24
3 x = 2 y = 2	**200–202 (1.5 mm.)**	1.4722	0.9931	72.57	10.60	72.45	10.49
4 x = 2 y = 3	**210–211 (3.5 mm.)**	1.4713	.9928	73.05	10.73	72.18	10.76
5 x = 3 y = 3	216–218 (3 mm.)	1.4710	.9811	73.45	10.86	73.43	10.82
6 x = 2 y = 4	**208–210 (2.5 mm.)**	1.4710	.9817	73.45	10.86	73.30	10.76

TABLE III

DI-(ω-CYCLOHEXYLALKYL) ACETIC ACIDS

$C_6H_{11}(CH_2)_x—CH(CO_2H)—(CH_2)_yC_6H_{11}$			B. p., °C.	M. p., °C.	n^{25}_D	d^{20}_4	Analysis Calcd. C	H	Found C	H
1	x = 0	y = 2	182–186 (4 mm.)	.....	1.4852	0.9915	76.14	11.18	76.07	10.98
2	x = 1	y = 2	207–208 (5 mm.)	50–51	....	....	76.63	11.34	76.59	11.33
3[a]	x = 2	y = 2	210–213 (1.5 mm.)	73–76	(Neut. equiv.:		280.3		279.8)	
4	x = 2	y = 3	213–214 (3 mm.)	**46.5–47**	....	....	77.49	11.65	77.14	11.52
5	x = 3	y = 3	**216–218 (3** mm.)	**42.5–45**	....	....	77.91	11.79	78.00	11.73
6	x = 2	y = 4	221–223 (4 mm.)	.....	1.4831	0.9647	77.91	11.79	77.67	11.54

[a] This acid and the corresponding malonic ester have been described by G. H. Coleman in a Doctor's thesis, University of Illinois, 1928.

The bacteriological tests were kindly made by Mr. W. M. Stanley.

Summary

A number of di-(cyclohexylalkyl) acetic acids were prepared. They were no more effective bactericidally than those molecules containing the same number of carbon atoms which have only one ring present.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

FURYLANGELIC ACID[1]

BY ALBERT S. CARTER

RECEIVED JUNE 8, 1928 PUBLISHED AUGUST 4, 1928

In proving the structure of furfural, Baeyer[2] studied the condensation of furfural and sodium acetate, yielding furylacrylic acid in a manner exactly analogous to the condensation of benzaldehyde to yield cinnamic acid. Upon reduction, furylacrylic acid gave furylpropionic acid, which upon treatment with bromine and subsequent oxidation by silver oxide was converted into a so-called *furonic* acid, having the structure indicated by the formula $HOOCCH{=}CHCOCH_2CH_2COOH$. This was reduced by hydriodic acid to yield a dibasic acid identified as pimelic.

In the same general manner used to prepare furylacrylic acid, Baeyer[3] successfully prepared a so-called furylangelic acid from sodium butyrate and furfural, to which he assigned the structure $C_4H_3OCH{=}CHCH_2CH_2COOH$. Tonnies[4] reported the conversion of furylangelic acid into furylvaleric, butyrofuronic and finally azelaic acids in a manner analogous to the conversion of furylacrylic into pimelic acid, The azelaic acid thus obtained did not agree exactly in melting point with any of the known isomers of the formula $C_9H_{16}O_4$, but approximated most nearly that of n-azelaic acid. The literature definitely states that the resulting acid possesses a normal chain. The structure $C_4H_3OCH{=}CHCH_2CH_2COOH$ does not agree with the present conception of the course of the Perkin condensation, for in the light of the formation of a-methylcinnamic acid from benzaldehyde and sodium propionate and other similar condensations, we should be led to expect that Baeyer's furylangelic acid would have the structure represented by $C_4H_3OCH{=}C(C_2H_5)COOH$. This would lead to the formation of a-ethylpimelic acid instead of n-azelaic acid in the course of the reactions carried out by Tonnies, but this ethylpimelic acid has been prepared[5] and found to differ from the product which Tonnies reported.

Furylangelic acid was prepared and found to be identical with the product obtained by Baeyer. By treatment with ozone and hydrolysis of the ozonide, the products included carbon dioxide, propionic acid and possibly a-ketobutyric acid. It is impossible to obtain these products

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[1] From an investigation, carried out under the direction of Professor Richard Fischer, which constituted a part of a thesis presented by A. S. Carter to the Graduate School Faculty of the University of Wisconsin in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

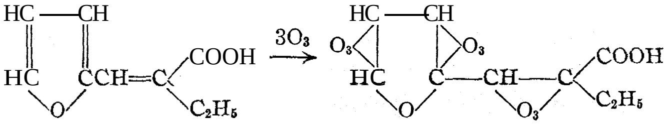
[2] Baeyer, *Ber.*, 10, 355, 395, 1358 (1877).

[3] Baeyer, *Ber.*, 10, 1364 (1877).

[4] Tonnies, *Ber.*, 12, 1200 (1879).

[5] Carter, THIS JOURNAL, 50, 1967 (1928).

from Baeyer's formula for furylangelic acid (δ-furylallylacetic acid), but they might, however, be the expected products from a-ethyl-@-furylacrylic acid, as shown below. This evidence indicates that furylangelic acid is an ethylacrylic acid derivative and the ozone oxidation proceeds as follows



the ring breaking to form HCOOH, CHOCHO and CHOCOOH, and the side chain giving $C_2H_5COCOOH$, which subsequently decomposes to form C_2H_5COOH, CO_2 and H_2O. The evidence throughout the remainder of this paper substantiates this view.

The products of permanganate oxidation of furylangelic acid included furoic acid, acetic acid and propionic acid, and from a study of the oxidation it was concluded that it could be understood only through the use of the ethylacrylic acid structure for furylangelic acid, oxidizing at the side-chain double bond to give ketobutyric acid, which decomposed in two ways to form acetic acid and propionic acid.

In an endeavor to correlate these facts with those of l'onnies, his work was repeated as exactly as possible. Having established the structure of furylangelic acid as possessing a branched chain, it was considered improbable that any means of reduction and ring opening could yield n-azelaic acid.

Reduction of furylangelic acid gave furylvaleric acid, which was undoubtedly the same as that obtained by Tonnies, though no analytical results or physical data can be found by which his product might be recognized. The composition of this product indicated that the reduction consisted in the addition of one molecule of hydrogen, which would be expected to enter at the most vulnerable point, namely, the double bond in the side chain. The reduction would then be analogous to the reduction of cinnamic to hydrocinnamic acid.

Furylvaleric acid was converted into butyrofuronic acid through the use of bromine and subsequent oxidation with silver oxide

$$C_4H_3OC_4H_6COOH \xrightarrow[H_2O]{Br_2} OCHCH{=}CHCOC_4H_6COOH + 2HBr \xrightarrow{Ag_2O}$$
$$HOOCCH{=}CHCOC_4H_6COOH$$

The product of this reaction was carefully purified and found to possess a melting point slightly higher than that recorded by Tönnies, but analysis indicated the same compound. The name given to this acid is misleading. In accord with his structure of furylangelic acid, butyrofuronic acid would be heptene-1-one-3-dicarboxylic acid-1,7; in accord with the structures established in this paper it should be heptene-1-one-3-dicarboxylic acid-1,5.

Upon hydriodic acid reduction of butyrofuronic acid, *n*-azelaic acid was not obtained. Instead, the products of the reduction were ethylpimelic acid and heptanone-3-dicarboxylic acid-1,5. The results of this work seem to warrant the conclusion that an acid melting at 117° similar to azelaic acid cannot be obtained by the method of hydriodic acid reduction employed. The melting point of the butyrofuronic acid used by Tonnies might indicate that it was impure and this might lead to the explanation of his different results. To speculate upon the hydriodic acid reduction; in the light of such anomalous results as the reduction of dibenzylcarbonyl to the phosphoric acid ester of the corresponding alcohol, as obtained by Grabe[6] and Johnson and Hodge,[7] it would not be highly improbable to expect the reduction of butyrofuronic acid to ethylacetone diacetic acid (heptanone-3-dicarboxylic acid-1,5) and the corresponding hydroxy compound which Tonnies found to be unstable, as intermediate reduction products. Heptanone-3-dicarboxylic acid-1,5 was evidenced by the products obtained by reduction at 190° for four hours; further reduction might next produce the hydroxyl group and subsequent decomposition of this acid take place, thus accounting for the water-insoluble resin and the low yields of the final product, ethylpimelic acid, mentioned in the experimental part of this paper.

Marckwald[8] subjected furylacrylic acid to the action of dry hydrogen chloride in alcoholic solution and obtained a diethyl ester of acetone diacetic acid. In a manner similar to this, the diethyl ester of heptanone-3-dicarboxylic acid-1,5 was prepared, which upon hydrolysis yielded the previously unprepared acid. Marckwald was unsuccessful in carrying out a similar reaction upon furylpropionic acid; the same failure to obtain results was found when the reaction was applied to furylvaleric acid. It is probable, therefore, that the double bond plays an important part in this reaction, which is essentially the addition of two molecules of water to furylangelic acid.

Heptanone-3-dicarboxylic acid-1,5 was successfully reduced to ethylpimelic acid by means of hydriodic acid. In all, fifteen reductions were made on butyrofuronic acid and heptanone-dicarboxylic acid and in no case was an acid similar to azelaic obtained, proving conclusively that furylangelic acid has the furylethylacrylic structure indicated by its oxidation products.

Experimental Part

Furylangelic Acid.—Forty g. of dry sodium butyrate, 40 cc. of freshly distilled furfural and 100 g. of butyric anhydride were heated under an air condenser for eighteen hours at 135–160°. The product, while warm, was washed out of the reaction flask

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[6] Grabe, Ber., 7, 1624 (1874).

[7] Johnson and Hodge, THIS JOURNAL, 35, 1014 (1913).

[8] Marckwald, Ber., 20, 2811 (1887); 21, 1398 (1888).

with 450–500 cc. of water, was neutralized with sodium carbonate and then treated for two or three hours with absorbent charcoal without boiling. Upon filtration, most of the tar and much of the color was removed; this was then again treated with charcoal, boiled for twenty minutes, allowed to settle and filtered, giving a light yellow solution. Boiling the solution during the first treatment causes the solution of some of the tar, which is otherwise carried down with the charcoal in the cold. Boiling the solution for twenty minutes during the second treatment was found to replace satisfactorily steam distillation of the excess furfural from the reaction mixture. Ice was then added and the free acid precipitated with dilute sulfuric acid. An excess of sulfuric acid is to be avoided, for it tends to bring out remaining furfural, contaminating the product. The cold solution was filtered by suction and the furylangelic acid dried; yield, 45–48 g. (80%) of crude, slightly colored product melting at 85–90". For much of the work this crude acid could be used without further purification but it was readily purified by dissolving in ethyl alcohol and precipitating with ice water or by crystallization from hot petroleum ether. The pure substance melted at 95.5–97° after drying at 40° in vacuum for six hours; it was soluble in alcohol, chloroform, hot petroleum ether and slightly in hot water.

Anal. Subs. 0.1500: CO_2, 0.3577; H_2O, 0.0806. Calcd. for $C_9H_{10}O_3$: C, 65.06; H, 6.02. Found: C, 65.04; H, 5.94.

The melting point recorded above is higher than that observed by Baeyer (87–88°). The melting point of the crude acid before purification checked more closely that of Baeyer. Two stereoisomeric forms are possible. Liebermann[9] isolated two forms of furylacrylic acid which were found to melt at 103 and 82–86°.

It was found impossible to obtain satisfactory yields of furylangelic acid using acetic anhydride as the condensing agent, as furylacrylic acid was the predominant product of the reaction in every case.

Ozone Oxidation of Furylangelic Acid.—Ten g. of dry furylangelic acid was dissolved in 200 cc. of dry chloroform in a tall cylinder, packed in ice and subjected to 5% ozonized oxygen at the rate of 10 liters per hour for four hours. The substance became yellow and then darkened to a brown with a definite green fluorescence and a brown, oily product separated on the sides of the tube. The ozonide was a thick, brown, tarry mass, insoluble in water and only partially soluble in chloroform, with a strong pungent odor resembling acetic acid. The chloroform was removed under diminished pressure after transferring the product to a 500-cc. flask. The ozonide was hydrolyzed by refluxing for three hours with 300 cc. of water. The product consisted of an acid solution and a tar from which nothing could be resolved. The acid solution was neutralized with dilute sodium hydroxide and evaporated to 2 cc. under diminished pressure. This solution was made acid with hydrochloric acid and a small amount of insoluble tar filtered off; the filtrate was treated with 1 cc. of a solution containing one part of phenylhydrazine to eight of a 50% solution of acetic acid. After standing for several hours, an oily hydrazone precipitated out, which was filtered off and recrystallized from chloroform; m. p. 138–142°. Upon standing for a few days, this hydrazone became liquid and underwent decomposition. Its behavior and properties resembled the phenyl hydrazone of a-ketobutyric acid, melting[10] at 144–145° which is probably the primary product of the hydrolysis.

It was found that the hydrolysis product was much more strongly acid if a small quantity of ferric chloride was added before hydrolyzing. The tar was filtered from this solution; it was made alkaline with ammonium hydroxide and again filtered to remove

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[9] Liebermann, *Ber.*, 27, 283 (1894); 28, 129 (1895).

[10] Wislicenus, *Ann.*, 246, 333 (1888).

ferric hydroxide. The solution was treated with ammoniacal silver nitrate and warmed to 40–50° for six hours; the resulting reduced silver was filtered from the warm solution, leaving a more completely oxidized product which was free from formaldehyde. This was made strongly acid with phosphoric acid, filtered and distilled to a volume of 30 cc. The acid distillate was redistilled and used for Duclaux determinations of the acid present. The values determined on two runs were 11.4, 11.2, 11.4 and 11.6, 11.6, 11.6 on the first three 10-cc. fractions. These values indicate propionic acid, which was checked by the preparation of propiono-p-toluide from the sodium salts obtained by evaporating the neutralized distillates from the Duclaux determinations.

Permanganate Oxidation.—Ten g. of furylangelic acid was dissolved in 150 cc. of water containing 10 g. of sodium hydroxide; this was rapidly titrated with saturated potassium permanganate (about 680 cc.), the manganese dioxide was filtered off and the solution was boiled down to a volume of 100 cc. Upon acidifying the solution with sulfuric acid, a white precipitate resulted, which was filtered off, dried and identified as furoic acid.

Anal. Subs. 0.2000: CO_2, 0.3916; H_2O, 0.0635. Calcd. for $C_5H_4O_3$: C, 53.57; H, 3.57. Found: C, 53.40; H, 3.53.

The acid solution was still found to reduce permanganate, so 100 cc. of the saturateti permanganate solution was added and the mixture distilled until salts began to crystallize out. The distillate was redistilled after addition of 10 cc. of sulfuric acid and an equal volume of permanganate, leaving about 20 cc. in the distilling flask to insure that no sulfuric acid was in the product. This was used for Duclaux determination of the acids present, the first four fractions giving the following values: 9.9+, 9.9—. 9.8—, 9.7+. These values do not check either propionic acid or acetic acid, but fall between them. The neutral solutions were evaporated and the resulting sodium salts were used for the preparation of *p*-toluides. The melting point of the resulting toluide was 104–120°, indicating a mixture. This was dissolved in 3 cc. of hot benzene and, upon cooling, aceto-*p*-toluide, melting at 146–147°, was obtained and a more soluble toluide remained in the benzene, which was recrystallized from petroleum ether, giving a product melting at 120–125°, probably indicating propiono-p-toluide (m. p. 123–124.5°).

Upon carrying out a similar run in which the furylangelic acid was dissolved in hot, concentrated sulfuric acid, considerable carbon dioxide was evolved during the addition of the oxidizing agent and no furoic acid was left at the end, indicating that the furane ring had been oxidized. The acid distillate, however, gave the same toluides and Duclaux values as had been found in the case of the basic oxidation. If phosphoric acid was substituted for sulfuric acid, the Duclaux values were lower, that is, 8.0, 8.2, 8.5, and the relative amount of the propiono-p-toluide obtained was very small. This evidence seems to indicate that acetic and propionic acids are both formed from some intermediate oxidation product, probably ketobutyric acid, for it was found that propionic acid was not oxidized to acetic acid under the conditions of this work.

Furylvaleric Acid.—Fifty grams of furylangelic acid was suspended in 2 liters of water and 800 g. of 3% sodium amalgam was added; frequent small additions of sulfuric acid hastened the action of the amalgam. The basic solution was separated from mercury, filtered and acidified with sulfuric acid, giving an oil which was collected in ether, dried over sodium sulfate and finally, upon evaporation of the ether, gave 50 g. of an oily acid (98% of the theoretical). This acid was distilled under diminished pressure; b. p. about 174° at 46 mm.

Anal. Subs. 02000: CO_2, 0.4698; H_2O, 0.1274. Calcd. for $C_9H_{12}O_3$: C, 64.3; H, 7.14. Found: C, 64.05; H, 7.08.

Butyrofuronic Acid.—By means of violent mechanical stirring, 4.5 g. of furylvaleric acid was suspended in one liter of water. To this was added 4.5 g. of bromine dissolved in water; stirring was stopped and the brominated mixture was immediately poured upon washed silver oxide, freshly precipitated from 28.5 g. of silver nitrate. Again the product was mechanically stirred and heated in a water-bath at 35–40° for two hours. The silver was precipitated with hydrochloric acid, filtered and the butyrofuronic acid extracted with ether. Continuous ether extraction for twenty-four hours was necessary because of the solubility of butyrofuronic acid in water. Evaporation of the ether gave brown crystals which were purified by dissolving in water, boiling with absorbent charcoal and evaporating to dryness in a vacuum desiccator over calcium chloride. This product was further purified by precipitating from warm ether by means of petroleum ether. Butyrofuronic acid was soluble in water, alcohol, warm chloroform and ether; m. p. 149–150° (Tonnies gives 140–142° with previous softening); yield about 1 g. (18–19%).

Anal. Subs. 0.1350: CO_2, 0.2669; H_2O, 0.0714. Calcd. for $C_9H_{12}O_5$: C, 54.0; H, 6.00. Found: C, 53.90; H, 5.88.

Reduction of Butyrofuronic Acid.—One g. of butyrofuronic acid, 8 g. of hydriodic acid (sp. gr. 1.70) and 0.5 g. of red phosphorus were sealed in a Pyrex bomb tube and heated at 195–200° for six hours. Upon opening the tube there was slight pressure and an inflammable gas escaped; the contents were decolorized with sulfurous acid and extracted with ether Evaporation of the ether left brown, tarry material, a part of which was soluble in hot water. This portion was precipitated from hot water three times, giving a colorless product which was further purified by precipitation from hot benzene. This entire oily mass crystallized upon the introduction of a crystal of ethylpimelic acid and proved to be identical with ethylpimelic acid (heptane-dicarboxylic acid-1,5), melting at 41-43°, and the silver salt corresponded to silver ethylpimelate.

Anal. Subs. 0.2000: AgCl, 0.1430. Calcd. for $C_9H_{14}O_4Ag_2$: Ag, 53.73. Found: Ag, 53.81.

The temperature and the duration of heating were varied in a number of runs but in no case was a product melting at 117° obtained. By adding only 0.3 g. of phosphorus and heating for four hours, a very small amount of heptanone-3-dicarboxylic acid-1,5 was recognized in the product.

Heptanone-3-dicarboxylic Acid-1,s.—Thirty g. of furylangelic acid was dissolved in 100 cc. of 95% alcohol and subjected to dry hydrogen chloride until a turbid solution was obtained (twenty-five minutes). Continuing the current of hydrogen chloride, this was refluxed on a water-bath for one hour, then treated with the gas for two hours longer, during which period it was allowed to cool. The alcohol and hydrogen chloride were distilled off on a water-bath, leaving a thick, brown oil possessing a pleasant aromatic odor. This ester was shaken with an equal volume of saturated sodium carbonate solution, collected in a small volume of ether and fractionated under diminished pressure. The major portion of the product distilled at 198–200° (25 mm.), giving 45 g. (96%) of colorless ester. Free heptanone-3-dicarboxylic acid-1,5 was obtained by refluxing with 150 cc. of 20% potassium hydroxide solution until the hydrolysis was complete. This solution was acidified with sulfuric acid and continuously extracted with ether for a period of forty-eight hours. Evaporation of the ether gave 32.5 g. (92.4%) of crystalline acid from 45 g. of the ester. Heptanone-dicarboxylic acid was readily obtained in a high degree of purity by recrystallizing from hot benzene; m. p. 83–84.5°. The silver salt was prepared and analyzed.

Anal. Subs. 0.3000: AgCl, 0.2061. Calcd. for $C_9H_{12}O_5Ag_2$: Ag, 51.9. Found: Ag, 51.7.

Heptanone-dicarboxylic acid was soluble in water, ether, acetone, chloroform and hot benzene; insoluble in cold benzene and petroleum ether; it crystallized in small white rosets from the sirup resulting by evaporation of a water solution.

Reduction of Heptanone-3-dicarboxylic Acid-1,5.—As before in the reduction of butyrofuronic acid, **9** g. of the acid was reduced by means of 1.8 g. of phosphorus and 60 cc. of hydriodic acid for eight hours at 190–200°. The product, extracted from the reduction mixture after decolorizing with sulfur dioxide and purifying by precipitation from hot water and benzene, consisted of **1** g. of colorless liquid which crystallized upon the introduction of a crystal of ethylpimelic acid. Analysis and melting point indicated that the reduction product was identical with that obtained from butyrofuronic acid, namely, ethylpimelic acid. The analysis of the silver salt gave the following results.

Anal. Subs. 0.5000: AgCl, 0.3601. Calcd. for $C_9H_{14}O_4Ag_2$: Ag, **53.73.** Found: Ag, **54.20.**

Summary

1. A method has been developed whereby furylangelic acid can be produced in yields of over 80% of the theoretical from furfural, sodium butyrate and butyric anhydride.

2. The structure of furylangelic acid and the course of the Perkin reaction when applied to furfural and butyric acid have been established through the isolation and identification of the products of oxidation of furylangelic acid.

3. Furylvaleric acid has been prepared and the ring opened by bromination and oxidation to yield heptene-1-one-3-dicarboxylic acid-1,5.

4. Butyrofuronic acid has been reduced to heptane-dicarboxylic acid-1,5 and heptanone-3-dicarboxylic acid-1,5.

5. The previously unprepared heptanone-3-dicarboxylic acid-1,5 and its ethyl ester have been prepared from furylangelic acid, and this product has been reduced to heptane-dicarboxylic acid-1,5.

WILMINGTON, DELAWARE

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

THE ACIDIC AND BASIC CATALYSIS OF ACETYLATION REACTIONS

BY JAMES B. CONANT AND GEORGE M. BRAMANW

RECEIVED JUNE 18, 1928 PUBLISHED AUGUST 4, 1928

The acetylation of hydroxy compounds by means of acetic anhydride is frequently catalyzed by the addition of sulfuric acid, sodium acetate or pyridine. Since acetic acid is often the initial solvent and is always formed by the reaction, the behavior of these catalysts in this solvent may afford the clue to the explanation of their action. Sulfuric acid is obviously an acid catalyst which furnishes hydrogen ions in excess of those provided by acetic acid itself. Sodium acetate and pyridine are examples of basic catalysts, since it has been shown[1] that these substances are strong bases in acetic acid.

The development of methods of studying the hydrogen ion activity

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[1] **Hall** and **Conant,** THIS JOURNAL, 49,3047 **(1927).**

of glacial acetic acid solutions[1] makes possible a further investigation of the influence of the acidity or basicity of the medium on the rate of acetylation. The results presented in this paper are in the nature of a preliminary survey of the field. They are limited by the accuracy of the present methods of determining hydrogen ion activities in glacial acetic acid and, in their interpretation, by our inadequate knowledge of the physical chemistry of the behavior of acids, bases and salts in this solvent. Furthermore, it was not found possible to obtain precise measurements of the rate of any of the acetylation reactions we studied. In spite of these limitations the results clearly show the fundamental factors which affect the speed of acetylations with acetic anhydride. This suggests wide possibilities in regard to controlling such reactions for preparative and analytical purposes. We shall report experiments along these lines at another time.

The Rate of Acetylation of β-Naphthol

After some experimentation with a variety of substances, β-naphthol was chosen for the rate measurements. It is readily acetylated by acetic anhydride with the formation of a crystalline acetate which is insoluble in water and resistant to hydrolysis by cold water. The β-naphthol and a four-fold excess of acetic anhydride were allowed to interact in glacial acetic acid solutions of definite acidity. The extent of the reaction was determined by diluting with water, filtering off the mixture of β-naphthol and o-naphthyl acetate on a Gooch crucible, washing with water and saponifying the residue with standard sodium hydroxide. Experiments with mixtures of pure β-naphthyl acetate and β-naphthol showed that the precipitation by water was not complete. We, therefore, standardized our procedure by operating always with such volumes that the recovery of the acetate was 70 ± 5% as shown by numerous blank runs with varying proportions of β-naphthol and β-naphthyl acetate dissolved in acetic acid. In calculating the extent of the reaction, we corrected the actual titration figures on the assumption that only seven-tenths of the acetate was recovered. The correctness of this procedure was demonstrated by the fact that the final constant value for the amount of acetate formed in each buffer was 100 ± 10% on the corrected basis. The necessity for this correction as well as the difficulty of the uniform precipitation and washing make the method only an approximate one, as shown by the figures exhibited below. A qualitative check of some importance was afforded by the determination of the melting point of the product. The acetate melts at 68°, β-naphthol at 122°, while a 50–50 mixture when precipitated from acetic acid by water melts at 48–51°. The melting points of the products showed the general correctness of the results of the analytical procedure, Analytical Procedure.—In starting each experiment, 5 cc. of a 0.5 molar solution of 0-naphthol in glacial acetic acid was placed in a tube in a thermostat at 25°; 5 cc. of the buffer solution (see Table I) was then added. One cubic centimeter of acetic anhydride was added rapidly and the mixture shaken; the time was taken from this point (with a stop watch if necessary). The tube was closed by a cork or by sealing off the glass and allowed to stand in the thermostat for the allotted time. The contents were then added to 100 cc. of water and the mixture was shaken rapidly. The coagulated precipitate was filtered off on a Gooch crucible, pressed on the filter and washed with 100 cc. of water. The crucible was then transferred to a 250-cc. wide-mouthed flask, containing 25 cc. of alcohol and 25 cc. of 0.1 N sodium hydroxide. The mixture was heated for ten minutes on the steam-bath under a reflux condenser attached to a soda lime tube. The excess of sodium hydroxide was titrated with 0.1 N hydrochloric acid using phenolphthalein as the indicator; the end-point is difficult to ascertain because of the color of the solution. The following results, obtained with a 0.2 molar benzamide solution, 0.4 neutralized with sulfuric acid, as the buffer, are typical.

TABLE I

TYPICAL RESULTS

Time, minutes	Percentage reacted By titration	Percentage reacted Corrected	$k \times 10^2$	Melting point of product, °C.
5	17	24	4.6	
10	25	35	4.4	
15	31	44	3.8	
20	36	51	3.5	55
25	52	74	5.4	
30	62	88	7.0	
40	68	97		63
50	68	97		
60	67	96		68
80	71	102		
140	70	100		

The results are summarized in Table II. The values of k given are the reaction velocity constants calculated from the monomolecular formula using natural logarithms and the time in minutes. Only experiments in which the extent of the reaction was between 10 and 85% were used in calculating k; the number of such experiments is given in the fourth column. In addition, there were always a number of experiments for longer periods of time to show that the reaction proceeded essentially to completion and thus to check our analytical procedure. The $P_{\mathrm{H}}^{(\mathrm{HAc})}$ values were determined by means of the chloranil electrode as previously described; they agreed within 0.2 of a unit of the values predicted from the titration curves. Solutions 5 and 6 were intended to be identical but actually varied 0.3 in $P_{\mathrm{H}}^{(\mathrm{HAc})}$; this slight difference was reflected in the rate measurements. The use of buffer solutions containing magnesium acetate partially neutralized with perchloric acid (Nos. 7, 9, 10) was suggested to us by Dr. N. F. Hall as a result of his further study of the behavior of acids and bases in glacial acetic acid.[2] Primary and secondary

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[2] To be published shortly.

amines and even urea were not suitable materials for preparing buffer solutions for our work since they are rapidly acetylated by acetic anhydride. Even benzamide and acetanilide are acted upon slowly, but not at a rate which seriously affects the validity of the results given in Table II.

TABLE II

RATE OF ACETYLATION OF β-NAPHTHOL IN GLACIAL ACETIC ACID BUFFER SOLUTIONS AT 25°

Concn. of β-Naphthol, 0.22 molar; of acetic anhydride, 0.88 molar

Soln. no.	Composition of buffer solution	P_H(HAc)	No. of expts.	Range of values of k X 10^2	Average value of k X 10^2	k X 10^2 calcd. from Eq. 2
1	0.2 *M* $HClO_4$	−4.5	2	Too fast to measure	*ca.* 5000	2800
2	0.2 *M* H_2SO_4	−3.3	4	100–200	160	200
3	0.2 M $C_{10}H_7SO_3H(\beta)$	−2.3	9	10–30	21	20
4	0.2 M $C_6H_5CONH_2$, 0.4 neut. with H_2SO_4	−1.8	5	3.5–5.0	4.2	6.3
5	0.2 M CH_3CONH_2, 0.65 neut. with H_2SO_4	−1.3	7	1.5–1.9	1.6	2.0
6	0.2 M CH_3CONH_2, 0.55 neut. with H_2SO_4	−1.0	6	0.9–1.5	1.1	1.0
7	0.05 N $Mg(OCOCH_3)_2$, 0.9 neut. with $HClO_4$	−0.6	5	0.06–0.15	0.12	0.4
8	0.2 M H_3PO_4	−0.2	3	0.13–0.17	0.12	0.16
9	0.05 N $Mg(OCOCH_3)_2$, 0.5 neut, with $HClO_4$	+0.5	5	0.029–0.050	0.039	0.037
10	0.05 N $Mg(OCOCH_3)_2$, 0.1 neut. with $HClO_4$	$1.5	11	0.0074 031	0.017	0.0084
11	0.05 M CH_3COONa, 0.5 neut. with $HClO_4$	+2.9	5	0.006–0.011	0.009	0.013
12	0.2 M CH_3COONa	+3.3	5	0.017–0.040	0.028	0.025
13	0.77 M Pyridine	+4.0	6	1.0–1.5	1.3	1.6
14	2 M CH_3COOK	+4 5	7	0.10–0.18	0.13	0.32
15	3 M Pyridine	+4 8	3	7–10	8 0	6.2

The most detailed recent studies of acid and base catalysis in aqueous solutions have been carried out by Lowry[3] and by Bronsted[4] in connection with the investigation of the mutarotation of glucose. The results of these two investigators show that in this process both an acid and a base (in Bronsted sense of the terms) are involved. If the acetylation of β-naphthol by acetic anhydride is subject to the same fundamental laws, the catalysts which would be effective would be the solvated hydrogen ion (the acetonium ion $CH_3COOH_2^+$), undissociated acid molecules, the acetate ion (or other ion of a weak acid) and relatively strong basic molecules such as pyridine. Just as the hydrated hydrogen ion and the hydroxyl ion are usually the most effective catalysts in aqueous solution, so in glacial acetic acid the solvated hydrogen ion and the acetate ion would

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[3] Lowry, J. *Chem. Soc.*, 1927, 2554.

[4] Brönsted and Guggenheim, THIS JOURNAL, 49, 2554 (1927).

be expected to be of predominant influence. The molecules of acetic acid, like those of water, may act as either acid or basic catalysts by virtue of their ability to donate or receive a proton with the formation of the acetate and acetonium ions, respectively. The effectiveness of these catalysts would be expected to be expressed by an equation such as the following

$$k = k_o + k_{\mathrm{H}^+}C_{\mathrm{H}^+} + k_{\mathrm{Ac}^-}C_{\mathrm{Ac}^-} + k_{\mathrm{B}}C_{\mathrm{B}} \qquad (1)$$

In this equation, k is the specific reaction constant as measured, k_o the constant in pure acetic acid, k_{H^+}, k_{Ac^-}, k_{B}, the constants characteristic of the solvated hydrogen ion, the acetate ion and any strongly basic ion and C_{H^+}, C_{Ac^-}, C_{B} the concentrations of these acids and bases. The effect of very weak acids and bases has been neglected since the recent work of Bronsted shows that, at least in certain cases, the value of each catalytic constant is closely related to the strength of the acid or base.

Unfortunately we have no certain information in regard to the concentrations of the ions in the case at hand so we cannot substitute the proper values in Equation 1. However, we have found that our experimental results may be formulated in terms of the hydrogen ion activity of our solutions by means of an equation similar to Equation 1. This empirical equation is as follows:

$$k \times 10^2 = 0.005 + 0.1\,a_{\mathrm{H}^+} + \frac{10^{-5}}{a_{\mathrm{H}^+}} + 2.0\,C_{\mathrm{Pyridine}} \qquad (2)$$

In this equation a_{H^+} denotes the hydrogen ion activity referred to an aqueous solution of $P_{\mathrm{H}} = 0$ as the reference state as in the previous work; it is defined experimentally as $\log a_{\mathrm{H}^+} = -P_{\mathrm{H}}^{(\mathrm{HAc})}$.

The values of k calculated according to Equation 2 are given in the last column of Table II. In Fig. 1, where log k is plotted against $P_{\mathrm{H}}^{(\mathrm{HAc})}$, the curve of Equation 2 omitting the last term is shown. For solutions 1 to 8 only the second term of Equation 2 is involved and there is, therefore, a straight line relationship between log k and a_{H^+}. With solution 14 only the third term is significant and the factor of 10^{-5} was obtained by a consideration of this point. The value of k_0 (0.005) was found empirically as that necessary to give the proper values with those solutions in which both the second and third terms are small. The introduction of the last term in the cases of the solutions containing pyridine is necessary to correspond to the increased catalytic activity; that such a term should appear would be expected from Bronsted's theory.

It is obvious that the factors 0.1 and 10^{-5} in the second and third terms of Equation 2 are not k_{H^+} and k_{Ac^-}, but include also a factor which relates the activity of the hydrogen ion, in the one case to the concentration of the acetonium ion ($CH_3COOH_2^+$) and in the other case to the concentration of the acetate ion. If in a 0.2 M solution of perchloric acid $C_{\mathrm{H}^+} = 0.2$, k_{H^+} is about 10^4 and if in a 0.2 M solution of sodium acetate $C_{\mathrm{Ac}^-} = 0.2$,

$k_{Ac^-} = 0.1$. It is extremely unlikely that such a simple state of affairs is actually the case even in the strong acid and basic solutions in glacial acetic acid; the assumption, however, may not be very greatly in error. It is interesting that k_B for pyridine (2.0) was found to be only about twenty times the value of k_{Ac^-} (0.1) derived on this simple assumption. It is impossible to estimate, at present, the concentration of the solvated hydrogen ion in solutions 2–15 except on the simple assumption that there is a direct proportionality between C_{H^+} and a_{H^+}, as has been done in writing Equation 2. To evaluate the catalytic activity of the other components of these buffer solutions will require work of a greater accuracy than that presented in this paper.

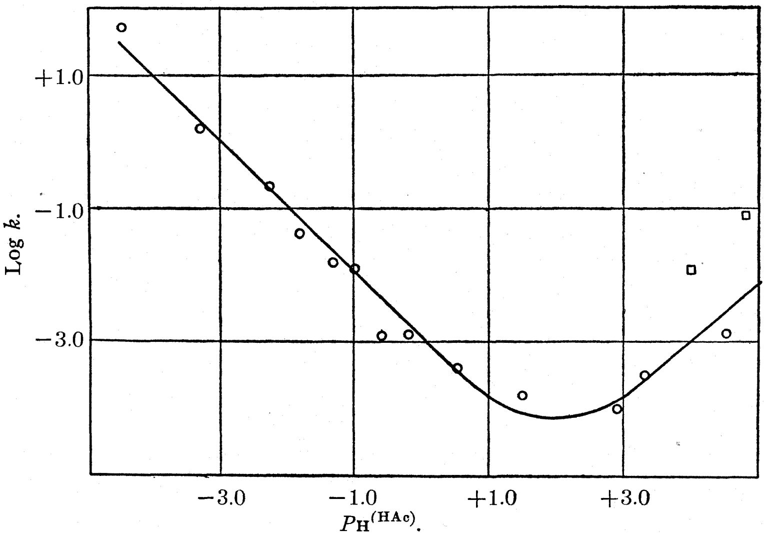

Fig. 1.—The rate of acetylation of β-naphthol in glacial acetic acid solutions. The smooth curve corresponds to Equation 2 with the omission of the last term. The experimental values are shown by the circles; the squares indicate the experiments using pyridine.

From the preparative point of view, it should be noted that the results reported in Table II cover a very wide range in the rates of reaction. Thus, in the perchloric add solution (No. 1) the time required for 50% reaction is less than six seconds as compared with five days in the slowest reaction (No. 11) and ten minutes with a 3 molar pyridine solution. It is thus possible by choosing the proper buffer solution to regulate quite closely the rate of the reaction between acetic anhydride and hydroxy compounds.

Summary

Measurements have been made of the rate of acetylation of β-naphthol by acetic anhydride in glacial acetic acid solutions of definite hydrogen ion

activity. The rate varies nearly a million-fold and is dependent on the acidity or basicity of the medium. The maximum rate is at $P_H^{(HAc)}$ -4.5, the minimum at about $P_H^{(HAc)}$ $+2.0$; over this range the rate is approximately proportional to the hydrogen ion activity. Between $+2.0$ and $+5.0$ the rate increases again showing that the process is one which is subject to both acid and basic catalysis.

CAMBRIDGE 38, MASSACHUSETTS

NOTE

A Simpler Derivation of the Cook Formula for the Determination of the Acetyl Value of Fats and Oils.—It is now generally conceded that the André–Cook[1] method of determining the acetyl number is more accurate and more rapid than the older method of Lewkowitsch.[2] The André–Cook method consists merely in determining the saponification value of the oil before and after acetylation. The acetyl value is then calculated by means of the formula

$$A = \frac{S' - S}{1 - 0.00075S}$$

where A is the acetyl value, and S and S' are the saponification values before and after acetylation. The derivations of this formula given by André and by Cook are rather involved.

In this note the same formula is derived by a simpler method. Let x represent the weight of acetylated oil which will contain 1 mole (59 g.) of *acetate* radical. Then x g. of acetylated oil will yield one mole of acetic acid on hydrolysis, and this quantity of acetic acid will require 1 mole or 56,000 mg. of potassium hydroxide for neutralization. Therefore, the acetic acid from 1 g. of acetylated oil will require $56{,}000/x$ mg. of potassium hydroxide, and

$$A = \frac{56{,}000}{x} \text{ or } x = \frac{56{,}000}{A} \qquad (1)$$

By definition of x it is obvious that x g. of acetylated oil was derived from a quantity of original oil which contained 1 mole (17 g.) of hydroxyl radical. The gain in weight during the acetylation of this quantity of oil was 59—17 or 42 g. Therefore x g. of acetylated oil was derived from $(x-42)$ g. of original oil.

Since A is equal to the number of mg. of potassium hydroxide needed to neutralize the acetic acid from 1 g. of acetylated oil, Ax mg. of potassium hydroxide will be needed for the acetic acid from x g. of acetylated oil. Similarly $S'x$ mg. of potassium hydroxide will be needed to saponify x g. of acetylated oil; and $S(x-42)$ mg. will be needed to saponify $(x-42)$ g. of

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[1] André, *Bull. soc. chim.*, [4] 29, 745 (1921); Cook, THIS JOURNAL, 44, 392 (1922).

[2] Lewkowitsch, *J. Soc. Chem. Ind.*, 16, 503 (1897).

original oil, which is equivalent to x g. of acetylated oil. In other words, x g. of acetylated oil require $S(x-42)$ mg. of potassium hydroxide to react with the glycerol esters, Ax mg. to react with the acetate esters and $S'x$ mg. for complete saponification. Therefore

$$S(x - 42) + Ax = S'x \tag{2}$$

Substituting (1) in (2)

$$S\left(\frac{56{,}000}{A} - 42\right) + A\,\frac{56{,}000}{A} = S'\,\frac{56{,}000}{A}$$

Multiplying by $A/56{,}000$

$$S(1 - 0.00075A) + A = S'$$

Solving for A

$$A = \frac{S' - S}{1 - 0.00075S} \tag{3}$$

Equation (3) is identical with the Cook formula.

CONTRIBUTION FROM THE
CHEMICAL LABORATORY OF
RUTGERS UNIVERSITY
NEW BRUNSWICK, NEW JERSEY

WILLIAM RIEMAN III
ALFRED T. HAWKINSON

RECEIVED MARCH 2, 1928
PUBLISHED AUGUST 4, 1928

NEW BOOKS

Das Periodische System in Neuer Anordnung mit Tabellen über Fünfzehn Physikalische Konstanten in Anordnung nach der Ordnungszahl der Elemente und nach der Grosse der Konstanten. (The Periodic Table in a New Form with Tables of Fifteen Physical Constants Arranged According to the Atomic Numbers of the Elements and the Magnitude of the Constants.) By DR. DARWIN O. LYON. Franz Deuticke, Leipzig and Vienna, 1928. vi + 40 pp. Illustrated. 17.5 X 26 cm. Price, unbound, M 8; bound, M. 10.

In an introduction the author first discusses rather broadly the origin and structure of matter. Next there is a cursory presentation of the Thomsen-Bohr arrangement of the elements followed by a brief discussion of several other arrangements of the elements particularly spiral ones. Special attention is devoted to magnetic relationships.

In the concluding section there are thirteen diagrams where curves are drawn connecting thirteen physical properties such as density, melting point, specific heat, electrical conductivity, entropy, etc., plotted against atomic numbers. There is then a large table where the numerical values of all these properties and the atomic numbers and atomic weights are arranged in fifteen columns with increasing values downward.

There is a clear tendency for the elements to occur at about the same level in the various columns of this table, although almost every element shows marked and violent irregularities. The most regular of all the elements is tin (No. 50) which comes at almost precisely the same level in all the columns except that for the melting points. It is not clear, however, that this marked regularity would persist if data for these properties were available for all the elements, or *a fortiori* if still other physical properties were similarly listed.

A final table lists the numerical values of these properties in the order of the atomic numbers.

ARTHUR B. LAMB

The Phase Rule and its Applications. By ALEXANDER FINDLAY, M.A., D.Sc., F.I.C., Professor of Chemistry, University of Aberdeen. Sixth edition, revised and largely rewritten. Longmans, Green and Company, 55 Fifth Avenue, New York, 1927. xv + 326 pp. 165 figs. 14 X 22 cm. Price $3.50.

In this sixth edition the author has undertaken a more thorough revision than in any of the preceding new editions. It is evident that a careful consideration has been given to the many recent advances in the wide field covered by this treatise.

To accomplish this thorough revision the author has made somewhat extensive alterations in the general framework of the book. The introductory chapters on systems of one component have been rewritten from a general and systematic rather than a specific point of view; the chapters on systems of two components have also been rewritten and considerably enlarged. A discussion of the nature of the equilibria in intensively dried systems and of Smits' theory of allotropy has been added as well as an entirely new chapter on the applications of equilibrium diagrams.

It is a tribute to the utility and excellence of this treatise that new editions of it have been in such constant demand. We predict a similar popularity for this latest edition—which, by the way, is aptly dedicated to Wilder D. Bancroft.

ARTHUR B. LAMB

Lehrbuch der Organischen Chernie. (Textbook of Organic Chemistry.) By JULIUS VON BRAUN, Ph.D., Professor and Director of the Chemical Institute of the University of Frankfort. S. Hirzel, Konigstrasse 2, Leipzig, Germany, 1925. xxii + 508 pp. 18 × 25.5 cm. Price, unbound, 22 M.; bound, 24 M.

This comprehensive text of organic chemistry is divided into four parts: (I) Introduction, (II) General, (III) Special and (IV) Historical. The chapter headings demonstrate in a general way the manner in which the subject has been presented.

(I). The introduction comprises a description of the analysis, principal characteristics and investigational methods of organic compounds.

(II). The general part contains the following chapters: (1) Methane and its Closest Derivatives; (2) General Survey of the Formation of Organic Compounds; **(3)** Hydrocarbons; (4) Halogen Compounds; (5) Metallo-organic Compounds; (6) Sulfonic Acids; (7) Nitro Compounds; (8) Reduction Products of Nitro Compounds; (9) Phosphorus, Arsenic, Antimony, Bismuth, Silicon and Boron Derivatives; (10) Hydroxyl Compounds; (11) Carbonyl Compounds; (12) Carboxyl Compounds; (13) Heterocyclic Compounds; (14) Summary and Critical Discussion (methods for determining constitution, value of physical properties for constitution, rearrangements, etc.).

(III). The special part is divided as follows: (1) Proteins; (2) Carbohydrates; (3) Fats; (4) Purines; (5) Alkaloids and Synthetic Medicinals; (6) Terpene Compounds and Rubber; (7) Resins, Styrols, Tannins, Ferments; (8) Dyes.

(IV). The historical part takes up the development of the theories of organic chemistry from the earliest time.

It will be noticed in the general part that the subject is developed by discussing in detail the character, formation and reactions of each functional group in turn. The first chapter in this part deserves special comment because it introduces immediately to the new student almost all of the common functional groups. Thus, after discussing methane, it is shown how this is converted to methyl chloride, the latter in turn to methyl alcohol. Then follow dimethyl ether, the dimethyl esters of inorganic acids, nitromethane, methylamine, dimethylamine, trimethylamine, dimethylhydrazine, tetramethyl ammonium hydroxide, methyl mercaptan, methyl sulfide, methyl sulfonic acid, zinc methyl, methyl magnesium iodide, formaldehyde, formic acid, formamide, hydrogen cyanide.

All of the chapters include a description of both aromatic and aliphatic compounds, and a comparison of the formation and reactivity of the corresponding groups in these two classes is carefully discussed. The heterocyclic compounds are left to a special chapter on account of the many unusual reactions in this field.

The fourth part is an excellent summary of the historical development of organic chemistry and is particularly to be recommended to the average student.

The book covers an extraordinarily large number of individual reactions and topics and it is difficult to see how it could be used in an introductory course in organic chemistry as this subject is usually taught in the various universities of the United States. It could be used as a text in a second course, and would unquestionably be a valuable reference book to one who has some knowledge of organic chemistry and who desires to have the outstanding facts about many of the fields of modern interest and importance. The author has made no attempt to include a discussion of the commercial applications of organic compounds or of industrial processes.

This book should certainly be added to the list of those which the student with some knowledge of organic chemistry, and which the teacher of this subject, should have at their disposal.

ROGER ADAMS

The Journal of the
American Chemical Society

VOL. 50 SEPTEMBER, 1928 No. 9

[COMMUNICATION FROM THE CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

HOMOGENEOUS GAS REACTIONS AT HIGH CONCENTRATIONS.
I. DECOMPOSITION OF HYDROGEN IODIDE

BY GEORGE B. KISTIAKOWSKY

RECEIVED MARCH 12, 1928 PUBLISHED SEPTEMBER 5, 1928

Kinetic studies of homogeneous gaseous reactions have revealed in a number of cases a perfect agreement between the predictions of the mass action law as deduced from the stoichiometric equation of the process and the observed influence of concentration on the reaction velocity. It has been generally assumed that, in these cases, the observed reactions directly follow a collision of two molecules in the case of bimolecular and of three molecules in the case of trimolecular reactions. There exist, however, many reactions which follow a more complicated course even in the small concentration interval investigated and the postulation of intermediary processes seems to be necessary for their kinetic interpretation. Moreover, the mechanism of bimolecular reactions may not be quite as simple as it appears, although this cannot be definitely established by the existing experiments. It is possible that experiments on a larger scale of concentrations would reveal deviations from the simple bimolecular law. Hibben[1] found, for example, that the decomposition of nitrous oxide is no longer bimolecular at very low concentrations. This deviation is due, apparently, to the predominance of a heterogeneous wall reaction and is therefore in no direct relation to the mechanism of the homogeneous reaction. The increase of relative probability of a wall reaction with increasing mean free path of the gaseous molecules is of course inherent in all bimolecular gaseous reactions and may considerably complicate their investigation at very low concentrations. Conversely, reactions which are homogeneous at ordinary concentrations will very probably remain so at higher concentrations and their investigation in this region, therefore, should not meet the difficulty mentioned above. Here, however, the homogeneous rate itself may become influenced by factors, the effect of which is negligible under ordinary experimental conditions ("atmospheric pressure" and below) owing to an increasing probability of three-

[1] J. H. Hibben, *Proc. Nat. Acad. Sci.,* 13,626 (1927).

and poly-molecular collisions or, speaking more generally, owing to the close proximity of the molecules. A hypothesis concerning a retarding effect of "three body" collisions on the rate of bimolecular reactions which the writer had in mind when starting these experiments has not been substantiated and its discussion therefore appears to be unessential; the experiments, however, offer one the possibility of drawing certain conclusions concerning the mechanism of bimolecular processes and should, therefore, be of some interest in connection with the theory of gaseous reactions.

The decomposition of hydrogen iodide was chosen as the object of study partly from considerations of an experimental nature, partly because this reaction has been most thoroughly investigated at ordinary concentrations and is known to have no complicating side reactions.

The rate of hydrogen iodide decomposition, the rate of its formation from molecular iodine and hydrogen and the position of the gaseous equilibrium have been extensively investigated by Bodenstein[2] over a wide range of temperatures (283–508°). He obtained good agreement between the rate and the equilibrium measurements, showing furthermore that the rate of decomposition is bimolecular—at least in the somewhat narrow concentration interval (around 0.042 mole per liter) investigated—and that this reaction is homogeneous in glass vessels. The more recent experiments of Taylor,[3] who found the rate of decomposition to be influenced by extensidn of the surface of the Pyrex glass used by him, can hardly affect Bodenstein's last conclusion, since his velocity constants are throughout considerably larger than those of Bodenstein. Furthermore, from Bodenstein's values of $d \ln k/dT$, a constant heat of activation[4] is calculable, whereas Taylor's results give a heat of activation decreasing with temperature. His experiments only show, therefore, that, in addition to the homogeneous decomposition, a wall reaction can be created by a suitable choice of the material for the containing vessels. Quite recently, Lewis and Rideal[5] doubted the simple bimolecular character of the reaction, suggesting that the decomposition is caused by free iodine atoms and finding that the rate (and similarly the position of the equilibrium) is influenced by minute quantities of water vapor. Bodenstein and Jost[6] pointed out, however, that phosphorus pentoxide, used by Lewis and Rideal as the drying agent, reacts at the temperature of their experiments with hydrogen iodide and probably causes all the observed effects. The experiments of Lewis and Rideal, therefore, do not prove the active influence of water vapor on the reaction velocity, but, as Bodenstein and

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[2] Bodenstein, *Z. physik. Chem.*, **13**, 56 (1894); **22**, 1 (1897); **29**, 295 (1899).

[3] H. A. Taylor, *J. Phys. Chem.*, **28**, 984 (1924).

[4] W. C. McC. Lewis, *J. Chem. Soc.*, **113**, 471 (1918).

[5] B. Lewis and E. K. Rideal, THIS JOURNAL, **48**, 2553 (1926).

[6] M. Bodenstein and W. Jost, *ibid.*, **49**, 1416 (1927).

Jost conclude, there is on the other hand no experimental evidence available contradicting the existence of such influence.

Experimental Details

The method chosen for the purpose of the present investigation was the static one and was in principle very similar to that used by Bodenstein. Sealed vessels filled with hydrogen iodide were heated in a thermostat for a desired length of time and their contents later analyzed.

Since, however, the details of both methods are somewhat different and the technique of rate measurements on gases at pressures up to about 500 atmospheres is not yet quite developed, the more important details will be here briefly described.

Gas Preparation.—Hydrogen iodide was prepared by passing a mixture of hydrogen and iodine through a heated furnace. It was distilled once in a vacuum to free it from larger quantities of iodine and was stored in a glass vessel cooled by liquid air.

Preparation of Gas Samples.—In order to fill the experimental vessels with hydrogen iodide they were sealed (through a graded seal) to a larger glass bulb (about 200 cc.) provided with a Daniels[1] glass membrane manometer and a dry inner ground glass stopper, magnetically operated, which connected it through a trap and, further, through a greased stopcock with the hydrogen iodide container. The only greased stopcock in direct connection with the filling bulb was at the end of a long capillary (to prevent decomposition of larger quantities of hydrogen iodide) and connected it through a mercury vapor trap to a mercury diffusion pump. After thorough evacuation of the system some hydrogen iodide was distilled into the intermediary trap with the pump still working. This operation resulted always in a slight decomposition due to the passage of hydrogen iodide through the greased stopcock but the iodine formed remained during the subsequent operations in the trap on account of its low vapor pressure. The stopcocks to the container and to the pump were now closed and hydrogen iodide in the trap was slowly warmed up until a desired pressure (from 50 to **300** mm.) was created in the system. Then the inner glass stopper was closed and the trap and one of the experimental vessels were simultaneously cooled by liquid air. Experiments showed that practically no hydrogen iodide diffused from the large bulb through the stopper but that all condensed in the vessel. After about two minutes the stopcock to the pump was opened again and a few minutes later the vessel, which had been filled, was sealed off. It was found impossible to prevent slight decomposition of hydrogen iodide, particularly during the sealing off; the liquid hydrogen iodide, after the vessels were warmed up, was always slightly colored by iodine. Analysis of the contents of those vessels, which were somewhat more than usually dark colored and thus were considered unsuitable for experiments, showed that the free iodine content of these was not greater than 0.02%. The amount of iodine present initially in other vessels must, therefore, be lower than this figure. The experimental vessels were made of fused quartz, since the only other possible material—Pyrex glass—has been shown by H. A. Taylor to be catalytically active. The vessels were of cylindrical shape of some 50 cc. volume (2 × 15 cm.) for low pressure experiments, of about 8cc. volume (0.8 × 15 cm.) for medium pressures and of about **3.3** cc. (0.5 × 15 cm.) and 0.7 cc. (0.2 × 20 cm.) for high pressures. The 3.3cc. vessels (two of them) used initially were found to be impractical. On account of their very thick walls (10 mm.) the quartz showed signs of considerable inner strain, manifested from time to time by small cracks in the surface. One of these vessels exploded

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[7] Daniels and Bright, THIS JOURNAL, 42, 1131 (1920).

a few minutes after cooling, the other during the first experiment after about five minutes of heating in the thermostat. The hydrogen iodide concentrations were in both cases only about one-fifth of those which the smaller vessels with the same ratio of internal diameter to wall thickness (1:2) were later found to withstand.

One end of each vessel was drawn to a fine tip, the other to a capillary about **0.5** mm. in diameter used in sealing the vessels to the filling system. The volume of all vessels, determined by weighing, varied slightly from experiment to experiment on account of the impossibility of sealing off the capillaries at exactly the same length. The errors so introduced are negligibly small for the larger vessels; for the small ones they were partly corrected for, the length of the capillary being measured each time and also the average area, the volume thus determined being added to the main volume. The errors introduced through the somewhat irregular shape of the capillaries may amount to as much as **0.5%** of the total volume.

Conduct of the Reaction.—For heating the vessels a large lead-bath thermostat, electrically heated, was used. The temperature, measured by a Chromel-Alumel thermocouple, was read on a potentiometer to 0.2°. The thermostat contained an efficiently working stirrer, an additional knife heater and a mercury thermoregulator. Due to a special design this latter was very sensitive; it responded to a sudden change of temperature of **0.5**" within ten seconds and the periodic variations of the temperature in the thermostat did not amount to more than **0.2".** During longer periods of time, however, the temperature of the thermostat, when left without attention, showed a slow drift amounting sometimes to as much as **1.5**" in twenty-four hours. The insertion of the cold quartz vessels into the thermostat lowered its temperature by a few degrees and several minutes were required for the temperature to become stationary again. In the later part of the work this inconvenience was avoided by heating the thermostat before each experiment to an appropriately higher temperature, so that even initially the temperature was within **0.5°** of the average.

To obtain a rapid cooling, the vessels, after taking them out of the thermostat, were immediately put into a steel pipe attached to a carbon dioxide tank and were cooled by a stream of cold gas. Two minutes were found to be sufficient (except for the 3.3cc. vessels) to bring them below room temperature.

Analysis.—The analysis was initially beset with considerable difficulties They were overcome by applying a cotton pad soaked in liquid air to one side of the vessel[8] and breaking the fine tips in distilled and degassed water under a specially designed small gas receiving apparatus. The rush of evaporating hydrogen iodide was so violent, however, that sometimes a fraction of it escaped from the receiver and more than one analysis was ruined in this way. It was fortunate that escaping hydrogen iodide immediately formed a fog in the air and so was easily detected. The tip of the capillary at the other end of the vessel was finally broken off and the vessel washed out with a degassed potassium iodide solution. For the subsequent titration of iodine and hydrogen iodide a standard solution of sodium thiosulfate approximately **0.1** N and two potassium hydroxide solutions **0.1** and **0.03 N** were used. Before each titration a **0.01** or **0.005 N** solution was freshly prepared from the standard thiosulfate by dilution. All titrating solutions were checked at regular time intervals according to the usual standard methods. For the iodine determination a certified micro buret was used almost exclusively. The other volumetric apparatus was recalibrated. The volumetric determination of free hydrogen, which, as a check, proved to be so useful to Bodenstein, had to be abandoned here on account of considerable complications resulting in the method of analysis

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[8] The simpler procedure of freezing one end of the vessels failed, hydrogen iodide melting first at the far end of the narrow and relatively thin-walled capillary and the resulting expansion cracking the quartz.

adopted. However, Bodenstein had to use this determination only in order to correct errors in analysis due to a reaction of hydrogen iodide with the alkaline constituents of his soft glass vessels. Pure quartz, which was used in the present work, is very unlikely to react in this way and therefore the omission of the hydrogen determination is more or less admissible (see, however, later pages)

Calculation of Results

By integrating the equation

$$-\frac{d[HI]}{dt} = k[HI]^2 - k_1[I_2][H_2] \tag{1}$$

Bodenstein has derived an expression which gives the velocity constant k of the decomposition reaction as a function of the time t, the fraction decomposed, x

$$x = \frac{I_2}{I_2 + {}^1/_2HI} \tag{2}$$

and of the fraction decomposed at equilibrium ζ. The equation is

$$k = \frac{\log\left[\frac{\frac{\zeta}{2\zeta - 1} - x}{\zeta - x}(2\zeta - 1)\right]}{0.8686\,\frac{1-\zeta}{\zeta}\,t} \tag{3}$$

This equation is valid for experiments in which pure hydrogen iodide was present initially. The reaction of hydrogen iodide being bimolecular, the constant k of the above equation is still proportional to the concentration and must therefore be divided by this latter in order to obtain a bimolecular velocity constant independent of concentration. The measurements of the equilibrium between gaseous hydrogen iodide, iodine and hydrogen at total concentrations not far from 0.04 mole per liter have been summarized by Bodenstein in the following interpolation formula for the equilibrium decomposition, ζ

$$\zeta = 0.13762 + 7.221 \times 10^{-5}t + 2.5764 \times 10^{-7}t^2 \tag{4}$$

where t is the temperature in centigrade degrees. Prom this equation the equilibrium decomposition can be calculated for every temperature.

Equation *(3)* shows immediately that the closer the observed decomposition is to that at equilibrium, the more sensitive will the calculated value of the velocity constant k be to small errors or to changes in the equilibrium constant. For this reason the time of heating in the following experiments was always chosen so as to give only a small and almost uniform decomposition. Such a decision, however, in conjunction with the bimolecular character of the reaction, limited the choice of convenient temperatures to the lower part of the range investigated by Bodenstein.

Experimental Results

Table I gives the results of rate measurements at an average temperature of 321.4°. The temperature of each experiment is **a** graphical average of all readings during the time of heating. The constant k given in the seventh column has been calculated by means of Equation (3), using for ζ

TABLE I

THE RATE OF HI DECOMPOSITION AT 321.4°

No.	Average temp., °C.	Time, secs.	Decomp., %	Vol. of the vessel, cc.	Initial concn. of HI, mole/liter	k(sec.$^{-1}$) × 10^6	k_0 × 10^6 (moles/liter. sec.)
1	322.4	82800	0.826	51.38	0.02337	0.1004	3.96
2	321.6	172800	2.567	59.80	.03838	.1543	3.98
3	322.1	180000	3.286	59.80	.04333	.1900	4.22
4	322.7	173100	3.208	51.38	.04474	.1927	3.98
5	321.6	81000	2.942	51.38	.1027	.3763	3.61
6	321.6	57560	2.670	7.899	.1126	.4778	4.20
7	322.4	61320	4.499	7.899	.1912	.7792	3.85
8	321.4	19200	2.308	7.899	.3115	1.235	3.96
9	321.6	18000	2.202	7.899	.3199	1.255	3.87
10	321.3	16800	2.071	7.899	.3279	1.262	3.87
11	321.4	17400	2.342	7.899	.3464	1.383	3.99
12	321.4	17700	2.636	7.899	.4075	1.537	3.77
13	320.4	18000	2.587	7.899	.4228	1.482	3.80
14[a]	321.3	23400	4.343	7.899	.4736	1.967	4.18
15	321.6	6000	2.224	3.280	.9344	3.802	4.03
16	321.7	5400	1.903	0.778	.9381	3.597	3.76
17	321.1	8160	3.326	.781	1.138	4.251	3.81
18	321.2	3600	1.986	.703	1.201	5.642	4.74
19	321.7	5400	2.741	.713	1.231	5.253	4.19
20	321.7	5400	3.089	.779	1.317	5.940	4.42
21	321.1	8160	4.116	.715	1.339	5.305	4.04
22	321.1	3600	1.830	3.280	1.351	5.187	3.92
23[a]	321.3	4380	2.972	0.810	1.624	7.033	4.36
24	321.2	3600	2.369	3.280	1.714	6.767	3.99
25	321.4	3600	2.959	0.777	2.067	8.520	4.12
26	321.1	3600	3.360	3.280	2.414	9.523	4.02
27	321.2	3600	3.710	0.782	2.532	10.80	4.31
28	321.4	3600	4.224	.785	2.678	12.40	4.63
29	321.3	3600	3.912	.729	2.680	11.43	4.31
30	321.4	3600	4.505	.777	2.682	13.29	4.95
31	321.4	1560	1.786	.788	2.742	11.68	4.26
32	321.5	2400	2.947	.780	2.762	12.72	4.56
33	321.4	3600	4.316	.729	2.822	12.68	4.50
34	321.6	2400	3.168	.732	2.886	13.72	4.71
35	321.6	2400	3.215	.710	2.982	13.94	4.63
36	321.6	1560	2.093	.735	2.999	13.74	4.54
37	321.3	1440	2.078	.740	3.310	14.78	4.51
38	321.3	1440	2.214	.780	3.360	15.77	4.74
39	321.1	1500	2.415	.785	3.751	16.56	4.50
40	321.4	1470	2.865	.782	3.769	20.17	5.35
41	321.4	1470	2.687	.731	3.914	18.87	4.82
42	321.1	1500	2.936	.720	4.093	20.28	5.05
43	321.4	1470	2.822	.780	4.146	19.87	4.79

TABLE I (*Concluded*)

No.	Average temp., °C.	Time, secs.	Decomp., %	Vol. of the vessel, cc.	Initial concn. of HI. mole/liter	k(sec.$^{-1}$) $\times 10^6$	$k_0 \times 10^6$ (moles/liter, sec.)
44	321.4	1470	3.047	.718	4.353	21.52	4.94
45	321.2	1140	3.426	.773	5.742	31.38	5.52
46	321.4	1200	4.178	.709	6.272	36.77	5.86
47	321.4	1200	4.607	.778	6.502	40.83	6.28
48	321.4	1200	4.646	.835	6.722	41.22	6.09
49	321.4	1200	4.976	.657	6.807	44.40	6.52
50	321 4	1200	5.487	.712	7.131	49.43	6.93

the value 18.745% computed from Bodenstein's interpolation formula and counting the time in seconds. In order to obtain the constant k_0 of the last column, the k's were divided by the initial concentration of hydrogen iodide expressed in moles per liter (sixth column) and were reduced to the same temperature, 321.4°, by using a value 1.061 as the temperature coefficient of the rate at 321° per degree, calculated from Bodenstein's data. The table reproduces actually the results of all the experiments made which were not interrupted by an explosion of the vessel or by a failure in the analysis of the contents. A group of seven experiments in vessels which, contrary to the usual procedure, were not heated and degassed thoroughly during the evacuation process previous to filling, have been recorded separately in Table II. All these experiments, scattered throughout the range of concentrations investigated, yield values of k_0 considerably larger than the rest of the experiments and indicate, therefore, the presence of some additional catalytic decomposition. Supporting this view is an observation made occasionally when degassing the reaction vessels, that microscopic amounts of some yellow substance—possibly of mercuric iodide—were deposited in the colder parts of the apparatus.

TABLE II

CATALYZED DECOMPOSITION

No.	Av. temp., °C.	Time, secs.	Decomp., %	Vol., cc.	Init. HI, mole/liter	k $\times 10^6$ (sec.$^{-1}$)	k$_0$ $\times 10^6$ (mole/liter/sec.)
51	321.4	61200	6.501	10.015	0.1130	1.171	10.4
52	321.6	18000	3.674	7.899	.3128	2.152	6.81
53	321.3	8160	4.879	0.779	1.194	6.685	8.03
54	321.5	6120	4.806	.733	1.514	8.367	5.50
55	321.4	3600	5.384	.732	3.092	16.13	5.22
56	321.3	1500	3.175	.733	3.772	22.02	5.87
57	321.7	1200	5.141	.763	5.873	46.02	7.75

Experiments with Specially Dry Hydrogen Iodide.—In order to investigate how far the rest of the experiments represented the true velocity of decomposition of pure hydrogen iodide and were not influenced by the presence of some unknown impurities (water), the filling apparatus was modified at the end of the present work. The stopcock and the capillary leading to the pump were removed and replaced by a wide tubing with a constriction for sealing off; between the trap, mentioned in the description of the apparatus, and the hydrogen iodide container were introduced three additional traps with inner glass seals at both ends of the line. Freshly prepared hydrogen iodide was used. All the separated (by the inner seals) parts of the system were baked out in a vacuum at 450400' for ten hours. The quartz part of the apparatus with the reaction vessels sealed to it was heated to a somewhat higher temperature than the rest. Hydrogen iodide was distilled four times in a vacuum from a bath of melting carbon disulfide ($-112°$), only the first fraction being used each time and the rest being sealed off after cooling. Unfortunately the glass membrane manometer failed to work after the heating and the pressure of hydrogen iodide in the filling system had to be guessed. The result was that too much was filled into two of the vessels and they exploded on heating; the remaining two experiments are Nos. 14 and 23 of the first table. Hydrogen iodide prepared in this way must have been not only extremely dry but also incomparably freer from all foreign matter than the quality normally used. Incidentally, it contained only very small quantities of free iodine and appeared to the eye absolutely colorless. This was secured by allowing a long time for complete condensation of hydrogen iodide before the vessels were sealed off.

The Influence of Temperature.—Table III represents nine experiments made at a lower temperature. The value of ζ used in the calculation of the constants k was computed from Bodenstein's data to be $\zeta = 18.247\%$. The bimolecular constants k_0 of the last column have been corrected to the mean temperature of 300.0".

TABLE III

THE RATE OF HI DECOMPOSITION AT 300 0°

No.	Temp., °C.	Time, secs.	Decomp., %	Vol., cc.	Coocn.	$k \times 10^6$	$k_0 \times 10^6$
58	299.7	10500	1 075	0.702	1.000	1 036	1 05
59	299.7	10500	1.433	.838	1.353	1.387	1.04
60	300.0	9600	1.523	.830	1.455	1.614	1.11
61	300.0	9600	1.946	.655	1.957	2.070	1.06
62	300.0	9600	1.933	.709	1.959	2.125	1 09
63	299.6	2400	0.6966	.827	2.405	2.818	1.20
64	300.0	9600	2.745	.835	2.482	2.956	1.19
65	299.6	2400	1.547	.645	4.847	6.558	1.38
66	299 8	1320	1.145	.613	5.998	8.818	1 49

Equilibrium Measurements.—Table IV gives the results of equilibrium measurements at 321.4°. The analysis of these experiments was particularly difficult on account of large amounts of non-condensable hydrogen present and a considerable number were rendered useless by losses of hydrogen iodide. The number of experiments offered is somewhat limited also because the quartz vessels did not seem to withstand well the long heatings necessary to attain equilibrium. Numerous explosions which, of course, ruined the rather costly quartz vessels were the unpleasant result.

Table IV

The Thermal Equilibrium at 321.4°

No.	Time, secs.	HI init., moles per liter	Decomp., %	Time, secs., calcd.
67	275400	1.02	18.67	139000
68	357000	1.30	19.03	109000
69	198000	1.64	18.68	86000
70	198000	1.79	18.93	79000
71	357000	1.92	19.72	74000
72	230400	2.08	19.27	68000
73	230400	2.12	19.40	67000
74	194400	2.21	18.78	64000
75	172800	2.24	18.48	63000
76	108000	2.29	18.71	62000
77	108000	2.30	18.81	61500
78	141000	2.65	19 02	53500
79	126000	3.73	20.75	38000
80	68700	5 39	19.46	26200

Errors

Influence of Impurities.—Before discussing the theoretical significance of the experiments made, it is well worth while to consider in detail the possible errors. Table II shows quite plainly that hydrogen iodide decomposition is rather sensitive to the presence of impurities. Whether the observed catalytic acceleration is really due to the mercuric iodide noticed or is due to oxygen occluded in quartz and driven off in most of the experiments by heating cannot be decided. It is important to note that the results of Table I very probably represent the true velocity of decomposition of pure hydrogen iodide, as is best demonstrated by the complete agreement between the main body of the results and those of experiments Nos. 14 and **23** made with unquestionably pure and dry hydrogen iodide.

Accidental Errors.—The mean of the first 14 experiments up to 0.5 mole per liter concentration (the reasons for this limitation will be seen from a later discussion) is $k_0 = 3.95 \times 10^{-6}$ with an average deviation of single values amounting to 3.1% and with a probable error of the mean itself of 0.73%. But, aside from one or two values with larger deviation—and these are very likely due to unobserved small losses of hydrogen iodide or of iodine (in the broken tip of the capillary)—the average deviation is even much smaller. It is fully accounted for by unavoidable errors in buret readings and other uncertainties of the analysis and of volume determinations and also by errors made in averaging the temperature;

these latter may amount easily for longer time intervals (overnight) to **0.3'** and will therefore account for about 2.0% deviation in the constants, k_0. All this shows that the rate measurements gave completely reproducible results.

Systematic Errors.—The calculated probable error of the mean does not include, however, systematic errors. The more important of these are: **(1)** Incorrect titers of solutions used and errors in the calibration of the volumetric apparatus. Assuming an error of 0.5% to be thus involved in each titration, we are on the safe side. This gives a possible error of **1.5%** in k_0, since iodine determination enters here in the first power, that of hydrogen iodide as the square. *(2)* More important still is the error in determination of the absolute temperature of the thermostat. The Chromel-Alumel thermocouple was calibrated in boiling water, mercury and sulfur. As the result of these determinations, repeated several times with almost identical results, a three-constant equation has been calculated which gives the temperature of the thermostat, designated in Table I as **321.4** to 321.6°. Independent check of the temperature was made by means of a platinum resistance thermometer and a high-precision Mueller type bridge. The first determination—in an early part of the work—yielded **321.2';** the second one, made somewhat later, **321.3'.** Attributing a statistical weight unity to the thermocouple determination and a weight **2** to the mean of the platinum thermometer temperatures, the final mean temperature is calculated to be 321.4° with an uncertainty of not more than **0.3'** or with an error in the k_0 not exceeding 2%.

Errors at **High** Concentrations.—The experiments at higher concentrations of hydrogen iodide are, of course, equally subject to all these errors and, in addition, to two others which will now be considered. The time intervals required for the heating up and for the cooling down of the vessels have been neglected so far, the "true" time of heating being equated to the actual time of immersion in the thermostat. This source of error will obviously affect the results more considerably the shorter the time of immersion. Therefore, four experiments, represented in Table V, have been made of only very short duration; the "true" time of heating has then been calculated after assuming an appropriate velocity constant

TABLE V
THE CORRECTION OF HEATING TIME

No.	Av. temp., °C.	Decomp., %	Vol., cc.	HI, moles per liter	$k_0 \times 10^6$, assumed	Time in seconds Immersion	Time in seconds Calcd. "true"
81	321.4	0.339	0.783	2.052	4.35	365	381
82	321.4	.316	.783	2.062	4.35	365	352
83	321.4	.389	.704	2.225	4.40	365	399
84	321.4	.526	.731	2.809	4.55	365	413
					Av.	365	388

k_0 (see the latter part of the article) for each experiment. The difference between the mean "true" and the actual immersion time amounts to only twenty-three seconds, the iodine initially present and the decomposition during the cooling apparently more or less compensating the slower rate during the warming up period. Therefore, the systematic error of time determination even in the shortest experiment (No. 45, Table I, 1140 seconds) amounts to only 2% and a correction of the results in Table I in this respect was considered unnecessary. The other error may arise from a change in the equilibrium decomposition due to the non-ideal character of the gases at high concentrations. The observed deviation of the decomposition velocity under these conditions from the normal course is rather in favor of such possibility. Table IV, containing the equilibrium measurements, could also be interpreted as supporting it. A closer comparison shows, however, that there is no systematic change of equilibrium decomposition with concentration of hydrogen iodide but rather a steady, although a slow, increase with time of heating for about equal concentrations. Different interpretations of the effect can be offered. (1) The time of heating was possibly too short. The last column of the table gives, however, the calculated times at which the equilibrium should be reached within 1% (that is, $x = 0.18558$ for $\zeta = 0.18745$) and shows that this time is throughout much shorter than the actual time of heating. It would remain so even if the equilibrium decomposition was shifted to $\zeta = 0.22000$ (this last calculation of course, was made with a suitably modified value of k_0). (2) The equilibrium mixture becomes inhomogeneous, liquid iodine being separated. Unfortunately a calculation of the iodine vapor pressure at 321° would be of no value since the composition of a liquid phase under the experimental conditions is unknown. Another consideration, however, will help. If a condensation does take place, there must be a critical concentration of hydrogen iodide with which at equilibrium a saturation concentration of iodine obtains. Above this, the extent of decomposition would increase very rapidly with increase of initial concentration of hydrogen iodide. No evidence of such behavior, at least in the concentration range investigated, can be found in Table IV. (3) Hydrogen is slowly consumed in the walls of the quartz vessels. The vessels showed, however, no visible signs of any change on the inner surfaces and so a reduction of silica appears improbable. It is more likely that hydrogen under high pressure is slowly diffusing through quartz. That helium diffuses through quartz even at room temperature has been shown by Elsey[9] and it is well known that at temperatures considerably higher than 320° quartz is quite permeable to hydrogen. The presence of such a diffusion process would not only account for the observed slow shift in the equilibrium decomposition but would also indi-

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[9] H. M. Elsey, THIS JOURNAL, **48**, 1600 (1926).

cate that the true decomposition values at high concentrations are somewhat lower than the figures recorded in Table IV and, hence, either about equal to or slightly lower than Bodenstein's value, $\zeta = 0.18745$, obtained for concentrations not in excess of 0.08 mole per liter. The velocity constants k_0 in the upper range of concentrations represent therefore in all probability either the true or slightly smaller values.

Kinetic Interpretation of the Results

For convenience in the following discussion the results of the first table have also been represented in Fig. 1. The ordinates give the velocity constant k_0, the abscissas the initial concentration of hydrogen iodide plotted on a logarithmic scale. The constants k_0 obtained at the mean temperature, 300.0" (Table 111), have also been plotted on Fig. 1 (as large circles) after having been multiplied by a factor of 3.85. This graphical representation will be of value in showing that the bimolecular velocity constant k_0 (the range 0.02 to 1.0 mole/liter) is quite independent of the size of the vessels used. Since, however, the surface–volume ratio of the different quartz vessels varied by at least a factor of 10, it means that the decomposition velocity measured was at least almost exclusively that of the homogeneous reaction. The experiments with dried hydrogen iodide mentioned earlier show, furthermore, that it was the true velocity of decomposition uninfluenced by the presence of impurities. Possibly even more convincing in this respect is a comparison with Bodenstein's results. His empirical interpolation formula for the velocity constant k_0[10] yields for the temperature 321.4° a value 1.10 X 10^{-5} (mole/22.4 liters, minutes). Converted to our units (mole/liter, seconds) the value is 4.12×10^{-6}. The same value 4.12 is obtained when for the calculation of the reaction velocity at 321.4° the equation

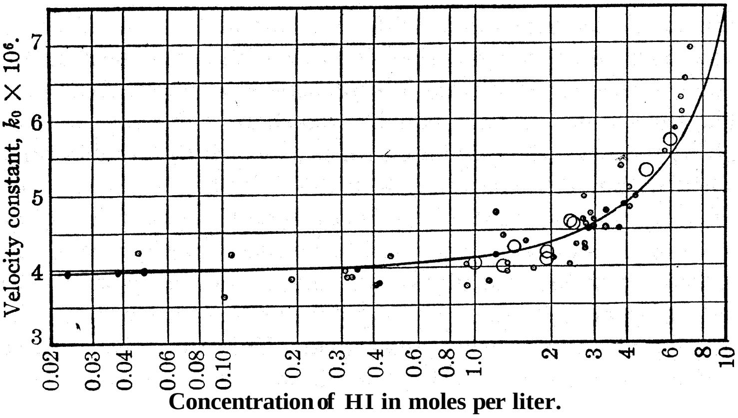

Fig. 1.—The bimolecular velocity constant of HI decomposition.

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[10] Bodenstein, Z. physik Chem., 29,295 (1899).

$$\ln \frac{k_{T_1}}{k_{T_2}} = A\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{5}$$

and the two nearest values (302 and 356°) of Bodenstein are used. The agreement between Bodenstein's and the present values is quite unusually good. The difference amounts to only 4% and is thus even within the limits of the maximum possible error estimated for these experiments alone, although about the same error *(5%)* must be inherent in Bodenstein's measurements. In consideration of the fact that he used soft glass vessels instead of pure quartz and that his method of filling the vessels (and therefore the amount of impurities) was quite different from ours, such agreement is the best proof that in both cases the true homogeneous rate has been measured.

Fig. 1 shows quite clearly that the velocity constant, k_0, which remains unchanged in a wide range of concentrations, starts to rise from about 1 mole per liter, reaching a value higher by more than 50% for the concentration of 7 moles per liter. Furthermore, as the values of k_0 at 300.0° indicate, the slope of the rise is essentially independent of the temperature; the temperature coefficient of the reaction rate at different concentrations therefore is the same.[11] The most natural explanation of this rise, that does not involve a postulate of some tri- or of still higher order molecular processes, is that the reaction rate is strictly proportional to the number of bimolecular collisions, but that the number of these latter is not proportional to the square of the concentration, provided the concentration is rather large. Indeed, van der Waals[12] has already shown that the equation for the total number of collisions

$$Z = 2\sqrt{\pi}\, N^2 \sigma^2 \sqrt{\frac{RT}{M}} \tag{6}$$

(N the number of molecules per unit volume of the only kind present, σ their diameter, M the molecular weight, R the gas constant and T the absolute temperature) is only a first approximation and that the next step in refining it is the multiplication of it by a factor

$$\frac{1}{1 - Nb} \tag{7}$$

The constant b has been found to be equal to four times[13] the volume of a molecule assumed to be a sphere. The same correction of course must be applied to the constants k_0 in order to retain the proportionality between the collision number and the reaction velocity. In Fig. 1 the curve has been drawn with a value of Nb equal to 47 cc. per mole or with σ =

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[11] It is appropriate to point out that the factor 3.85, by which the constants at 300.0" have been multiplied, is within 1% of the temperature coefficient of the rate between 300.0 and 321 4° determined from Bodenstein's data.

[12] J. D. van der Waals, "Over de continuiteit van den gas-en vloeistoftoestand," Leiden, 1873.

[13] O. E. Meyer, "Die kinetische Theorie de Jase," Breslau, 1899.

3.33×10^{-8} cm. This value of b fits best the numerous experiments between $c = 2.5$ and $c = 4.5$ moles per liter concentration. The experiments at very high concentrations are unsuitable for the determination of b because, as Jaeger[14] pointed out, even the corrected collision equation is only an approximation and must fail when Nb approaches unity. The experiments in the region $c = 0.9$ to $c = 2.5$ moles per liter show somewhat too large irregular deviations to be used for the calculation of b. They yield, however, a mean ($k_0 = 4.14 \times 10^{-6}$; $c = 1.31$ moles/liter), which is within 1% of the curve[15] drawn. The introduction of the quantity b into the expression for the collision number is equivalent to the introduction of the volume correction b into the equation of state of van der Waals. The other correction "a" which takes care of the attracting forces between the molecules has, however, a different influence on the form of the collision equation. As Sutherland[16] has shown, only the apparent diameter of the molecules is increased by forces of attraction, whereas, at least as long as only forces acting between two (colliding) molecules are considered, the number of collisions remains proportional to the square of the molecular concentration. No more general calculations taking care of the influence on the collision frequency of forces exerted by other neighboring molecules are recorded in the literature.

The agreement of the value of a obtained ($a = 3.3 \times 10^{-8}$ cm.) with that calculated by Rankine[17] from viscosity data, $a = 3.5 \times 10^{-8}$ cm., is rather good.

Summarizing, the conclusions arrived at can be stated as follows. The decomposition of hydrogen iodide is kinetically strictly bimolecular; Bodenstein's measurements of the reaction velocity seem to be very accurate; an exact value for the velocity constant at 321.4° and a fairly accurate value of the molecular diameter[18] have been obtained.

Activation Energy and Collision Area.—With these data on hand an investigation of the mechanism of activation[19] and reaction can now be attempted. The writer has repeated the graphical determination of the

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[14] G. Jaeger, *Sitz. Akad. Wien*, 105 (2A), 111 (1896).

[15] The larger deviations of these experiments arise partly from uncertainties in the analysis of the very small amounts of iodine formed in the small 0.7cc. vessels. The two experiments with the 3 28cc. vessel (Nos. 24 and 26) have not been included in the above average. It is very doubtful whether the "true" time of heating coincides with the time of immersion in the thermostat so well for this large and very thick walled vessel, as it does for the small 0.7cc. vessels.

[16] Sutherland, *Phil.* Mag, 36, 507 (1893).

[17] Rankine, *Trans. Faraday Soc.*, 17,719 (1922).

[18] The probable error in this latter is somewhat uncertain. It is easy to show, however, that a change of b by 25% (therefore a change in σ by about 8%) completely destroys the agreement between calculation and experiments in Fig. 1.

[19] For the following considerations compare, for instance, C. N. Hinshelwood, "The Kinetics of Chemical Change in Gaseous Systems," Oxford, 1926

activation energy[4] from the temperature coefficient data of Bodenstein. The values of ln $k_0 - {}^1/_2 \ln T$, from the equation

$$\ln k = {}^1/_2 \ln T - E/RT + C \tag{8}$$

have been plotted on a large scale against $1/T$. All values of Bodenstein from 508 to 302° lie on a straight line with maximum deviation not exceeding 5% in the value of k (not ln k). The slope yields for E, 44,300 cal.[20] In order to estimate the probable limit of error of this figure, we may assume that the velocity constants at 508 and 302° are wrong each by 20%—a rather exaggerated error in view of the agreement earlier demonstrated. The upper limit of E under these conditions is calculated to be 45,900 cal. Assuming that the reaction occurs on each collision in which the energy of both molecules exceeds the above value, we may calculate the rate of hydrogen iodide decomposition at 321.4°.

$$k_0c^2 = 2Z\, e^{-E/RT} \tag{9}$$

Z, the total number of collisions per cc. per second at unit concentration (1 mole per liter), is calculated to be 2.82×10^{31}, if $\sigma = 3.3 \times 10^{-8}$ cm. The exponential with $E = 45{,}900$ cal. is equal to 1.28×10^{-17}, so that the number of molecules reacting, which is twice the number of effective collisions, is calculated to be at least 7.25×10^{14}. This must be compared with the experimentally determined number ($k_0 = 3.95 \times 10^{-6}$) 2.39×10^{14}. The agreement obtained cannot be considered as quite good because, it must be remembered, the calculated reaction velocity represents the lower limit, still consistent with Bodenstein's measurements of the temperature coefficient, and should probably be raised by a factor close to 2.

As has been frequently pointed out, Equation 9 holds strictly only if the energy of activation of the colliding molecules is assumed to be distributed in two degrees of freedom only. It is of some interest to consider another possible source of activation energy: the total kinetic energy of relative motion of colliding molecules.

In such a case the number of collisions (therefore half the rate of decomposition) with the relative kinetic energy larger than a given one is expressed not by Equation (9) but by[21]

$$k_0c^2 = 2Z\left(1 + \frac{E}{RT}\right) e^{-\frac{E}{RT}} \tag{10}$$

To calculate the theoretical reaction velocity of hydrogen iodide decomposition with Equation 10 it must be first noted that the temperature coefficient of the reaction rate is given now by

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[20] The value of k_0 at 283° is considerably off the straight line (by some 20% in k) and its inclusion would *decrease* the average activation energy. The deviation is possibly due to a wall reaction becoming marked at this low temperature. Since we are interested here in the upper limit of ϵ only, the value of k at 283° has been neglected.

[21] Tolman, "Statistical Mechanics with Applications to Physics and Chemistry," The Chemical Catalog Company, New York, 1927.

$$\frac{d \log k_0}{dT} = \frac{1}{2T} + \frac{E}{RT^2} - \frac{1}{T} \tag{11}$$

(the term $(1 + E/RT)$ being substituted in Equation (10) with a sufficient degree of accuracy by E/RT) and that therefore RT must be added to the previously determined value of E.

The upper limit of E at 321° now becomes 47,100 cal., and from this and Equation 10 the *minimum* number of effective collisions is calculated to be 4.45×10^{15}, the rate therefore to be 8.9×10^{15}. The experimentally determined value was 2.4×10^{14}.

Without going into further calculation it may be pointed out here that the discrepancy between the calculated and experimental rates will be still considerably increased if the assumption is made that all forms of energy present in a diatomic molecule, that is, energy of translation, of rotation and of oscillation, contribute to the activation of hydrogen iodide.[22] The only error which could have entered into the calculations of the theoretical reaction rate (provided the theory of activation is correct generally) lies in the assumption that the diameter of the reacting molecules or, better, their effective cross section, is the same as the kinetic cross section of an average molecule. And, since the calculated rate was found to be greater than the observed, it means that the effective cross section of molecules in collisions leading to reaction is considerably smaller than the average. If only two degrees of freedom are acting in the activation, the effective cross section is still not far from the normal—probably one-half to one-fourth of it. But if we assume that at least three—the translational—degrees of freedom are responsible for the activation, the effective cross section of reacting molecules must be smaller than 0.03 of the normal. This result is rather striking because, as has been shown repeatedly,[23] atoms (and probably also molecules) in the state of electronic excitation have cross sections considerably greater than the calculated kinetic averages for normal atoms. Some light on the process of activation in thermal reactions could possibly be obtained by similar studies of the cross sections of molecules excited to higher oscillation and rotation quantum states by absorption of light in their infra-red absorption bands. At present very little can be said definitely as to the origin of the small effective cross sections of the activated molecules. They may be due to a "steric factor"[24]—the

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[22] For the form of equations determining the number of collisions with energy greater than a given one, as a function of the number of degrees of freedom, see Herzfeld, "Die Kinetische Theorie der Wärme," Braunschweig, 1925; Hinshelwood, Proc. *Roy. Soc., London,* **113A,** 230 (1926); Fowler and Rideal, *ibid.,* **113A,** 570 (1926); O. K. Rice and H. C. Ramsperger, THIS JOURNAL, 49, 1617 (1927).

[23] K. A. Stuart, *Z. Phyrik,* 36, 262 (1925); Schutz, *ibid.,* 35, 260 (1925); compare also Franck and Jordan, "Anregung von Quantenspriingen durch Stosse," Berlin, 1926, p. 243.

[24] Herzfeld, *Ann. Physik,* 59, 635 (1919); Tolman, THIS JOURNAL, 47, 1524 (1925).

orientation of the molecules in the moment of their collision—or to some other causes. Prior to deciding this question, it is necessary to know the exact origin of the activation energy.

The Molecular Volume Factor in the Velocity Experiments.—The experiments here described offer—at least in principle—the possibility of solving this last problem. A more careful consideration of the meaning of the term Nb which, according to the suggested interpretation, caused the observed increase of the velocity constant at high concentrations, will show that this quantity is somewhat different from the ordinary Nb entering the van der Waals equation of state. In this equation b determines, so to speak, that part of the total volume of a gas which, being occupied by the rest of the molecules, is excluded from the space which can be occupied by an average molecule. Therefore, b of van der Waals is determined by the nearest distance to which the centers of two average molecules can approach each other, that is, by the sum of their radii. In contrast to this the experiments on reaction rate describe not the behavior of average molecules but the behavior of certain[25]—activated—molecules; Nb, therefore, represents that fraction of the total volume which is excluded to these particular molecules, is thus determined by the nearest distance to which the center of an activated molecule can approach the center of an average molecule in an average collision. The knowledge of this distance will make possible at least an indirect conclusion as to the forms of energy sharing in the thermal activation. If it is the kinetic energy we may expect[15] that b, determined from the rate measurements, will be somewhat smaller than the usual b at the same temperature. On the other hand it is quite likely that increased energy of rotational and vibrational degrees of freedom[26] increases somewhat the dimensions of the molecules and should be therefore manifested by a larger volume correction in the rate experiments. Unfortunately, the present state of knowledge of the exact volume of average molecules of hydrogen iodide at the temperature of the experiments here recorded as also possible errors in b, determined, from the rate measurements, make a successful comparison rather improbable.

[25] The case is equivalent to the case of a mixture of two kinds of molecules, although we must assume that there is a continuous exchange of individual molecules, of which each has a chance to be either activated or deactivated. Provided the concentration of one (the "activated") kind is negligibly small, the volume correction for it is given by $4N[4/3\pi((r' + r)/2)^3]$, r' and r being the radii of both kinds, whereas for the other kind (the "average") the correction is $4N(4/3\pi r^3)$. In reality molecules in different (higher) rotational or oscillational quantum states or molecules with different velocities are probably capable of reaction on collision with a suitable other molecule. The above calculation gives, therefore, only their average cross section.

[26] A Sommerfeld, "Atombau und Spectrallinien," Vieweg und Sohn, Braunschweig, 1924.

In conclusion the writer wishes to thank Professor Hugh S. Taylor for his active interest and encouragement during the course of this work.

Summary

1. The decomposition of gaseous hydrogen iodide has been investigated at concentrations from 0.02 to 7 moles per liter.

2. The rate of decomposition is bimolecular in the whole range of concentrations investigated and is not influenced by extreme drying.

3. At higher concentrations a correction taking care of the volume of the molecules in the expression for the number of bimolecular collisions must be introduced in order to retain the bimolecular character of the reaction rate.

4. Calculations of the reaction rate from the data on the activation energy show that the effective cross section of activated molecules in collisions leading to reaction are smaller than the average kinetic cross section of molecules.

5. A way of deciding which forms of molecular energy are contributing to the activation process has been indicated from considerations on the nature of the volume correction obtained from the rate measurements here recorded.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE PHYSIKALISCHES INSTITUT AND CHEMISCHES LABORATORIUM DER UNIVERSITÄT, LEIPZIG]

THE DIELECTRIC CONSTANTS OF BINARY MIXTURES. VII. THE ELECTRIC MOMENTS OF CERTAIN DIPHENYL DERIVATIVES. THEIR RELATION TO THE SEVERAL STRUCTURES

BY JOHN WARREN WILLIAMS[1] AND ARNOLD WEISSBERGER[2]

RECEIVED APRIL 16, 1928 PUBLISHED SEPTEMBER 5, 1928

A study of the chemical properties of diphenyl and its derivatives has led to interesting speculations concerning the structures of the various molecules. For the purpose in hand it is considered unnecessary to review the work which has been done in this field; it will be sufficient simply to state the conclusions given in two more recent publications These articles contain numerous references to previous investigations.

Adkins, Steinbring and Pickering,[3] as a result of their studies, conclude that the non-formation of the anhydrides is due to the fact that in the dinitro and dihydroxy acids the rings are extended as in the conventional formula, while in the amino or benzidine type of acids the rings are super-

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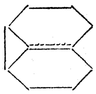
[1] National Research Council Fellow in Chemistry.

[2] Privatdozent an der Universität, Leipzig.

[3] Adkins, Steinbring and Pickering, THIS JOURNAL, 46, 1917 (1924).

imposed. Kuhn and Albrecht,[4] discussing the same question, "come to the conclusion that it is not possible to explain diphenyl and its derivatives by means of a single space formula." In the case of the *p,p'*-disubstituted diphenyl compounds, two types of formula are discussed, as follows. (1) A formula in which the axes of the two benzene rings lie in a straight line. (2) A formula in which the axes of the two benzene rings make an angle with each other or are directed parallel to each other, as indicated in the following diagram.



In the previous papers of this series,[5] the use of electric moment data for the solution (in many cases at least) of problems of chemical structure has been suggested. The purpose of this article is to demonstrate the utility of these data as applied to the question of the structure of certain derivatives of diphenyl.

Experimental

The electric moments of the molecules in question, as well as that of *p*-phenylenediamine, which is necessary for the discussion, have been determined from dielectric constant and density data of their dilute solutions in benzene at 25°. The limited solubility of the diphenyl derivatives in benzene requires that the difference in dielectric constant between the solution and that of the solvent be determined with a high degree of accuracy. For this purpose an apparatus shown diagrammatically in Fig. 1 was built.

It differs from that previously described[6] in that it consists of three distinct circuits, two of which are oscillators and the other a receptor. The heterodyne principle was used as before; in fact, the method of making a dielectric constant measurement was very similar to that previously described. The dielectric constant of benzene was assumed to be 2.2820; that of the solutions was determined by noting the change in capacitance produced when the solution was substituted for the solvent between the plates of the measuring condenser. In the tables the dielectric constants have been expressed to four significant figures only. A fifth and doubtful figure was used in the calculation of the molar polarization of the solution, and therefore in the calculation of the molar polarization of the solute molecule. The uncertainty in the molar polarization of the solute molecule, P_2, is of the order of magnitude of 5%.

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[4] Kuhn and Albrecht, *Ann.*, 455, 272 (1927).

[5] Williams and collaborators, THIS JOURNAL, 49, 1676, 2408, 2416 (1927); 50, 94, 362 (1928).

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

All substances used for the measurements reported were subjected to a careful purification by the usual methods of crystallization or distillation or both. The melting points of the various solutes were determined, and in no case was the observed melting point different by more than 1° from that given in the literature.

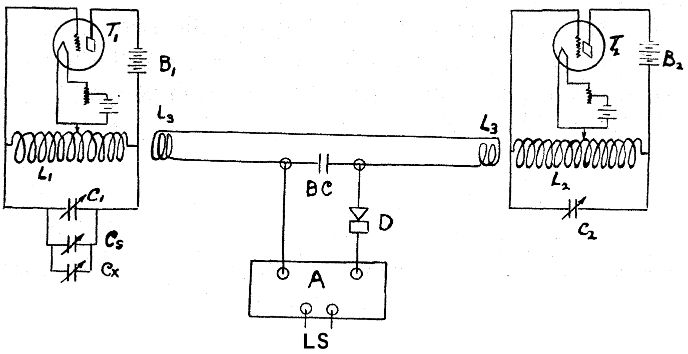


Fig. 1.—Diagram of circuits.

T_1,T_2—Telefunken RE 144 vacuum tubes, B_1,B_2—"B" batteries, 90 volts; L_1,L_2—inductances, 150 turns, C_1,C_2—capacitances, 1000 mmf.; C_s—standard variable air condenser; C_x—dielectric cell; L_3—coupling inductances, 25 turns; BC—block condenser, 0.1 μf; D—detector; A—two-step amplifier; LS—loud speaker.

TABLE I

DIELECTRIC CONSTANT AND DENSITY DATA FOR MIXTURES

MF, C_6H_6	d_4^{25}	ϵ	$P_{1,2}$	P_2
		p-Phenylenediamine		
100.00	0.8731	2.282	26.77	37.5
99.84	.8744	2.285	26.79	
		4,4′-Dichlorodiphenyl		
100.00	.8731	2.282	26.77	63
99.84	.8739	2.282	26.82	
99.68	.8752	2.283	26.87	
99.36	.8775	2.286	27.00	
		4,4′-Dinitrodiphenyl		
100.00	.8731	2.282	26.77	65
99.95	.8733	2.281	26.79	
		4,4′-Diaminodiphenyl		
100.00	.8731	2.282	26.77	100
99.75	.8758	2.294	26.94	
		4,4′-Diethoxydiphenyl		
100.00	.8731	2.282	26.77	150
99.82	.8741	2.295	27.03	
99.63	.8755	2.302	27.21	

The results of the experimental determinations are given in Tables I and II. The symbols used in the earlier articles have been retained throughout; therefore their significance need not be repeated here.

TABLE II

ELECTRIC MOMENTS OF SOLUTE MOLECULES AT 25°

Molecule	P_2	P_2''	P_2'	$\mu \times 10^{18}$
p-Phenylenediamine	37.5	35	2.5	0.3[a]
4,4'-Dichlorodiphenyl	63	63	0	0
4,4'-Dinitrodiphenyl	65	65	0	0
4,4'-Diaminodiphenyl	100	60	40	1.3
4,4'-Diethoxydiphenyl	150	75	75	1.9

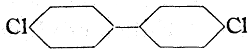
[a] Moment indistinguishable from zero by the method used.

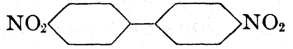
Discussion

In the discussion of these results it is necessary to consider the data not only for the particular derivatives of diphenyl but also for the corresponding derivatives of benzene. The data for *p*-dichlorobenzene,[7] *p*-dinitrobenzene[5] and hydroquinonediethylether[8] are available in the literature; that of *p*-phenylenediamine is reported above.

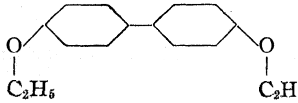
With regard to the structure of the several derivatives of diphenyl, the following statements may be made.

(1) Since the electric moments of the compounds *p*-dichlorobenzene and 4,4'-dichlorodiphenyl, and of *p*-dinitrobenzene and 4,4'-dinitrodiphenyl, are zero, and since the introduction of a single Cl atom or NO_2 group into the benzene nucleus causes a highly unsymmetrical molecule," the conclusion is definite that in the case of the compounds 4,4'-dichlorodiphenyl and 4,4'-dinitrodiphenyl the rings of the diphenyl nucleus are co-axial. They are represented diagrammatically in the following sketches.





(2) The electric moments of the compounds hydroquinonediethylether and 4,4'-diethoxydiphenyl (1.7 and 1.9 × 10^{-18} e. s. u., respectively) must be considered to be of the same order of magnitude. The reason why hydroquinonediethylether gives a finite moment has been discussed previously.[8,9] Since the magnitude of the moment of the corresponding diphenyl derivative is the same, it is highly probable that its structure is similar. The conclusion to be drawn from these considerations is, again, that the benzene rings are extended. This structure is suggested in the following diagram.



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[7] Smyth and Morgan, THIS JOURNAL, 49, 1030 (1927).

[8] Williams, *Physik.* Z.,, 29, 271 (1928). In this connection see also Williams, THIS JOURNAL, 50, 2350 (1928).

[9] Weissberger, *Physik. Z.*, 29, 272 (1928).

In this connection it may be pointed out that until more accurate experiments are available for this and similar substances, the possibility of a slight deformation from the extended position is not excluded.

(3) The electric moment data for the compounds *p*-phenylenediamine and 4,4′-diaminodiphenyl distinctly indicate a collapsed or folded structure for the latter substance, in benzene solution, at least.[10] The electric moment of the similar benzene derivative is zero; thus there is no tendency for the NH_2 groups to be bent from the plane of the benzene ring. 4,4′-Diaminodiphenyl has a comparatively large moment, $\mu = 1.3 \times 10^{-18}$ e. s. u. If the benzene rings of the diphenyl were extended, as has been shown to be the case for the dichloro, dinitro and diethoxy derivatives, there can be little question that a moment indistinguishable from zero would have resulted for the benzidine molecule as well.

Thus the electric moment data reported in this article indicate the truth of the statement quoted above from the article of Adkins, Steinbring and Pickering, namely, that in the dinitro and dihydroxy derivatives of diphenyl the rings are extended as in the conventional formula, while in the amino or benzidine type the rings are folded. They are also in accord with the conclusions of Kuhn and Albrecht. It is evident, however, that these data are insufficient to establish the general truth of these conclusions; therefore the work is being continued.

The authors take pleasure in thanking Professor P. Debye for facilities placed at their disposal, for his kindly interest in the work and for the inspiration he has given it.

Summary

1. Dielectric constant and density data at 25° have been obtained for benzene solutions of *p*-phenylenediamine, 4,4′-dichlorodiphenyl, 4,4′-dinitrodiphenyl, 4,4′-diethoxydiphenyl and 4,4′-diaminodiphenyl. The electric moments of the various solute molecules have been calculated from these data.

2. The electric moment data have been shown to indicate the truth of statements made by Kuhn and by Adkins with regard to the structure of certain derivatives of diphenyl. In the case of the dinitro and dihydroxyl derivatives, the rings of the nucleus are extended. In the case of the amino derivative the rings cannot be extended.

LEIPZIG, GERMANY

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[10] For discussion of effect of solvent, see Kuhn and Zumstein, Ber., 59, 488 (1926).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY, No. 581]

THE OXIDATION POTENTIAL OF THE PENTAVALENT–TRIVALENT COLUMBIUM SYSTEM. II

BY SAMUEL J. KIEHL AND DAVID HART

RECEIVED APRIL 30, 1928 PUBLISHED SEPTEMBER 5, 1928

Introduction

During our study of the reduction of columbic acid at a mercury electrode[1] the behavior of the reduced columbium upon reoxidation to the pentavalent state indicated that the trivalent columbium might possess a rather high reducing potential. Consequently, inasmuch as the literature contained no potential measurements whatever upon the pentavalent–trivalent columbium system, it was deemed worth while to make a study of this phase of the chemistry of columbium.

Apparatus

On account of the oxidation of a reduced columbium solution by contact with the air, it was necessary to devise and construct an hermetically sealed apparatus in which measurements could be made and solutions could be introduced, withdrawn and transferred. In an apparatus described below, which provided an atmosphere of hydrogen, the measurements were made. Platinum electrodes were first tried but the results were so inconstant and non-reproducible that, as with Forbes and Bartlett[2] in their measurement of the stannic–stannous potential and Forbes and Richter[3] in their determination of the chromic–chromous potential, they were abandoned and the mercury electrodes were employed instead. Forbes and Bartlett and Forbes and Richter concluded from their experimental work that with the mercury electrodes results were more quickly obtained, irregularities due to surface energy of the electrode were less pronounced and deviations due to traces of oxygen in the system were almost eliminated. Besides, mercury has, as an important and as an additional property in its favor, a free surface upon which hydrogen has a high overvoltage. Also it does not appreciably react with sulfuric acid of the concentrations used in these experiments when the solutions are at room temperature.

Mercury Electrode.—The mercury electrode employed in the measurement of oxidation potentials is shown in Fig. 1. It consists of a wide-mouthed bottle of 250cc. capacity, closed with a rubber stopper provided with seven holes through which, respectively, pass a glass tube with a

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[1] Kiehl and Hart, THIS JOURNAL, 50, 1608 (1928).

[2] Forbes and Bartlett, *ibid.*, 36, 2030 (1914).

[3] Forbes and Richter, *ibid.*, 39, 1140 (1917).

sealed-in platinum wire to make contact with the mercury on the bottom of the cell, a glass tube to furnish a stream of hydrogen, two burets to introduce the reduced and unreduced solutions, respectively, a glass tube leading into a bottle to act as a water seal to release the excess of hydrogen, a glass tube for the withdrawal of an analytical sample, and finally a glass tube to act as a salt bridge connecting the solution to be measured with the saturated calomel cell.

The instruments, the arrangement and the method used to measure the electromotive force were described by Hansen and one of us.[4]

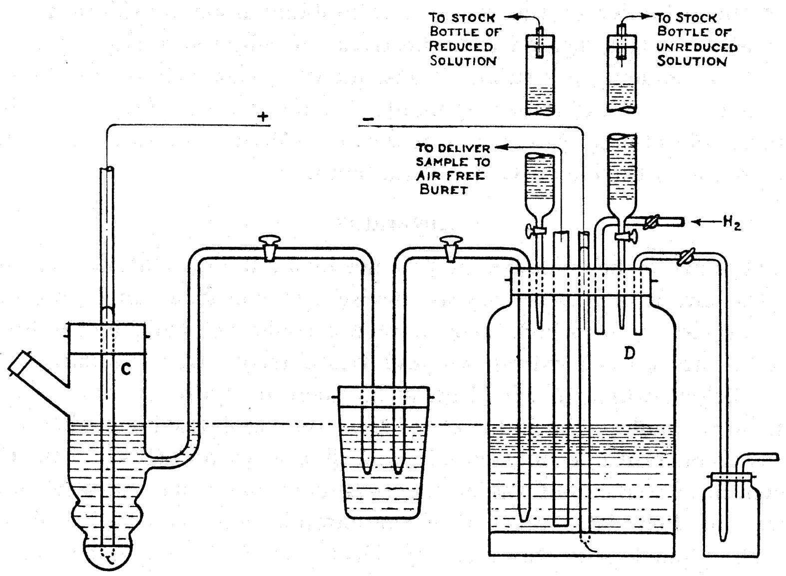

Fig. 1.

Experimental

Preparation of Solutions.—Solutions containing both pentavalent and trivalent columbium were prepared as follows. A solution of approximately 0.025 M Cb_2O_5 in the desired concentration of sulfuric acid was prepared and reduced completely to the trivalent state by the method previously described by us.[1] About one-half of this reduced solution was transferred to a stock bottle and rwxidized to the pentavalent state by passing purified air through it until the blue color disappeared. The excess oxygen was removed by a stream of hydrogen. This procedure insured the same sulfate concentration in the reduced as in the unreduced solution. This solution furnished the pentavalent columbium used below in the measurements.

Before the required amounts of the two solutions were introduced into bottle D, Fig. 1, the air was swept out by a stream of hydrogen. The whole system, including stock bottles, pipet for withdrawal of samples and titrating system used previously by us,[1] was connected hermetically and operated in an atmosphere of hydrogen. After the complete apparatus was ready, measured quantities of the solutions of trivalent

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[4] Kiehl and Hansen, This journal, 48,2802 (1926).

and pentavalent columbium sufficient to make a total of 100 cc. and to give the required reduction were introduced into bottle D of Fig. 1 through the burets connected to the stock bottle5 In this manner the approximate amount of reduction was secured.

The bottle D was connected to the saturated calomel–saturated potassium chloride half-cell C by a glass-stoppered siphon tube leading through an intermediate solution of saturated potassium chloride at 25° The value of this electrode at 25° according to Fales and Mudge[5] is 0 5266 volt The system was placed in a Freas electrically regulated thermostat at 25° and the electromotive force measurements were made by the null method with the standard apparatus previously mentioned. Wherever rubber connections were employed, they were covered with collodion.

After several hours, the potential assumed a value which remained constant within ±0.0003 of a volt, provided no leakage of air occurred. This was considered to be the potential of the combination at equilibrium for this particular system. Furthermore, this value remained the same whether the solution was stirred or not, whereas violent fluctuations occurred if the solution was stirred before a constant value was obtained. For further assurance of the equilibrium potential a trace of mercuric chloride, a test generally used, was introduced into the system. The trivalent columbium reduced the mercuric mercury to the mercurous condition and free mercury, a reaction which lowered the potential considerably. The original potential before the introduction of the mercuric chloride was restored after it stood for a short time unless equilibrium was not reached

After the equilibrium potential was recorded, 25 cc. of the equilibrium solution was delivered into a 250cc. Erlenmeyer flask previously swept by hydrogen and the amount of reduced columbium was determined by a standard potassium permanganate solution as heretofore.[1] The value thus obtained, in general, agreed closely with the amount of reduced solution originally added, so practically no oxidation had taken place during the transfer of solutions.

After each electromotive force measurement, the bottle D was thoroughly cleaned and dried. Fresh mercury prepared by the method of Hulett[6] was then introduced to serve as the electrode for the next measurement.

Tables I, II and III contain the results obtained with 0.024 molar solutions of Cb_2O_5 in approximately three molar, six molar and ten molar sulfuric acid, respectively.

TABLE I

RESULTS OF EXPERIMENTS

0.0240 M Cb_2O_5. Temperature, 25°. 3.14 M sulfuric acid

	25 cc of columbium solution							
Expt.	0 02 M $KMnO_4$, cc	Total Cb_2O_5, g.	Reduced Cb_2O_5, g.	Reduction, %	Obs e m f , v.[a]	Normal ox. potential, E_0, v.[b]	$^cK \times 10^{13}$	Time, hours
1	2.40[d]	0.1595	0.0016	1.0	-0.3125	-0.3714	2.6	14
2	4.76[d]	.1595	.0032	2.0	– .3225	– .3724	2.4	26
3	11.86[d]	.1595	.0075	5.0	– .3348	– .3725	2.4	17
4	23.42[d]	.1595	.0156	9.8	– .3443	– .3727	2.3	65
5	46.56[d]	.1595	.0311	19.5	– .3551	– ,3733	2.2	25
6	7.11	.1595	.0475	29.8	– 3618	– .3728	2.3	31
7	9.53	.1595	.0636	39.9	– .3681	– .3734	2.2	28
8	11.92	.1595	.0795	49.8	– .3735	– .3736	2.2	12
9	11.95	1595	.0798	50.0	– .3730	– .3730	2.4	17

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[5] Fales and Mudge, THIS JOURNAL, 42, 2434 (1920).

[6] Hulett, *Z. physik. Chem.*, 33, 611 (1900).

TABLE I (*Concluded*)

	25 cc. of columbium solution							
Expt.	0.02 M $KMnO_4$, cc.	Total Cb_2O_5, g.	Reduced Cb_2O_5, g.	Reduction, %	Obs. e.m.f., v.[a]	Normal ox. potential, E_0, v.[b]	[c]$K \times 10^{13}$	Time, hours
10	14.30	.1595	.0954	59.8	− .3782	− .3731	2.3	41
11	16.65	.1595	.1111	69.7	− .3840	− .3733	2.2	16
12	19.06	.1595	.1271	79.7	− .3908	− .3732	2.2	18
13	21.46	.1595	.1431	89.8	− .4014	− .3735	2.2	12
14	21.92	,1595	.1462	91.7	− .4045	− .3737	2.1	13
15	22.64	,1595	.1510	94.7	− .4102	− .3732	2.2	21
16	23.41	,1595	.1561	97.9	− .4211	− .3721	2.3	37
						Mean	2.3	
				Duplicate				
1	7.20	.1603	,0480	30	− .3622	− .3731	2.3	36
2	12.01	.1603	.0801	50	− .3732	− .3732	2.2	45
3	16.80	.1603	,1120	70	− .3845	− .3736	2.2	23
4	21.58	.1603	,1439	90	− .4012	− .3731	2.3	49
						Mean	2.2	

[a] Against sat. calomel–sat. KCl cell as zero.

[b] Referred to the sat. calomel–sat. KCl electrode as zero.

[c] $K = [\mathrm{Cb}^{+++}]e/[\mathrm{Cb}^{+++++}]e$.

[d] 0.002 *M* $KMnO_4$ was employed for these titrations.

TABLE II

RESULTS OF EXPERIMENTS

0.0241 M Cb_2O_5. Temperature, 25°. 5.91 M sulfuric acid

	25 cc. of columbium solution							
Expt.	0.02 *M* $KMnO_4$, cc.	Total Cb_2O_5, g.	Reduced Cb_2O_5, g.	Reduction, %	Obs. e.m.f., v.[a]	Normal ox. potential, E_0, v.[b]	[c]$K \times 10^{14}$	Time, hours
1	11.84[d]	0.1606	0.0079	4.9	−0.3464	−0.3844	9.3	18
2	24.52[d]	.1606	.0164	10.0	− .3570	− .3850	8.9	15
3	47.68[d]	.1606	.0318	19.8	− .3668	− .3847	9.1	12
4	7.20	.1606	.0480	29.9	− .3742	− .3851	8.8	27
5	9.56	.1606	.0638	39.7	− .3795	− .3849	9.0	15
6	12.02	.1606	.0802	49.9	− .3848	− .3848	9.0	19
7	12.04	.1606	.0803	50.0	− .3850	− .3850	8.9	47
8	14.38	.1606	.0959	59.7	− .3902	− .3854	8.6	18
9	16.82	.1606	.1121	69.8	− .3969	− .3862	8.1	10
10	19.21	.1606	.1282	79.8	− .4029	− .3854	8.6	17
11	21.61	.1606	.1441	89.7	− .4111	− .3834	10.8	25
12	22.86	.1606	,1524	94.9	− .4227	− .3852	8.8	23
						Mean	8.9	
				Duplicate				
1	47.72[d]	.1606	.0318	20	− .3672	− .3850	8.9	31
2	12.04	.1606	.0803	50	− .3845	− .3845	9.3	52
3	16.87	.1606	.1125	70	− .3973	− .3864	8.0	28
4	22.89	.1606	.1527	90	− .4117	− .3836	9.9	17
						Mean	9.0	

[a] Against sat. calomel–sat. KCl cell as zero.

[b] Referred to the sat. calomel–sat. KCl electrode as zero.

[c] $K = [\mathrm{Cb}^{+++}]e/[\mathrm{Cb}^{+++++}]e$.

[d] 0.002 M $KMnO_4$ was employed in the titrations.

TABLE III

RESULTS OF EXPERIMENTS

0.0240 *M* Cb_2O_5. Temperature, 25°. 9.87 *M* sulfuric acid

	25 cc of columbium solution							
Expt.	0 02 *M* $KMnO_4$, cc.	Total Cb_2O_5, g.	Reduced Cb_2O_5, g.	Reduction, %	Obs., e.m.f., v.[a]	Normal ox. potential, E_0, v.[b]	[c] $K \times 10^{14}$	Time, hours
1	2.40[d]	0.1602	0.0016	1.0	−0.3663	−0.4252	3.9	12
2	11.90[d]	.1602	.0079	5.0	− .3878	− .4255	3 8	17
3	23.93[d]	.1602	.0160	10.0	− .3975	− .4256	3.7	15
4	7.18	.1602	.0479	29.9	− .4155	− .4264	3.4	64
5	9.57	.1602	.0638	39.8	− .4208	− .4261	3.6	13
6	11.98	.1602	.0800	50.0	− .4265	− .4265	3.5	32
7	14.37	.1602	.0958	59.8	− .4314	− .4263	3.5	36
8	19.21	.1602	.1280	79.9	− .4444	− .4267	3.4	17
9	21.56	.1602	,1439	89.8	− .4545	− .4256	3.7	51
10	22.80	.1602	.1521	94.9	− .4645	− .4270	3.4	18
11	23.75	.1602	,1584	98.9	− .4834	− .4258	3.7	15
						Mean	3.6	
				Duplicate				
1	7.22	.1602	.0481	30	−.4153	−.4262	3.6	29
2	11.99	.1602	.0800	50	−.4270	−.4270	3.4	33
3	19.26	.1602	.1285	80	−.4440	−.4262	3.6	17
4	21.62	.1602	.1442	90	−.4548	−.4267	3.4	20
						Mean	3.5	

[a] Against sat. calomel–sat KCl cell as zero.

[b] Referred to sat. calomel-sat. KCl electrode as zero.

[c] $K = [Cb^{+++}]e/[Cb^{+++++}]e$.

[d] 0.002 M $KMnO_4$ was employed in the titrations.

All concentrations have been expressed in terms of Cb_2O_5 from which the solutions were always prepared. The analytical results in the tables are expressed in grams of Cb_2O_5 in 25 cc. because the total columbium content in the solution was so determined gravimetrically.

TABLE IV

RESULTS OF EXPERIMENTS

0.013 *M* Cb_2O_5. Temperature, 25°. 3 M sulfuric acid

	25 cc. of columbium solution							
Expt.	0.02 *M* $KMnO_4$, cc.	Total Cb_2O_5, g.	Reduced Cb_2O_5, g.	Degree of reduction, %	Obs. e.m.f., v.[a]	Normal ox. potential, E_0, v.[b]	[c] $K \times 10^{13}$	Time. hours
1	11.84[d]	0.0794	0.0079	10.0	−0.3440	−0.3721	2.4	31
2	35.53[d]	.0794	.0237	29.9	− .3620	− .3729	2.3	12
3	59.52[d]	.0794	.0397	50.0	− .3725	− .3725	2.4	75
4	8.32	.0794	.0555	69.9	− .3839	− .3731	2.3	35
5	10.75	.0794	.0717	90.3	− .4012	− .3727	2.3	15
						Mean	2.3	

[a] Against sat. calomel–sat. KCl cell as zero.

[b] Referred to sat. calomel–sat. KCl electrode as zero

[c] $K = [Cb^{+++}]e/[Cb^{+++++}]e$.

[d] 0.002 *M* $KMnO_4$ was employed in these titrations.

The Effect of a Change of Total Columbium Content.—In Tables I, II and III the total columbium content was the same in each case. To determine what effect a change in the concentration would make, a solution of one-half the total concentration used above was prepared in a **3** *M* sulfuric acid solution. The results recorded in Table IV show that in solutions of such low concentrations of columbium in the presence of such high concentrations of sulfuric acid there is but little change in the normal oxidation potential.

Table V contains the data from which the curves in Fig. 2 were constructed. It contains the ratio of the concentrations, the logarithm of the ratio and the corresponding electromotive force measurement for the three different acid concentrations, respectively.

TABLE V

RATIOS AND LOGARITHMIC RELATIONS

0.0240 M Cb_2O_5

3.14 *M* H_2SO_4			5.91 *M* H_2SO_4			9.87 *M* H_2SO_4		
A	B	C	A	B	C	A	B	C
0.01	−2.00	−0.3125	0.05	−1.29	−0.3464	0.01	−2.00	−0.3663
.02	−1.69	−.3225	0.11	−0.95	−.3570	.05	−1.28	−.3878
.05	−1.28	−.3348	.25	−.61	−.3668	.11	−0.95	−.3975
.10	−0.96	−.3443	.43	−.37	−.3742	.43	−.37	−.4155
.24	−.62	−.3551	.66	−.18	−.3795	.66	−.18	−.4208
.42	−.37	−.3618	1.00	.00	−.3850	1.00	.00	−.4265
.66	−.18	−.3681	1.48	.17	−.3902	1.49	.17	−.4314
1.00	.00	−.3730	2.31	.36	−.3969	3.98	.60	−.4444
1.49	.17	−.3782	3.95	.60	−.4029	8.80	.94	−.4545
2.30	.36	−.3840	8.71	.94	−.4111	18.86	1.27	−.4645
3.93	.59	−.3908	18.61	1.27	−.4227	89.90	1.95	−.4834
8.81	.94	−.4014						
11.05	1.04	−.4045						
17.86	1.25	−.4102						
45.62	1.67	−.4211						

A = $[Cb^{+++}]/[Cb^{+++++}]$. B = log $[Cb^{+++}]/[Cb^{+++++}]$. C = Obs. e.m.f., volts.

Discussion

In all the electrical potential measurements the probable error found experimentally was plus or minus one-half millivolt. The observed voltage represents the average of several readings taken after the system had reached equilibrium.

The potential was referred to a saturated calomel–saturated potassium chloride cell as zero to which it became progressively more negative as the acid concentration increased. With a large negative potential trivalent columbium may be classed, therefore, as a strong reducing agent within the range of our experiments.

By assuming that the degree of ionization and the activity were the same for both states of columbium, calculations of the normal oxidation potential tabulated in Tables I, II, III and IV were made by use of the[7] well-known equation

$$E = E_0 - \frac{RT}{nF} \times \ln \frac{C''}{C'}$$

developed from the Nernst formula. When the ratio of the concentrations was unity, the observed potential became the normal potential

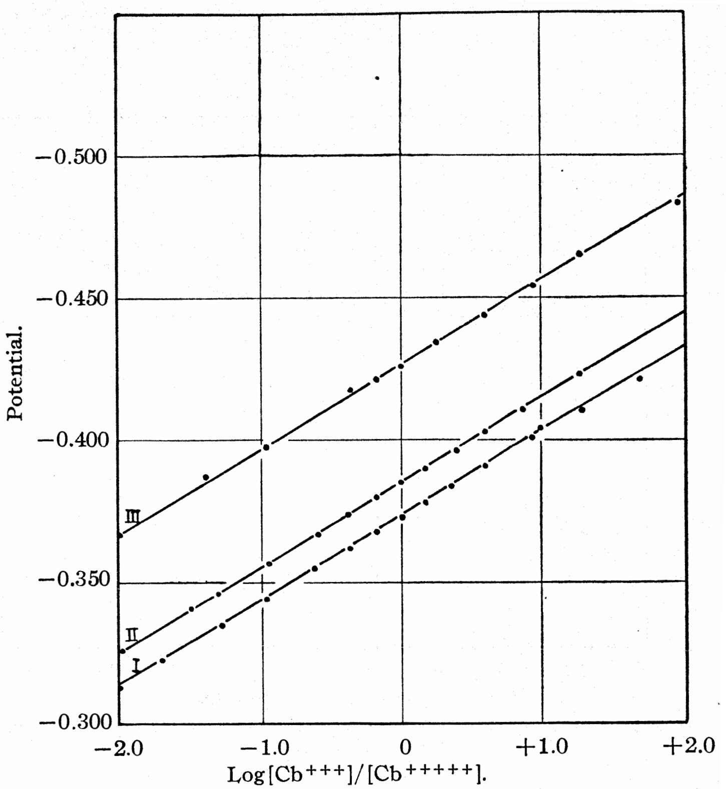

Fig. 2.—I, 0.024 *M* Cb_2O_5 in 3.14 *M* H_2SO_4; II, 0.024 *M* Cb_2O_5 in 5.91 *M* H_2SO_4; III, 0.024 *M* Cb_2O_5 in 9.87 *M* H_2SO_4; temperature, 25°.

By this value the valence of three for the reduced form determined by us[1] was confirmed. At 25° the final equation used for the calculations was

$$E = E_0 - 0.0295 \log \frac{[Cb^{+++}]}{[Cb^{+++++}]}$$

By use of the formula

$$\log K = \frac{E_0}{0.0295}$$

derived from the above relations, the average value of equilibrium con-

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? Peters, Z. *physik. Chem.*, 26,193 (1898).

stants for the system in three sulfuric acid concentrations, 3.14 M, 5.91 M and 9.87 M were found to be, respectively, 2.3×10^{-13}, 8.9×10^{-14} and 3.6×10^{-15}.

During the process of measurement, the potentials at extreme reduction were made and the extent of reduction determined by titration in the usual manner. In the 3.14 M, 5.91 M and 9.87 M sulfuric acid, respectively, the average corresponding potentials were −0.4580, −0.4795 and −0.5090, with the values of 99.87, 99.94 and 99.83% in order for the determined reduction.

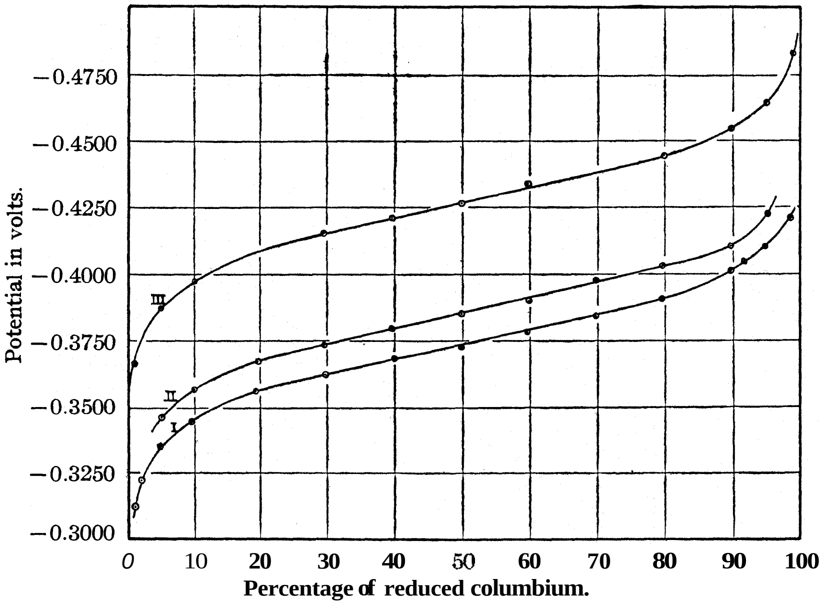

Fig. 3.—I, 3.14 M H_2SO_4; II, 5.91 M H_2SO_4; III, 9.87 M H_2SO_4; 0.024 M Cb_2O_5; temperature, 25°.

In Fig. 2 the data collected in Table V were used to construct nearly straight lines, the slopes of which are very nearly identical for the three acid concentrations and agree very closely with that of the ideal, 0.0295. The slopes for the system in the three acid concentrations were calculated also. Their average values were, respectively, for 3.14 M sulfuric acid, 0.0294; for 5.91 M sulfuric acid, 0.0293 and for 9.87 M sulfuric acid 0.0296. The plotted values were, respectively, 0.0298, 0.0295 and 0.0300 approximately.

When the percentage of reduced columbium is plotted against the corresponding potential, a set of curves set forth in Fig. 3 was obtained. These curves are similar in form and character to those obtained by Peters[7] in the ferric-ferrous system.

Summary

1. The oxidation-reduction potentials of the pentavalent-trivalent columbium system were measured with a mercury electrode in an atmosphere of hydrogen at 25°. Three concentrations of sulfuric acid, 3.14 M, 5.91 M and 9.87 M were used. The concentration of columbium in Tables I, II, III and V expressed as Cb_2O_5 was 0.024 M. In Table IV it was 0.012 M.

2. The trivalent columbium was found to be a strong reducing agent which increased markedly as the concentration of acid increased.

3. A valence of three was confirmed for the reduced state.

4. The average calculated normal electrode potentials for the three concentrations of acid, respectively, are: -0.3730, -0.3849 and -0.4261.

NEW YORK, N. Y.

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

PHOTOCHEMICAL STUDIES. VII. THE PHOTOCHEMICAL DECOMPOSITION OF FORMIC ACID LIQUID AND VAPOR

BY W. N. HERR AND W. ALBERT NOYES, JR.

RECEIVED MAY 3, 1928 PUBLISHED SEPTEMBER 5, 1928

The fact that formic acid decomposes under the influence of ultraviolet radiation has been known for many years. Thiele[1] found that the product of photochemical decomposition of the anhydrous acid was largely carbon dioxide, together with small amounts of oxygen, carbon monoxide and other gases. Berthelot and Gaudechon[2] state that long wave lengths (250 to 350 mμ) cause the formation of water and carbon monoxide, while shorter wave lengths cause the formation of carbon dioxide and hydrogen. Allmand and Reeve,[3] in a recent careful investigation of the photochemical decomposition of formic acid in aqueous solution, find that wave lengths below 350 mμ are effective and that practically the only gas formed is carbon dioxide. They think that the hydrogen (which would be formed simultaneously) is used in reducing formic acid to formaldehyde and other products. These authors also made accurate studies of the quantum efficiency and found the latter to be nearly independent of concentration but to depend on the wave length, being greater for short wave lengths.

Little work has been done on the photochemical decomposition of formic acid vapor. Ramsperger and Porter[4] have made a study of the absorption spectrum. They find that two types of molecule, HCOOH and $(HCOOH)_2$, exist in the vapor state and that each absorbs below about

[1] Thiele, *Ber.*, **40**, 4914 (1907).

[2] Berthelot and Gaudechon. *Compt. rend*, **151**, 478 (1910).

[3] Allmand and Reeve, J. *Chem. Soc.*, 129,2852 (1926)

[4] Ramsperger and Porter, THIS JOURNAL, **48**, 1267 (1926).

260 mμ. They exposed vapors of formic acid to radiation from the quartz mercury arc lamp until decomposition was complete. Under these conditions carbon monoxide and water formed 64% of the mixed products and carbon dioxide and hydrogen 36%. No details of the method of analysis and no measure of the quantum efficiency were given. Bates and Taylor[5] have studied the photochemical decomposition of formic acid vapor sensitized by excited mercury. They find that the sensitized reaction proceeds much more rapidly (400 times) than the unsensitized reaction and that of the products uncondensed by liquid air, 76% were carbon monoxide and 24% hydrogen.

Other work has been done but need not be mentioned at this time.

I. Experimental Procedure and Results

A. Decomposition of the Vapor.—The formic acid used in these experiments was prepared by the method of Schlesinger and Martin[6] by drying with boron trioxide. In part of the experiments phosphorus pentoxide was used as the drying agent. The formic acid used was outgassed after it had been admitted to the vacuum line. The line was first thoroughly flamed out with the highest vacuum obtainable and the formic acid distilled in with liquid air. The line was again evacuated with the formic acid frozen. The formic acid was then distilled from one trap to another and the evacuation repeated. This was continued until the amount of gas removed by a Toepler pump into a volume of 210 cc. was less than 10^{-4} mm. No excess liquid was present except in two of the preliminary runs.

After exposure to the radiation the formic acid was condensed with liquid air and the decomposition products remaining in the gas phase were removed by the Toepler pump. These consisted entirely of hydrogen and carbon monoxide. The formic acid was then distilled with liquid air and the free gas removed by the Toepler pump. This process was repeated until distillation liberated a negligible amount of gas. Carbon dioxide snow and ether ($T = -77°$) was then substituted for liquid air and the process repeated. Under these conditions carbon dioxide (and small amounts of water vapor) were removed by the Toepler pump.

Monochromatic light was not used in these experiments. The light intensities were measured by a thermopile calibrated by a standard source of radiation furnished by the Bureau of Standards. A perforated sheath was placed over the mercury arc lamp to approximate a point source of radiation. The light was made into a slightly diverging beam by means of a quartz lens, passed through a quartz cell 2 cm. in thickness containing water and then through a tube 92 cm. in length fitted with transparent quartz ends. The intensity was measured when the vapor was in the tube and when the vapor was condensed in liquid air The difference gave the deflection due to the light absorption. The area of the spot was not very definite due to the fact that monochromatic light was not used, since the index of refraction of the quartz in the lens varies with wave length.

Water absorbs practically all of the infra-red beyond 1.4μ. The infra-red intensity of a quartz mercury arc lamp is relatively low. In addition, while the authors were unable to find any data on formic acid vapor, most simple organic compounds in the vapor state do not possess infra-red absorption bands between 1.4μ and 0.7μ. The error due to infra-red

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

[6] Schlesinger and Martin, *ibid.*, **36,** 1589 (1914).

should not exceed 10%. Prom a consideration of the absorption spectrum and the energy distribution of the quartz mercury arc lamp as determined with a quartz spectrograph, the average wave length absorbed by the vapor was taken to be 250 ± 10 mp.

The average of ten determinations gave 6.6×10^{12} molecules uncondensed by liquid air formed per erg absorbed or 0.52 molecule per quantum with an average deviation from the mean of 0.16. In addition 0.39 molecule (with an average deviation of 0.10) not condensed by carbon dioxide snow and ether but condensed by liquid air was formed per quantum. The measurement of the light intensity was the most probable source of error since it involved the difference between two quantities. It would seem, however, that the quantum efficiency of the decomposition of the vapor is on the average less than unity.

B. Decomposition of the Liquid.—It is exceedingly difficult to measure the decomposition of anhydrous liquid formic acid because some thermal decomposition is unavoidable. However, the gas formed by thermal decomposition is uncondensed by liquid air, while the main gas formed by photochemical decomposition is condensed by liquid air but not at $-77°$. This agrees with the statement made by Allmand and Reeve for solutions, that the main gas evolved by photochemical decomposition is carbon dioxide.

Light intensity measurements were made by placing the thermopile In front and in back of the cell. By use of the change in area of the beam in traversing the **cell** and the decrease in deflection due to the empty cell, it was found that 15% of the radiation from the arc lamp (after passage through 2 cm. of water) was absorbed by 3.1 **cm. of** liquid formic acid. The average wave length is taken as 300 mp since the mercury line of greatest intensity in the region of strong absorption is at **313** mμ. The coefficient k in the equation $I = I_0^{-kl}$ (l is thickness in cm.) increases from 0.42 at 300 mp to about 1.5 at 250 mp (Measurements made with rotating sector in conjunction with quartz spectrograph.) Seven determinations gave 0 **46** molecule condensed by liquid **air but** uncondensed by carbon dioxide snow and ether per quantum absorbed with an average deviation of 0.16.

Five runs with light transmitted by Pyrex glass were made. From a consideration of the absorption coefficients of the liquid and the fact that of the ultraviolet lines transmitted by Pyrex glass by far the most intense are at **366** mμ and **313** mp, the average wave length was taken as **330** mμ The average number of molecules of gas condensed by liquid air but not at $-77°$ formed per quantum absorbed was 0.14 with an average deviation of 0 04.

Allmand and Reeve found the quantum efficiency for decomposition of formic acid in solution to be about 2.7 at 260 mμ and 1.0 at 300 mp. A very rough calculation shows that the quantum efficiency is about 1.1 on the average for those wave lengths transmitted by quartz but not by Pyrex glass. Since the average wave length in this case is nearer 300 mμ than 250 mμ, the quantum efficiency is not greatly different from that found by Allmand and Reeve for solutions.

II. Discussion of Results

The results of Ramsperger and Porter[4] and of Bates and Taylor[5] indicate that formic acid may decompose either directly or through the agency of excited mercury into carbon monoxide and water or into carbon dioxide and hydrogen. If these two primary reactions occur, measurement of the number of molecules of hydrogen and carbon monoxide together (both uncondensed by liquid air) would give an indication of the number of molecules of formic acid vapor decomposed. One run was made in which hydrogen to a pressure of 0.2 mm. was added. Normally, with the light intensity used, a pressure increase (with liquid air around the trap) of 0.03 mm. would have been observed. Actually the pressure change was negligible but showed, rather, a slight diminution. This may indicate that hydrogen is capable of reducing formic acid under the conditions of the experiment with formation of a product condensed by liquid air.

From the data of Ramsperger and Porter[4] it can be shown that at 25° and a total pressure of 39 mm. (the approximate conditions in the above experiments) over 95% of the pressure is exerted by the bimolecular form. Since the absorption coefficient of this form is higher than fot the monomolecular form, nearly all of the radiation is absorbed by $(HCOOH)_2$. While sufficient resolution was not used by Ramsperger and Porter to make an analysis of the absorption spectrum of the vapor, the absorption seems to be continuous and to increase in intensity with frequency. Whether a definite low frequency limit to the absorption exists or not cannot be ascertained. The heat of dissociation of the bimolecular form is about 14,000 calories per mole. This would correspond to a wave length of 2μ. This wave length may be absorbed. The ultraviolet absorption may cause the dissociation of the bimolecular form as follows: $(HCOOH)_2 = HCOOH + HCOOH^*$, where $HCOOH^*$ represents an activated molecule. The monomolecular form should then absorb at slightly longer wave lengths in the ultraviolet than the bimolecular form, since the heat of dissociation is small compared to the total energy absorbed. The activated molecule may decompose either directly or upon collision. Little information can be obtained on this point from the absorption spectrum measurements. While the error in the above experiments may be fairly large, the low value of the quantum efficiency indicates that direct dissociation probably does not result.

The question now arises as to whether all of the products found by Ramsperger and Porter[4] and by Bates and Taylor[5] result from the primary reaction. In solution and in the anhydrous liquid only one type of decomposition seems to result. The following possibilities may be considered.

(*a*) The monomolecular form may decompose in one manner and the bimolecular form in another. This would necessitate a large quantum efficiency for the decomposition of the monomolecular form and a relatively small one for the decomposition of the bimolecular form. Increase in the percentage of the monomolecular form by lowering of the pressure from **39** mm. to 18 mm. did not affect appreciably the ratio of gas uncondensed by liquid air to that condensed by carbon dioxide snow and ether.

(b) The activated molecules may decompose in two manners for the reasons given by Bates and Taylor.[5]

(c) The primary decomposition may be into carbon dioxide and monatomic hydrogen. The heat of the reaction is small (of the order of four thousand calories) and the production of monatomic hydrogen is possible. Production of formaldehyde might result by the action of the monatomic hydrogen on another molecule of formic acid. The formaldehyde might then decompose. By this mechanism the quantity of hydrogen should be equal to the quantity of carbon monoxide unless the hydrogen were partially used up. Formaldehyde was tested for but not found in the condensed formic acid vapor remaining after the gases had been removed by a Toepler pump with carbon dioxide snow and ether around the trap. The small amount of carbon monoxide in the gases given off from solutions[S] indicates that formaldehyde, if formed, does not decompose rapidly in solution due to the screening effect of the formic acid or to polymerization. Evidence is not satisfactory on these various points.

(d) It is possible that the bimolecular form might decompose directly into formaldehyde, carbon dioxide and water, the formaldehyde decomposing into carbon monoxide and hydrogen. The excess of carbon monoxide over hydrogen found by previous observers could be explained by reducing action of the hydrogen.

It seems not impossible, therefore, that the primary reaction in both liquid and vapor state may lead to the formation of carbon dioxide. While the errors in the determination of the quantum efficiencies are large, they are of the same general magnitude.

If the activated state for the vapor is the same as for the liquid, one might expect the heat of vaporization to be related to the effective frequencies for decomposing the liquid and vapor by the formula $AH = Nh(\nu_1 - \nu_2)$, where A H is the heat of vaporization, h is Planck's constant and ν_1 and ν_2 are the frequencies necessary to cause decomposition of the liquid and vapor, respectively. It is not possible to test this formula accurately with the present data due to difficulty in choice of frequency but we may say qualitatively that the formula does not give the wrong order of magnitude.

The authors wish to express their appreciation to Mr. W. E. Vaughan for aid in performing part of these experiments.

Summary

1. The number of molecules of gas uncondensed by liquid air formed per quantum absorbed has been determined for the photochemical decomposition of both liquid and gaseous formic acid. A similar determination of the number of additional molecules uncondensed by carbon dioxide snow and ether has been made.

2. The quantum efficiency increases with frequency in the case of the liquid. The vapor absorbs only at short wave lengths and variations of frequency were not made.

3. Possible mechanisms for the reaction have been discussed.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE PHYSIKALISCHES INSTITUT DER UNIVERSITÄT, LEIPZIG]

THE DIELECTRIC CONSTANTS OF BINARY MIXTURES. VIII. THE ELECTRIC MOMENT AS A VECTOR QUANTITY

BY JOHN WARREN WILLIAMS[1]

RECEIVED MAY 14, 1928 PUBLISHED SEPTEMBER 5, 1928

Electric moment data for a number of molecules, organic and inorganic in nature, have been presented in the previous papers of this series.[2] The moments have been calculated from dielectric constant and density data for suitable binary mixtures, using the Debye modification of the Clausius–Mosotti Law. The purpose of the present article is to give the results of further experimental work in this field and to suggest the significance of these data.

The apparatus used for the determination of the dielectric constants of the binary mixtures was designed and constructed especially for the purpose by the author. It has been very briefly described in a previous article.[2e] Dielectric constant and density determinations were made at 25°, using a carefully regulated thermostat and observing the usual precautions for precision work. In every case the solvent used was benzene.

Purification of Materials

All substances used for the measurements herein reported were subjected to a careful purification. For that purpose the customary methods of crystallization or distillation or both were resorted to. It is considered unnecessary to give the outline of the method for each particular substance—suffice it to say that in no case did the observed physical constants,

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[1] National Research Council Fellow in Chemistry.

[2] (a) Williams and Krchma, THIS JOURNAL, 49, 1676, 2408 (1927); (b) Williams and Allgeier, *ibid.*, 49, 2416 (1927); (c) Williams and Ogg, *ibid.*, 50, 94 (1928); (d) Williams and Schwingel, *ibid.*, 50, 362 (1928); (e) Williams and Weissberger, *ibid.*, 50, 2332 (1928).

melting point or freezing point, differ appreciably from those given in the standard tables.

Results

The results of the experimental determinations and calculations are given in Table I. The symbols of the previous articles have been retained throughout. In the interest of a saving of space the dielectric constant and density data for the binary mixtures have been omitted; they are in all respects similar to those previously given. Their accuracy is fully as great in practically every case.

Table I

Electric Moment Data for Solute Molecules

Molecule	P_2	P_2''	P_2'	$\mu \times 10^{18}$
Bromobenzene	82	33	49	1.51
Benzaldehyde	190	35	155	2.75
p-Nitrobenzaldehyde	158	38	120	2.4
p-Nitrobenzoic acid	300	40	260	3.5
p-Chlorobromobenzene	40	39	1	0.1
Hydroquinone diethyl ether[a,b]	116	50	65	1.7
Hydroquinone diacetate[a,b]	150	50	100	2.2
Mesitylene	42	41	1	0.1
sym.-Triethylbenzene	56	55	1	0.1
sym.-Trinitrobenzene	54	40	14	0.8
Phloroglucinol triacetate[b]	185	65	120	2.4

[a] Previously reported in a preliminary note, Williams, *Physik. Z.*, 29, 271 (1928).

[b] The author takes this opportunity to thank Dr. A. Weissberger of the Chemisches Laboratorium der Universitat, Leipzig, for the preparation and purification of these chemicals.

The polarization due to the deformation of the molecule, P_2'', was calculated by taking the sum of the atomic refractions or by means of the familiar Lorenz-Lorentz formula. In either case the molar refraction is obtained. That this method of procedure leads to a slight inaccuracy is well known;[2a] however, it does not in any way interfere with the significance of the results as discussed below.

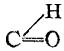
Discussion

The molecules for which electric moment data are presented above are derivatives of benzene of one form or another. They are discussed in the order of an increasing number of substituent atoms or groups of atoms. The simplest case is, of course, that in which only one of the hydrogens of the benzene is replaced. Since benzene itself is a non-polar substance, any such substitution of an atom or group will cause the formation of a polar molecule. Sufficient electric moment data are now available to indicate that an atom or group when introduced into a molecule may be considered as a vector and acting in a certain direction. For example, the introduction of an OH group into methane, ethane, propane or benzene gives a moment of magnitude, $\mu = 1.7 \times 10^{-18}$ e.s.u., while the NO_2 group substituted into benzene gives a moment of magnitude, $\mu = 3.9 \times 10^{-18}$ e.s.u. This statement must not be understood to mean that the moment of any compound formed by the substitution of an atom or group into methane will be exactly the same as the moment formed when the same atom or group is substituted into benzene or other non-polar molecule; the idea to be conveyed is that each atom or group is characterized by a more or less definite moment. There are many ways in which the vector value of this moment may be somewhat altered, since when such an atom or group is introduced the number of electrons present in the molecule is changed and internal compensations may take place. If such a group be introduced into the benzene nucleus (which for the purpose of discussion is considered as two-dimensional) it is natural to assume that the vector will act in the direction of the plane. On the basis of this assumption an approximate moment may be assigned to each of nine atoms or groups from the data of this and the previous articles.[2] The data are taken entirely from electric moment data for derivatives of benzene.

When two of these groups are substituted into benzene, the second in various positions with respect to the first, it is possible to assign an electrical character to each of these groups, the only limitation being that one of the groups must be used as a reference. In the table given below the CH_3 group is considered to be positive in nature. It was shown[3] from the data for the nitrotoluenes that if the CH_3 group has one kind of electrical effect, the NO_2 group must have the opposite kind of electrical effect. If, on the other hand, the data for the chloronitrobenzenes[4] are considered, it is seen that the electric moment of the molecule becomes smaller and smaller as the second substituent moves from the ortho through the meta to the para position. This indicates that the Cl atom and the NO_2 group have like electrical effects—also, if the CH_3 group is positive, then both must be negative. In this manner charges and approximate values have been assigned to the atoms or groups given in Table II.[5]

TABLE II

CHARACTERISTIC MOMENTS OF ATOMS OR GROUPS

Group	Moment	Group	Moment
NO_2	−3.9	OCH_3	−1.2
 $C(H){=}O$	−2.8	C—OH	−0.9
OH	−1.7	CH_3	+0.4
Cl	−1.5	NH_2	+1.5
Br	−1.5		

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[3] Williams, *Physik. Z.*, 29, 174 (1928).

[4] Höjendahl, *Nature*, 117, 892 (1926).

[5] The classification of the NH_2 group was made possible by the kindness of Dr. Hojendahl who communicated the results of unpublished data on the nitranilines.

To this point **Höjendahl**[4] and Smyth and Morgan[S] have discussed their data in a similar manner.

These data are of interest in connection with an article by Thomson[7] written before these and similar data were available. Considering the case when both substituents are of the same kind, this author concludes that "neglecting the deflection of the two doublets due to their action on each other that: 1. If the second constituent goes into the para position the resultant moment is zero. 2. If it goes into the ortho position the resultant moment is

$$(I^2 + I^2 + 21^2 \cos 60°)^{1/2} = \sqrt{3I}$$

3. If it goes into the meta position the resultant moment is

$$(I^2 + I^2 + 2I^2 \cos 120°)^{1/2} = I$$

where I = moment characteristic of the atom or group."

The results of recent researches[4,6,8] on disubstituted benzenes of this type have in every case been treated in the manner suggested above, assuming always that the vectors which represented the groups acted in the plane of the benzene ring. It was found that the experimental data could without serious difficulty be represented by the formulas of Thomson or their equivalent. However, the fact that hydroquinone diethyl ether and hydroquinone diacetate have rather large dipole moments indicates clearly that the simple assumption of no interaction between the two groups cannot always be made. It is becoming more and more evident that as the substituted groups become longer or more complex the greater is the interaction between them—in other words, it is only in the case of the substitution of atoms and smaller groups that the vectors may be considered to act approximately in the plane of the benzene ring, and that when sufficient data are accumulated the cases where there is appreciable interaction will be in the majority. It is only because the simplest substances have been investigated first that the para disubstituted benzenes have previous to this article appeared always to have moments indistinguishable from zero.

Thomson further considers the case in which the second substituent is not the same as the first. In this case the "moment of the molecule if the second substituent goes into: (1) the para position is $I - I$; (2) the ortho position is $(I^2 + I'^2 + II')^{1/2}$; (3) the meta position is $(I^a + I^2 - II')^{1/2}$; where I' = moment characteristic of the second atom or group." As in the case of two like substituents, it is found that in certain cases (atoms and smaller groups) the assumption of vectors directed in the plane of the benzene nucleus does not lead to any appreciable difficulty. This is rather nicely illustrated in the case of para chloro-

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[6] Smyth and Morgan, THIS JOURNAL, 49, *1030 (1927)*.

[7] Thomson, *Phil. Mag.*, [6] 46, *497 (1923)*.

Errera, *Physik. Z.*, *27*, *764 (1926)*.

bromobenzene tabulated above, which gives a moment indistinguishable from zero. The moments of chlorobenzene ($\mu = 1.52 - 1.55 \times 10^{-18}$) and bromobenzene ($\mu = 1.51 \times 10^{-18}$) are very nearly alike, so that when one vector acts in opposition to the other a cancellation results. Other cases of this type have been sufficiently discussed. However, it is becoming more and more apparent, as before, that this is true only in the cases where simple substituents are present in the benzene nucleus, and that as the substituent groups become more complex the effect of the interaction between the groups becomes more pronounced. As evidence for this statement Table III has been prepared. It contains data for several substituted nitrobenzenes. The moment has in each cast. been calculated in the manner suggested by Thomson.

TABLE III

ELECTRIC MOMENT DATA POR PARA DISUBSTITUTED BENZENES

	Molecule	Observed moment	Calculated moment
1.	$NO_2C_6H_4CHO$	2.4×10^{-18}	1.1×10^{-18}
2	$NO_2C_6H_4COOH$	3.5×10^{-18}	3.0×10^{-18}
3.	$NO_2C_6H_4NH_2$	7.1×10^{-18}	5.4×10^{-18}
4.	$NO_2C_6H_4Cl$	2.5×10^{-18}	2.4×10^{-18}
5.	$NO_2C_6H_4CH_3$	4.5×10^{-18}	4.3×10^{-18}

It is at once evident that in the case of the first three molecules there is appreciable interaction between the substituents. The data for the last two molecules, cases in which the second substituent (Cl or CH_3) is of simpler type, have been included only for purposes of comparison. Other tables might be prepared from data now available which would illustrate the same point.

To summarize: it would appear that when two atoms or groups of atoms (like or unlike) are substituted into the benzene nucleus, the assumption that there is no interaction between them can be made only when the groups are of very simple type. In general the vectors characterizing the groups *cannot* be considered to act in the direction of the plane of the benzene ring, so that in any vectorial considerations a three dimensional rather than a two dimensional molecule must be considered.

In the above discussion the various molecules have been considered as derivatives of benzene. Recent data of the author indicate that in the case of the substitution of certain groups (OH and OCH_3, for example) the role played by the benzene nucleus may become insignificant and that the molecules are best treated from another point of view. These data are reserved for a later communication.

The data for the symmetrical trisubstituted derivatives of benzene are of interest in connection with the question of the structure of the benzene nucleus. If the Korner formula[9] were the correct one, a finite electric

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[9] **Korner,** *Gazz. chim. ital.*, **4, 444 (1874). See also** Huggins, THIS JOURNAL, **44, 1607 (1922); 45,264 (1923).**

moment for every like trisubstituted compound of the symmetrical type should result. The same supposition may be made in the cases of the formulas of Baeyer[10] and of Ladenburg.[11] The evidence is conclusive that in the case of mesitylene and symmetrical triethylbenzene no such moment results. The same is true in the case of symmetrical tribromobenzene, where a moment indistinguishable from zero has been reported by Höjendahl.[4] In a previous article Williams and Schwingel[2d] reported a value, $\mu = 1.08 \times 10^{-18}$, for symmetrical trinitrobenzene, but stated that from theoretical considerations a zero value should have resulted. However, a value of such magnitude should be distinguishable from zero;[2] therefore this substance was reinvestigated with extreme care. The result given in Table I was kindly communicated to me by Mr. Schwingel from the Laboratory of Physical Chemistry, University of Wisconsin as the result of careful measurements on trinitrobenzene which had been "recrystallized from benzene ten times and dried *in vacuo* at 35° to constant weight." A repetition of the work by the author in this Laboratory gave a result 5% higher. Therefore the original result is essentially correct and it indicates that symmetrical trinitrobenzene has a finite electric moment. The explanation is, without doubt, to be found in a consideration similar to that given to the disubstituted compounds. The interaction between the groups causes them to be extended (only slightly in this case) above the plane of the benzene nucleus.

There can be no doubt that measurements of this type, made at a single temperature and using benzene as a solvent, will indicate a finite moment for *sym.*-trinitrobenzene. However, in order to remove any question, it would be desirable to supplement these measurements by others at different temperatures.

Concerning the data for phloroglucinol triacetate there can be no question. This substance, a symmetrically trisubstituted benzene, has a comparatively large dipole moment, the explanation of which is to be found in a strong interaction between the groups. The case is exactly analogous to that of hydroquinone diethyl ether and hydroquinone diacetate[12] and will not be discussed further at this point.

In the case of the trisubstituted benzenes, then, it is predicted that as the groups which are substituted into the benzene nucleus become more complex, the greater will be the interaction between them. This point is now being investigated more thoroughly by the author.

In the above discussion the phrase "the plane of the benzene ring" has been more or less frequently used, although it has not been directly proved that the six carbon atoms of the benzene nucleus are in one plane.

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[10] Baeyer, Ann., 245, 103 (1888).

[11] Ladenburg, *Ber.*, 2, 140 (1869).

[12] In this connection see also Williams, *Physik.* Z., 29, 271 (1928).

It is claimed that the data presented cannot be explained by the use of such a formula as that suggested by Korner, Baeyer or Ladenburg and that they can be accounted for by the assumption of a plane formula. The results are strongly indicative of the latter type of arrangement.

Smyth and Morgan,[6] from a consideration of their electric moment data for certain of the disubstituted benzenes conclude that "it appears logical to suppose that the benzene nucleus is a regular hexagon with all the carbon and hydrogen atoms in the same plane, although substitution may possibly distort the hexagon to a somewhat puckered ring." The results of the present investigation must be considered to strengthen materially the argument in favor of the plane ring, particularly in view of the limitations which must be placed upon any conclusions drawn from considerations of the disubstituted compounds. The limitations are, briefly, (1) the fact that any para like-disubstituted benzene forms a symmetrical molecule cannot be considered as proof for a special configuration of the benzene nucleus,[3] and (2) the effect of the interaction between groups which is emphasized in this article is certain to obscure the treatment.

The results of this article are also of interest in connection with those recently reported by Ebert and v. Hartel[13] for molecules of the type CX_4. Certain molecules of this type, CCl_4, CH_4, $C(CH_2Cl)_4$, and also from unpublished data of the author, $C(NO_2)_4$ and $C(CH_2Br)_4$ have zero moments and therefore are symmetrical, while others, such as $C(OCH_3)_4$, $C(OC_2H_5)_4$ and $C(CH_2OOCCH_3)_4$ are characterized by finite electric moments ($\mu = 0.8$, 1.1 and 2.6×10^{-18}, respectively). From these data as well it would appear that as the length or complexity of the substituent group is increased, the interaction between groups is increased. Thus electric moment data for molecules of the types $1,4—C_6H_4X_2$, $1,3,5—C_6H_3X_3$ and CX_4 are now available which indicate that in the case of simpler substituents (X) a symmetrical molecule is formed, but that as the substituent becomes more and more complex the effect of interactions between the groups becomes prominent and asymmetrical molecules result.

It would be desirable to have the x-ray diagrams in the cases of the molecules of the types $1,4—C_6H_4X_2$ and $1,3,5—C_6H_3X_3$ which give finite electric moments. One might expect in the case of compounds of the latter type, for example, that the ends of the substituted groups would be found in a plane above that of the benzene nucleus and that it should be possible to compare the results of such studies as these, that is, data concerning the structure of the molecules in the dissolved state, with their structure in the solid state as determined by x-ray analysis. However, at the present writing such a comparison is possible in but very few cases. It must be pointed out, too, that in certain of these cases, at least, the results are

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[13] Ebert and v. Hartel, *Naturwissenschaften*, 15, 668 (1927).

in direct conflict with each other, so that it cannot be said that such a comparison is always possible. This fact has been briefly discussed in another place.[14]

Conclusion

It appears from the data of this and previous articles that for both aliphatic and aromatic compounds an interaction between groups in a molecule is a common phenomenon. Thus formulas such as those of Thomson for the case of disubstituted benzene derivatives, which neglect the deflection caused by the interaction of two or more groups in a molecule, cannot be of general utility. In most cases the vectors characteristic of the groups must be considered to be acting in space rather than in a plane, making a three-dimensional analysis necessary.

The writer acknowledges with pleasure his indebtedness to Professor P. Debye for apparatus placed at his disposal and for the interest shown and counsel given by him during the progress of the work.

Summary

1. Dielectric constant and density data at 25° have been obtained for benzene solutions of bromobenzene, benzaldehyde, *p*-nitrobenzaldehyde, *p*-nitrobenzoic acid, *p*-chlorobromobenzene, hydroquinone diethyl ether, hydroquinone diacetate, mesitylene, *sym.*-triethylbenzene, *sym.*-trinitrobenzene and phloroglucinol triacetate. From these data the electric moments of the various solute molecules have been calculated and presented in a table.

2. It has been shown that an atom or group when substituted into a molecule is characterized by a more or less definite electric moment. This moment can be considered to be a vector quantity to which it is possible to assign an electrical character by making a simple assumption with regard to the electrical character of one group.

3. Interaction between groups in a molecule appears to be a common phenomenon; therefore the dipole moment of a molecule which contains several groups can be calculated in general only provided the vectors characteristic of the groups be considered to be acting in space.

4. The data are strongly indicative of a formula for benzene in which the six carbon atoms lie in one plane.

5. The possibility of comparing the molecular structure of molecules in the dissolved state, as indicated by electric moment data, with their structure in the solid state, as determined by x-ray analysis is briefly discussed.

LEIPZIG, GERMANY

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[14] Williams, *Physik. Z.*, forthcoming publication.

[CONTRIBUTION FROM THE LABORATORIES OF THE DIVISION OF AGRICULTURAL BIOCHEMISTRY, UNIVERSITY OF MINNESOTA]

THE MEASUREMENT OF THE ELECTROKINETIC POTENTIAL ON PROTEINS BY THE STREAMING POTENTIAL METHOD[1]

BY DAVID R. BRIGGS[2]

RECEIVED MAY 14, 1928 PUBLISHED SEPTEMBER 5, 1928

It has been shown by various investigators that chemically inert particles suspended in a protein solution take on the electrokinetic properties of the protein. Loeb[3] demonstrated this fact with collodion particles suspended in solutions of gelatin and of other proteins. Freundlich and Abramson[4] have recently shown that quartz particles act in the same manner. Svedberg and Tiselius[5] used this phenomenon as a means for measuring cataphoretically the mobility of egg albumin and therefrom its ζ-potential at various hydrogen ion concentrations. Abramson[6] repeated their work, using a simplified method and showed that an extremely dilute solution of the protein (10^{-3} g. per liter or less) could be used and that it was to be preferred to the more concentrated solutions.

The author has shown[7] that the electrokinetic potential, that is, the ζ-potential, may be accurately determined by the streaming potential method upon diaphragms of various materials, for example, of paper pulp, built up between two perforated gold electrodes, provided the specific conductivity of the liquid, as it exists within the diaphragm, is determined. An application of this method for measuring the ζ-potential on proteins at various PH values seemed desirable because of the ease and accuracy with which such measurements may be made.

Method

It was found that finely ground quartz powder could be made into a diaphragm between the two perforated gold plates in a manner already described for paper pulp.[7] Surface conductance, that is, increased conductivity of the liquid when in contact with the diaphragm material, was found to be relatively unimportant for such a crystalline diaphragm even when conductivity water was used for the interstitial liquid. When dilute electrolyte solutions were present in the diaphragm, surface conductance was found to be negligible and the specific conductivity factor, K,

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[1] Published with the approval of the Director as Paper No. 782, Journal Series, Minnesota Agricultural Experiment Station.

[2] National Research Council Fellow in the Biological Sciences.

[3] Loeb, J. Gen. *Physiol.*, 5, 395 (1922–23).

[4] Freundlich and Abramson, *Z. physik. Chem.*, **128**, 25 (1927).

[5] Svedberg and Tiselius, THIS JOURNAL, 48, 2272 (1926).

[6] Abramson, *ibid.*, 50, 390 (1928).

[7] Briggs, J. *Phys. Chem.*, 32, 641 (1928).

in the streaming potential formula could be taken as that of the solution in bulk.

Through such a quartz diaphragm could be forced a dilute solution of fairly pure commercial egg albumin from which had been separated the water-insoluble fractions. After an amount of solution which contained approximately 0.2 g. of albumin had passed through the diaphragm (the diaphragm contained 17.5 cc. of quartz powder), the quartz surface was found to be saturated with the protein and the diaphragm then acted as though it were a protein diaphragm. Subsequently, solutions of various hydrogen ion concentrations and containing approximately 10^{-3} g. of the protein per liter were forced through the diaphragm and the ζ-potential was determined in the usual manner. Svedberg and Tiselius used 1% egg albumin solutions of 0.02 M buffer mixtures of acetic acid and sodium acetate. Abramson used the very dilute protein solutions in the 0.02 *M* buffer mixtures. Such concentrations of electrolytes cannot be used in streaming potential measurements because the electrical conductivity of such solutions is so great as to prevent entirely the building up of a measurable potential across the ends of the diaphragm. The solutions used in the present work were 0.0004 *M* in hydrochloric acid and lithium chloride, a concentration great enough to eliminate surface conductance in the diaphragm and yet low enough to allow for the formation of a streaming potential which was easily measurable. After 50 cc. of any of the solutions had passed through the diaphragm (requiring about twenty minutes) equilibrium had been attained and the measurements could be taken. The PH of the solutions used was determined electrometrically.

Experimental

The application of the streaming potential method to the determination of the isoelectric points and the effects of ions upon the ζ-potential on water–soluble proteins, is well illustrated by the data presented in this paper. Egg albumin was used as the protein in order to make a comparison with the data offered by Abramson.[6]

The ζ-potential is calculated according to the formula

$$\zeta = \frac{HK}{P} \cdot \frac{4\pi\eta}{\epsilon}$$

where H is the streaming potential set up across the ends of the diaphragm at pressure P, K is the specific conductivity of the liquid as it exists inside the diaphragm and which, in this case, is equal to that of the liquid in bulk and η and ϵ are, respectively, the viscosity and the dielectric constant of the liquid, which may be taken as those of water for such dilute solutions of electrolytes and protein as are those used. The ζ-potential will be given in volts when H, P and K are given in millivolts, cm. of mercury, and reciprocal ohms, respectively, and multiplied by the factor 1.0596×10^2.

In Table I are shown the PH values of a series of 0.0004 M mixtures of hydrochloric acid and lithium chloride, in which was dissolved the egg albumin in a concentration of 10^{-3} g. per liter. Such solutions have no buffer capacity and may vary a few hundredths of a PH from solution to solution of the same concentration of electrolyte. Because of this variation the PH was determined individually for every solution used.

TABLE I

SHOWING PH OF MIXTURES OF LITHIUM CHLORIDE AND HYDROCHLORIC ACID WHERE NUMBERS OF CC. INDICATED ARE DISSOLVED IN A LITER OF THE DILUTE PROTEIN SOLUTION

Cc. of *N*/100 HCl	26.0	16.0	12.0	8.4	6.0	4.0	3.3	2.8	2.0	1.6	1.0	0.0
Cc. of *N*/100 LiCl	14.0	24.0	28.0	31.0	34.0	30.0	36.7	37.2	38.0	38.5	39.0	40.0
PH		3.63	3.86	3.99	4.20	4.38	4.65	4.86	5.00	5.31	5.57	5.84	6.21

Table II gives the values of H, P and K, and of the ζ-potential of the albumin in the solutions at various PH values. Three different quartz diaphragms were prepared and the values obtained on each (*A*, B and *C*) were found to check very closely, although the porosity of the different diaphragms was found to vary to some extent, as indicated by the rate at which water flowed through each at a given pressure.

TABLE II

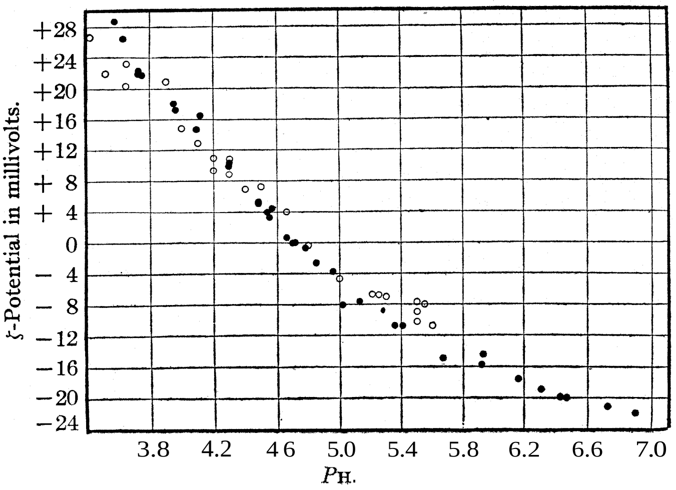
SHOWING CHANGE IN THE ζ-POTENTIAL IN EGG ALBUMIN WITH CHANGE IN THE PA OF 0.0004 *M* MIXTURES OF LITHIUM CHLORIDE AND HYDROCHLORIC ACID WITH WHICH THE PROTEIN IS IN CONTACT

P, cm. of Hg	*H*, mv.	K × 10^6, mho	$\frac{HK}{P} \times 10^6$	ζ, mv.	PH
		Diaphragm (A)			
38.15	+69	15.00	+27.20	+28.82	3.58
40.42	73	13.70	24.80	26.28	3.63
41.26	75	11.20	20.40	21.62	3.75
40.11	74	8.82	16.30	17.27	3.96
40.24	55	6.72	9.20	9.75	4.29
37.27	+33	5.80	+ 5.14	+ 5.45	4.48
41.01	−4	5.33	− 0.52	− 0.55	4.78
36.89	74	4.98	10.05	10.65	5.36
40.06	60	5.04	7.56	8.01	5.02
36.18	−106	4.62	−13.47	−14.27	5.93
		Diaphragm (B)			
40.19	+70	11.90	+20.72	3-21.95	3.73
36.23	68	9.06	17.00	18.01	3.95
41.00	75	7.70	14.10	14.93	4.09
41.15	61	6.54	9.72	10.30	4.30
37.09	31	5.78	4.84	5.13	4.48
40.88	+ 4	5.24	+ 0.51	+ 0.54	4.66
41.61	− 30	5.02	− 3.63	− 3.84	4.96
41.41	61	4.88	7.20	7.63	5.13

TABLE II (*Concluded*)

P, cm. of Hg	H, mv.	$K \times 10^6$, mho	$\frac{HK}{P} \times 10^6$	ζ, mv.	PH
41.11	86	4.74	9.91	10.50	5.41
37.95	120	4.45	14.10	14.94	5.67
39.98	135	4.38	14.80	15.68	5.94
41.51	154	4.48	16.60	17.59	6.17
39.87	150	4.76	17.90	18.97	6.31
40.48	170	4.48	18.80	19.92	6.43
43.18	180	4.50	18.85	19.97	6.47
39.33	178	4.38	19.85	21.03	6.73
40.78	194	4.35	20.70	21.93	6.90
36.25	−180	4.09	−20.30	−21.51	7.50
40.47	+ 75	11.40	+21.10	+22.36	3.73
		Diaphragm (C)			
37.45	+ 78	7.60	+15.80	+16.74	4.12
38.30	+ 24	6.00	+ 3.77	+ 3.99	4.54
...	0	..	0	0	4.69
38.83	+ 18	6.88	+ 3.19	+ 3.38	4.55
40.30	0	..	0	0	4.70
37.44	− 18	5.15	− 2.48	− 2.63	4.85
37.54	+ 29	5.57	+ 4.30	+ 4.56	4.57
42.12	0	..	0	0	4.72

Fig. 1 shows the values given in Table II in comparison with those obtained by Abramson for the same protein by the cataphoretic measurements. It will be noted that through the range of PH between 3.8 and 5.2 there is shown a remarkable agreement between the values of the ζ-



●, By streaming potential method; ○, by cataphoresis, measurements by Abramson.

Fig. 1.—The variation of the ζ-potential with PH on egg albumin.

potential as obtained by the two methods. Through this range the ζ-potential is influenced almost entirely by the hydrogen and hydroxyl ion concentrations of the solution. Beyond this range on either the alkaline or acid side, the values obtained in the 0.0004 *M* solutions diverge to a greater extent from zero potential than those measured in 0.02 M solutions. The higher concentrations of the other ions begin to show their effect toward reducing the ζ-potential soon after that function moves away from the zero value in either direction, but this effect is very small compared to that of the H^+ and OH^- ions until the hydrogen ion concentration has moved out of the above mentioned range. While this divergence between the two curves is primarily a concentration effect, it is not entirely unlikely that the kind of ion used may also have some influence. Recent work by the author[8] has shown that the lithium ion reduces the ζ-potential on a negatively charged surface to a less extent, at any given concentration, than does the sodium or the potassium ion. It was for this reason that lithium chloride was used in the present experiment instead of the more common alkali chlorides. The chloride ion, likewise, should have a greater effect toward lowering the ζ-potential at a positively charged surface than the acetate ion, which may account for the fact that the two curves lie together for a longer range of PH on the acid side of the isoelectric point than they do on the alkaline side.

Incidentally, the streaming potential method for measuring the ζ-potential offers an accurate means for determining the isoelectric point on a water-soluble protein. The solution, which is being streamed through the diaphragm covered with the protein, may be adjusted to a hydrogen ion concentration such that there is no streaming potential set up. The PH of this solution can then be accurately determined, this PH being the isoelectric point of the protein. By such a procedure it is possible to determine this point to within the experimental error of the PH determination.

Further work is being done both upon proteins and upon other colloidal materials which are peptized in water or in dilute acid, alkali or alcohol solutions, and which have a marked effect upon lowering the interfacial tension, such as saponin and lecithin. It is not improbable that the electrokinetic properties of many dyestuffs and other organic compounds may be similarly studied.

Summary

1. The streaming potential method of measuring electrokinetic potentials has been applied in a study of egg albumin by utilizing the property of the protein to adsorb onto a quartz surface so as to give that surface the properties of the protein.

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[8] Briggs, *J. Phys. Chem.*, 32, October, 1928.

2. Data, upon comparison with the work of Abramson with the same protein on quartz surfaces but by the cataphoresis method, show excellent agreement between the values of the ζ-potential obtained by the two methods between P_H 3.8 and P_H 5.2. Divergence of the values of ζ-potential beyond this range is explained by the differences in the concentration of the electrolyte utilized in the two experiments and probably, to some extent, by the differing effects of the ions used.

ST. PAUL, MINNESOTA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ALBERTA]

DIPHENYLCARBAZIDE AS A TEST FOR CHROMIUM

BY NORMAN M. STOVER

RECEIVED JUNE 1, 1928 PUBLISHED SEPTEMBER 5, 1928

A search of the literature has revealed a number of organic reagents which have been used for the detection and estimation of chromium when present as chromate or dichromate. Of these organic compounds, diphenylcarbazide, $CO(NHNHC_6H_5)_2$, seemed very promising. Cazeneuve[1] used this reagent to detect chromic acid in a dilution of 1:1,000,000. Brandt[2] proposed the use of diphenylcarbazide as an inside indicator in the titration of iron with potassium dichromate, while more recently Snoddy[3] has made it the basis of a colorimetric method for estimating small amounts of chromium in fats. Scott[4] mentions the use of this reagent in detecting chromium as chromate.

Since the test is very simple to carry out and the reagent produces a distinctive violet or reddish-violet color with exceedingly small amounts of dichromate, it seemed desirable to compare the sensitivity of diphenylcarbazide with that of the ether—hydrogen peroxide test usually employed in qualitative analysis and to determine the best conditions under which the test might be applied.

Experimental Work

I. Tests with Potassium Dichromate

Solutions of potassium dichromate containing varying amounts of chromium were first tested with diphenylcarbazide and also by the ether–hydrogen peroxide method in order to determine which method was the more sensitive. Further, the tests with diphenylcarbazide were carried out in solutions acidified with different. acids, namely, sulfuric acid, acetic acid and citric acid.

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[1] Cazeneuve, *Bull. soc. chim.*, [3] 23, 592, 701, 76R (1900).

[2] Brandt, *Z. anal. Chem.*, **45**, 95 (1906).

[3] Snoddy, *J. Oil Fat Ind.*, **2**, 20 (1925).

[4] Scott, "Standard Methods of Chemical Analysis," D. Van Nostrand Co., New York, 1918, p. 132

The reagent was made by dissolving 0.2 g. of diphenylcarbazide in 10 cc. of glacial acetic acid and diluting to 100 cc. with 95% ethyl alcohol. The solution remains colorless for about one day, but thereafter gradually turns to a slightly reddish-brown color, even when kept in a brown bottle. This change in color, however, did not seem to render the reagent less sensitive.

The following procedure was used. A stock solution of potassium dichromate was made up to contain 10 mg. of chromium per cc. This solution was then diluted to a definite concentration as required and that volume pipetted out which gave four times the amount of chromium needed for the test at that particular dilution. This solution of potassium dichromate was treated with 4 cc. of 6 *N* ammonium hydroxide, diluted to 100 cc. and divided into four equal portions. One portion was acidified with 6 *N* sulfuric acid, an excess of about 2 cc. being added, followed by the addition of 3 to 5 cc. of ether and 3 cc. of 3% hydrogen peroxide solution. The mixture was shaken vigorously and the appearance of the ether layer noted. The three remaining portions were slightly acidified with sulfuric acid, acetic acid and citric acid, respectively, and 2 cc. of the diphenylcarbazide reagent was added to each. The solutions were allowed to stand for ten minutes before recording the formation of a red or reddish-violet color. When using 2 cc. of the reagent a deep red color is produced with relatively large amounts of dichromate while with small amounts of dichromate the solution assumes a distinctly violet color, the intensity of which varies with the amount of dichromate present. The 25cc. portions of solutions tested contained from 0.04 mg. to 0.00005 mg. of chromium, these concentrations representing 1 part in 625,000 and 500,000,000, respectively. A duplicate series of tests was carried out, the results of the two series being almost identical. It was found that the highest dilutions giving positive tests were as follows: for the ether–hydrogen peroxide method, 1 part of chromium in 1,250,000; for diphenylcarbazide, 1 part in 100,000,000 to 250,000,000 when using sulfuric acid, 1 part in over 71,000,000 when using acetic acid, and 1 part in 12,500,000 when in the presence of citric acid. These results indicate that diphenylcarbazide affords a much more sensitive test than does the ether–hydrogen peroxide method and that diphenylcarbazide is more sensitive when used in the presence of sulfuric acid than in the presence of either acetic or citric acid.

A series of blank tests was next run in duplicate on solutions containing 10 mg. of zinc, or 5 cc. of 3% hydrogen peroxide or both the zinc and hydrogen peroxide, and when acidified with 2 cc. of either 6 N sulfuric, hydrochloric or acetic acid. The final volume of each solution was between 25 and 30 cc. The zinc used was in the form of zinc nitrate. In every case a negative test was obtained upon adding 2 cc. of the reagent.

These blank tests were made on solutions containing zinc and hydrogen peroxide because these two substances might be present in a solution at the point of testing for chromium in the usual qualitative procedure.

Also, since the color produced by the reagent is probably due to oxidation by chromate or dichromate, it was thought that the nitrate ion in acid solution might itself cause a color change. The nitrate ion, of course, would normally be present in a solution at this point in the qualitative procedure if nitric acid were used to acidify the filtrate from the sodium hydroxide–sodium peroxide treatment preliminary to removing aluminum. Accordingly, three solutions were made as follows: (1) 25 cc. of water, 1 cc. of 6 *N* ammonium hydroxide and sulfuric acid until acid; (2) same as (1) but with 1 g. of sodium nitrate added; (3) same as (1) but with 1 g. of ammonium nitrate added. Two cc. of reagent was added to each solution. No color developed in any of the solutions.

II. Tests with Chromic Nitrate

The diphenylcarbazide reagent having been found to be very sensitive to dichromate ions, it was thought advisable to determine the sensitivity toward solutions obtained by starting with chromic ions and subjecting them to the usual Group III procedure of qualitative analysis. For this purpose chromic nitrate solutions containing definite amounts of chromium were used, while the procedure followed was that given by Reedy[6] for the analysis of Group III. After precipitating aluminum hydroxide, the filtrate (about 50 to 60 cc.) was cooled and divided into two equal portions. One part was acidified with acetic acid and 2 cc. of the diphenylcarbazide reagent added. The other portion, which would normally be used for the test for zinc, was tested for dichromate by the ether–hydrogen peroxide method already described under the tests with potassium dichromate. A comparison of the two tests for chromium was thus made from the same solution at the same time. It was found that the highest dilution giving a positive test with diphenylcarbazide was 1 part of chromium in approximately 1,666,000, while a dilution of 1 part in 250,000 failed to give a positive test by the ether–hydrogen peroxide method. Although the diphenylcarbazide reagent is again shown to be more sensitive than the ether–hydrogen peroxide method, it is to be noted that a smaller amount of chromium was detected when originally present as dichromate than when present as chromic ions and the latter put through the usual Group III procedure of qualitative analysis.

Another series of tests similar to those just described for chromic nitrate was carried out, but with 10 mg. each of aluminum, zinc and iron added to each solution tested. The aluminum was added in the form

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[6] Reedy, "Elementary Qualitative Analysis," McGraw-Hill Book Co., New York, 1924.

of the ammonium alum, the zinc as zinc nitrate, and the iron as ferric nitrate. The procedure was the same as when using chromic nitrate alone. The results obtained were almost the same as those obtained when using chromic nitrate alone, indicating that little or no chromium was lost during the precipitation and removal of other cations that might normally be present.[6]

It should be mentioned why, in the tests made on solutions originally containing chromic ions, acetic acid was used instead of sulfuric acid to acidify the solutions prior to adding diphenylcarbazide. In performing blank tests on the individual cations used in the various mixtures above, namely, aluminum, zinc and iron, several slight positive tests were obtained when using sulfuric acid to acidify the solutions before adding diphenylcarbazide, although the salts used were supposedly free from chromium. When the same blank tests were repeated, using acetic acid instead of sulfuric acid, no positive tests were obtained. The slight positive tests given when using sulfuric acid may have been due to very minute traces of chromium in the salts used, together with the fact that diphenylcarbazide is extremely sensitive when used in sulfuric acid solutions. Hence, acetic acid was to be preferred.

Acetic acid has the added advantage in that it is the acid used to acidify the solution prior to adding potassium ferrocyanide in making the test for zinc by this method. Thus the filtrate from the aluminum precipitation has only to be acidified with acetic acid, divided into two parts, one part treated with diphenylcarbazide to test for chromium and the other portion with potassium ferrocyanide for zinc.

The use of diphenylcarbazide possesses two other advantages.

1. It involves adding only one solution, whereas the ether–hydrogen peroxide method requires two. 2. It dispenses with the use of ether, which is usually regarded as a source of danger when used by beginning students in chemistry, due to its inflammability.

Summary

1. The sensitivity of diphenylcarbazide toward dichromate ions has been compared with the sensitivity of the ether–hydrogen peroxide method, the diphenylcarbazide proving to be much more sensitive.

2. The advantages offered by the use of diphenylcarbazide in place of ether and hydrogen peroxide have been pointed out.

EDMONTON, ALBERTA, CANADA

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[6] The author gratefully acknowledges the assistance of Dr. R. B. Sandin, of the University of Alberta, who also carried out some of the analyses in order to eliminate the personal factor which might be involved in reading the various tests

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

A STUDY OF SUPERACID SOLUTIONS. III. THE TITRATION AND DILUTION CURVES OF BASES DISSOLVED IN ACETIC ACID[1]

BY NORRIS F. HALL AND TYRRELL H. WERNER

RECEIVED JUNE 2, 1928 PUBLISHED SEPTEMBER 5, 1928

In the first papers of the present series[2] it was shown that the chloranil electrode, when combined with a suitable salt-bridge and reference electrode, is very well adapted to the study of titrations in glacial acetic acid. Titration curves were there reproduced for a number of bases in 0.2 *M* concentration. The acid used was sulfuric acid. Here we propose to study the effect of changes in the acid, the concentration and other conditions on the titration curves of bases. The increased precision of the newer measurements permits a more complete study of the form of the titration curves, and also of certain related questions, such as the variation in hydrogen-ion activity when solutions of various bases in acetic acid are diluted.

Effect of the Solvent

The general relationships between acids and bases, while essentially similar in a variety of solvents, may also exhibit significant differences. This has been more or less clearly stated or demonstrated by a number of investigators such as Franklin,[3] Brönsted,[4] Hildebrand,[5] Folin[6] and others. No really precise and comprehensive study of the question appears to have been made, however, and such an investigation is under way in this Laboratory, with the aid of both electrometric and colorimetric methods.

Our preliminary results indicate that certain other solvents may be as superior to acetic acid as the latter is to water, in the titration of certain bases, but that few if any solvents can be found which have all the advantages of acetic acid for a general survey. The first important characteristic of a solvent is the size of the "break" in the titration curve of a given base at a given concentration in that solvent when titrated with a given acid.[6a]

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[1] Part of the material in this paper was presented at the St. Louis Meeting of the American Chemical Society on April 18, 1928.

[2] Hall and Conant, THIS JOURNAL, 49, 3047 (1927); Conant and Hall *ibid.*, 49, 3062 (1927).

[3] Franklin, *ibid.*, 46, 2137–51 (1924).

[4] Bronsted, "The Theory of Strong Electrolytes," *Trans. Faraday Soc.*, April, 1927, pp. 431–2; *Chemical Reviews*, September, 1928 (in press).

[5] Bishop, Kittredge and Hildebrand, THIS JOURNAL, 44, 135–40 (1922).

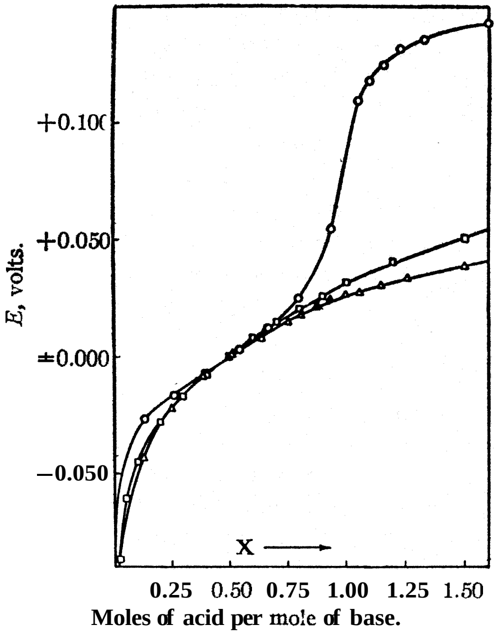
[6] Folin and Wentworth, *J. Biol. Chem.*, 7, 421–6 (1910); Folin and Flanders, THIS JOURNAL, 33, 1622–6 (1911); *J. Biol. Chem.*, 11, 257–63 (1912); THIS JOURNAL, 34, 744–9 (1912).

[6a] See W. M. Clark, "The Determination of Hydrogen Ions," Williams and Wilkins Co., Baltimore, Md., 3d ed., p. 543.

This point is emphasized in Fig. 1, which shows the character of the curves when 99.5% acetic acid, commercial absolute ethyl alcohol, and water are used, respectively, as solvents in the titration of a 0.1 M solution of a weak base, acetoxime ($K_B = 6.5 \times 10^{-13}$).[7]

In each case 100 cc. of the 0.1 M solution of the base was prepared and titrated with a solution of perchloric acid (approximately 1.0 M) in the appropriate solvent, except that in the alcohol titration a 1 M solution of perchloric acid in acetic acid was used for the titrating solution. The quinhydrone electrode was employed and the potentials were measured against the saturated calomel half-cell through a glass-stoppered joint, using a quadrant electrometer. The point where $\Delta E/\Delta V$ has a maximum value was taken as the point of complete neutralization in every case. The exact form of the curves is not significant in this particular case, as it may be affected by electrode and liquid junction errors.

The curves have been shifted vertically as a whole by adding a constant to the observed potentials, so as to bring the points of half neutralization into coincidence in the three cases (in order to mask the grosser differences of liquid junction potential). It is plain that this base, which is so weak as to give no break at all in either water or alcohol, gives a break of 0.1 volt when dissolved in acetic acid. This large break is due to the exceptionally high hydrogen-ion activity of solutions of perchloric acid (and some others) in acetic acid (and certain other solvents). Solutions of this sort have been called "superacid."[2]



○, CH_3COOH; □, C_2H_5OH; △, H_2O.

Fig. 1.—Effect of the solvent in the titration of a weak base (acetoxime) with perchloric acid.

Aside from this "superacidifying" character, other properties of the solvent are of importance. In particular it must dissolve appreciable quantities of the bases selected for study, and also of the salts of these bases with the titrating acid, if the titration curves are not to be complicated by the appearance of precipitates. In the main, acetic acid meets

[7] Lundén, Ladolt-Barnstein, "Tabellen."

this requirement very well, although there are numerous exceptions, as noted in a later paper.

Choice of the Titrating Acid

In the earlier work sulfuric acid was used in all the titrations, although it was remarked that the acidity of equivalent solutions of perchloric acid was apparently higher and although the titration curves showed that the second as well as the first hydrogen of sulfuric acid occasionally entered into reaction (especially with the stronger of the bases). Further, there are certain bases which have insoluble sulfates or acid sulfates but whose perchlorates are soluble. For these reasons it seemed desirable to make a comparative study of the two acids, and as hydrochloric acid also might be supposed to present certain advantages, it was included in the preliminary survey.

This was conducted as follows. Five bases were selected with strengths fairly evenly distributed over the measurable range. Three equal portions of 0.05 M solutions of each of these in acetic acid were titrated, respectively, with 1.0 M $HClO_4$, 1.0 M H_2SO_4 and 1.0 M HCl (all in acetic acid), and the curves plotted in the usual way. Fig. 2 gives the results of the titrations.

The six families of curves are plotted on the same vertical scale with the same zero. The horizontal scales are the same but the zero is shifted in each case 0.5 unit to the right. The abscissa is the fractional neutralization. The ordinate is the measured potential of a cell such as that sketched in Fig. **3,** and constituted as follows

Pt	$C_6Cl_4O_2$ (Sat.) $C_6Cl_4(OH)_2$ (Sat.) **Base** (Cb) **Acid** (Ca)	LiCl Cx	KCl Sat	KCl Sat. HgCl Sat.	Hg
	in HAc		in H_2O		

The convention

$$(P_{\mathrm{H}})^{\mathrm{HAc}} = \frac{E - 0.566}{0.0591} \text{ at } 25^\circ$$

(where E is the electromotive force of the cell, regarded as positive when the platinum is positive to the mercury) was used as in the earlier papers,[2] to which the reader is referred for experimental details. The following changes may be noted in the technique. The early difficulties with electrode poisoning were almost completely absent, perhaps because the electrodes were always ignited before every new run. We did not warm the solutions to saturate them with chloranil, as we found that stirring for ten minutes at 25° was uniformly effective. The acetic acid used was in all cases the P. W. R. analytical reagent. The perchloric acid was prepared as described below (footnote 9). The hydrochloric acid was prepared by passing the pure gas, dried with sulfuric acid, into acetic

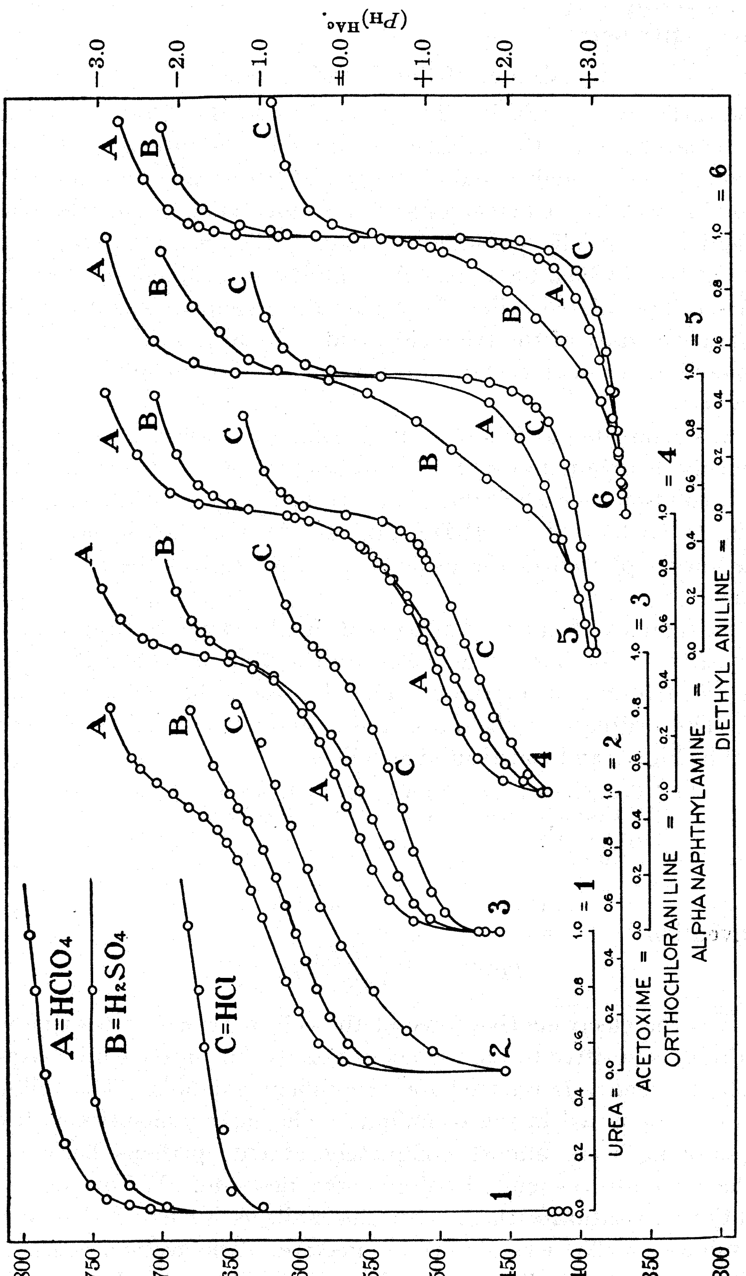


Fig. 2.—Comparison of $HClO_4$, H_2SO_4 and HCl as titrating acids. Abscissas are moles of acid added per mole of base.

acid until the proper concentration was reached or exceeded, and then diluting if necessary. The other materials were of the same nature, as described in the earlier paper.

Beginning in the upper left hand corner of Pig. 2, the first family of curves is not one of titration curves but simply represents the effect of adding the three acids to the pure solvent in amounts corresponding to those used in the other cases (titrations). These curves show clearly that equal concentrations of the three acids are far from being equally "acid." The individual character of strong acids, masked in water by the relatively basic solvent, is here permitted to exhibit itself. It is further apparent that certain bases which would give no break at all with hydrochloric acid could be titrated quite satisfactorily with perchloric acid. The next family of curves (titrations of urea) brings out just this phenomenon. This base is so weak that even in acetic acid it gives no break with hydrochloric acid and only a slight bend with sulfuric acid, while with perchloric acid the break, though slight, is clearly marked. The next two bases, acetoxime and o-chloro-aniline, are appreciably stronger, as shown by the increasingly negative potential of their half-neutralization points, and with them first two, and then all three of the acids give a good break.

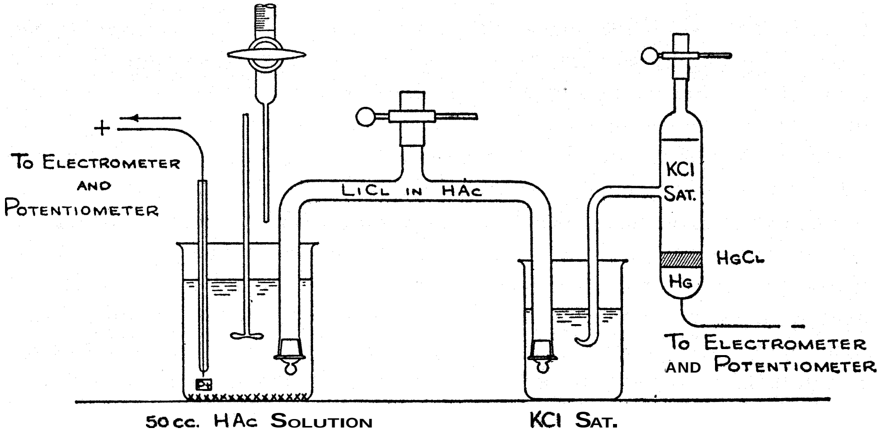


Fig. 3.—Cell for titrations in glacial acetic acid using the chlorauil electrode.

The three curves are also coming closer together as potentials are reached which lie far below those characteristic of the acids alone, but at the same time the sulfuric acid curve (B) is rising rather more rapidly over the range from 50 to 95% neutralization, due to a quite different cause. This is clearly apparent in the case of the much stronger base α-naphthylamine (No. 5). Here the break is in all three cases very pronounced—the form of the curves A and C recalls those characteristic of strong bases in water, by comparison with the weak base types 2, **3** and 4, and the sulfuric acid curve, B, has bent sharply upward at the halfway point and lies far above the other two. This is of course due to the fact that the base is now strong enough to react with the second hydrogen of sulfuric acid, and the sulfate thus formed is progressively converted to the acid salt as the neutralization proceeds. An essentially similar state of affairs is shown by Curve 6 (diethylaniline). This base has a K_B in water of about 4×10^{-8},[8] and therefore behaves in this solvent like a strong base (in respect to its titration curve) as will be more explicitly shown below. The break (with perchloric acid) from 50 to 150% neutralization, is about six PH units, while with hydrochloric acid it is about two units less.

Only one base (cocaine) has been found whose curve obtained under comparable conditions lies appreciably (as much as 15 millivolts) below that of diethylaniline, while many substances known to be stronger bases, such as diphenylguanidine, triphenylguanidine and triethylamine, have curves practically coincident with the diethylaniline curve. On the other hand, some stronger bases such as eserine, strychnine, ammonia, quinine, quinidine, nicotine, brucine, cinchonine, dimethylamine, diethylamine and piperidine give curves that lie from 5 to 30 millivolts *above* it. It seems probable, in view of all the data at hand, that the curve of diethylaniline represents the limiting value (at this concentration) for a normal base which is "strong" as regards its titration in the solvent and that all bases with curves lying appreciably above this value are definitely not completely "strong," but that minor variations of 15–30 millivolts about this limiting value are to be attributed to unknown chemical influences and not to differences in base strength. The individual behavior of particular bases will form the subject of a later communication.

It is obvious from these diagrams that perchloric acid is far preferable to the other two as far as its purely electrical character is concerned in the titration of bases of all measurable strengths. There are, however, other considerations involved.

A great many of the bases we have studied have rather insoluble perchlorates (pyridine, K, Rb, NH_4, nicotine, brucine, cinchonine, cinchonidine, pamido-acetophenone, arylcarbinols, etc.) or sulfates or acid sulfates (Na, Li, Ca, Sr, Ba, Pb, β-naphthylamine, dianisal acetone, semicarbazide, *-bromo-aniline, etc.). We have not tried hydrochloric acid in all of these cases but it seems probable that the chlorides of many of these bases are much more soluble, so that hydrochloric acid might be used in a comparative study of certain (of the stronger) bases which give curves of irregular form when titrated with perchloric or sulfuric acid. On the other hand, the partial pressure of hydrochloric acid from

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[8] Pring, *Trans. Faraday Soc.*, 19, 705–10 (1923–24); Bourgeaud and Dondelinger, Bull. *soc. chim.*, [4] 37, 277 (1925).

acetic acid solutions is so large that a 1.0 *M* solution fumes about as strongly as 16 *M* hydrochloric acid in water, so that aside from their unpleasantness in use the solutions of this acid are variable in composition, due to the high rate of escape of hydrochloric acid.[9] On the whole it seemed best to use perchloric acid whenever possible, changing to the other acids for particular substances or classes of substances.

The Effect of Concentration

The curves given in the first paper were all obtained at a single concentration (0.2 M), and it was recognized that the observed potentials were in general influenced by concentration changes to a greater degree than is the case in aqueous solutions. We have therefore made a few experiments to determine the nature of this effect. In water the effects of concentration change are as follows. When a strong base such as sodium hydroxide is titrated with a strong acid in a series of concentrations each of which is one-tenth that of the preceding one, the titration curves obtained are all essentially similar and parallel, and are spaced about one P_H unit apart (see Fig. 4A). On the other hand, when a weak base such as ammonia is titrated with a strong acid the titration curves for different concentrations lie very much closer together and presumably almost intersect at the mid-point. In acetic acid as solvent the phenomena are notably different. The curves for a "strong" base are usually quite similar in shape to those determined in water, but the effect of a tenfold dilution is to move the curve only about one-half of a P_H unit instead of a whole one. On the other hand, the effect of dilution is very much greater on a weak base titration curve than it is in water. These relationships are exhibited in Figs. 4 and 5.

Fig. 4A shows calculated curves for the titration of aqueous sodium hydroxide with hydrochloric acid. In drawing these curves the volume has been assumed constant during the titrations and no account has been taken of the change of hydrogen-ion activity coefficient with change in the composition of the solution as the titration proceeds. The activity coefficients of the pure sodium hydroxide solutions were taken from the data of Harned,[10] and the curves are plotted on the assumptions that *(a)* the

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[9] We have found that in making up perchloric acid, by adding an approximately 8 N aqueous solution to the theoretical quantity of chilled acetic anhydride and diluting with acetic acid to 1 *M*, it is important that there be no excess of acetic anhydride left in the solutions, as otherwise high and irregular potentials are observed. These are due to the action of acetic anhydride on hydrochloranil. A thermal method has proved useful in gaging the exact proportions of acetic anhydride and aqueous perchloric acid to be used. After the two components are mixed in nearly correct proportions, it is found that adding a small amount of one of the components produces a temperature rise. This component is then added until further additions are without thermal effect and the mixture is then diluted with acetic acid to the desired concentration.

[10] Harned, THIS JOURNAL, 47, 676–689 (1925).

Ph of 0.0001 *N* NaOH is 10.00, (b) the activity coefficients of the two ions of sodium hydroxide are equal at each concentration and (c) the activity coefficient of 0.001 N NaOH can be calculated from the limiting equation of Debye and Hückel. On the scale of the diagram, the changes in the shape and relative position of the curves introduced by these approximations are negligible.

The curves in the right-hand half of the diagram reproduce the results of actual titrations of solutions of diethylaniline of the concentrations indicated, in glacial acetic acid. The titrating mixture was a solution of perchloric acid in acetic acid. The concentration of this solution was 2.0 *M* in the lowest two curves, 0.2 M in the middle curve, 0.02 M and 0.002 *M* in the two upper curves. The lowest curve is corrected for the volume change during titration, on the assumption that the measured e.m.f. is 0.018 volt too high when the concentration is halved. Corresponding corrections to the other curves would be negligible and were not applied. The curves show that between 0.02 and 0.002 *M* the $(P\mathrm{H})^{\mathrm{HAc}}$ of the solution changes approximately as the *square* root of the concentration of unneutralized base, while at both higher and lower concentrations the change in $(P\mathrm{H})^{\mathrm{HAc}}$ is greater, approaching that found in water solutions. These rather surprising results suggested the investigations reported below (Figs. 6, 7 and 8).

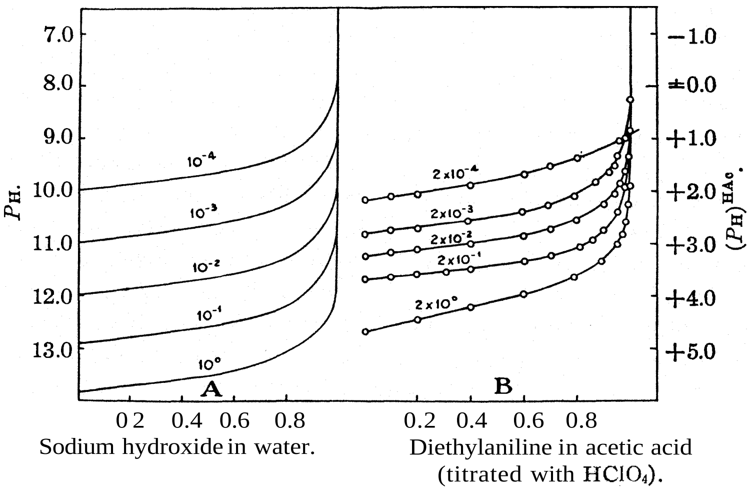
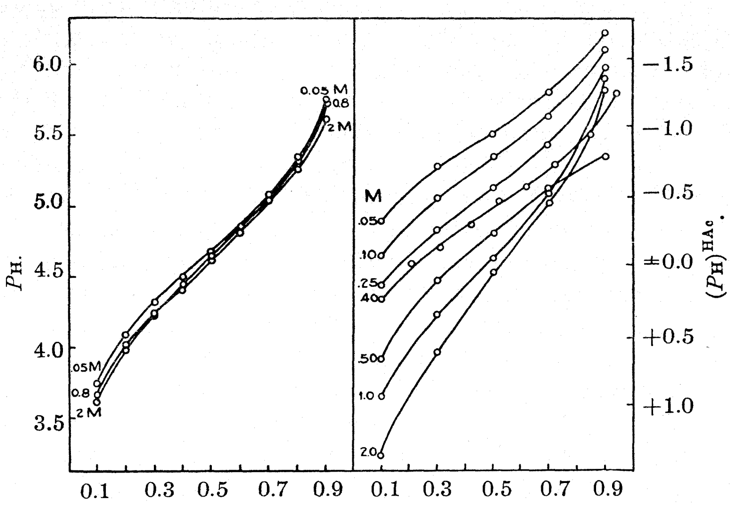


Fig. 4.—Titration curves of "strong" bases. Effect of concentration. Abscissas are moles of acid per mole of base.

In Fig. 5 are reproduced somewhat similar curves for "weak" electrolytes in the two solvents. As we know of no complete data on a weak base in aqueous solution, we decided to use the results of Cohn and his collaborators[11] on acetic acid. These investigators[12] report the values of $-\log \gamma$ for solutions containing varying proportions of acetic acid and sodium acetate at a number of fixed concentrations of total acetate. As $-\log \gamma$ is essentially the measure of the deviation of the actual titration curves from the theoretical curve whose mid-point is at $P_K = 4.73$, it is a simple matter to construct the actual titration curves from their data. This has been done for three concentrations of total acetate: 2 M, 0.8 M and 0.05 M. It is evident that the curves lie close together and do not greatly deviate from the ideal shape.



A. Acetic acid titrated with sodium hydroxide in water.

B. Urea titrated with $HClO_4$ in acetic acid.

Fig. 5.—Effect of concentration change on titration curves of weak electrolytes in water and in acetic acid. Abscissas indicate fractional neutralization.

On the right-hand side of Fig. 5 are found similar curves reproducing our measurements on the titration of urea with perchloric acid in acetic acid solution. Here it is seen that a corresponding concentration change produces an enormously greater effect than in water. Only one of the curves (that for 1.0 M urea) follows closely the theoretical form; the others are either too steep (2 M) or too flat (all others). At the point of 10% titration the change in $(P_H)^{HAc}$ is approximately one unit between 0.5 M and 0.05 M. At 90% titration it is two-thirds of a unit. Between 0.1 M and 1 M the corresponding changes are one unit and one-third of a unit.

Taken in conjunction with Fig. 2, these results show clearly that both the nature of the titrating acid and the concentration used have much

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[11] Cohn, Heyroth and Menkin, This Journal, **50,** 696–714 (1928).

[12] Ref. 11, p. 711.

more effect on the PH of mixtures of a weak base and its salt in acetic acid than is the case in water. The extrapolation involved in computing the dissociation constants of bases will therefore be much greater and more uncertain in the former solvent. Accurate values even of the relative strength of bases will evidently only be obtainable under carefully regulated conditions.

The Form of the Titration Curves

In the course of the earlier work it was noted that the curves there obtained (in the titration of 0.2 M bases with sulfuric acid) showed fair approximation to the theoretical form for a weak electrolyte.[13] As can be seen from the present results (Fig. 2 above) sulfuric acid tends to act to some extent as a dibasic acid even with fairly weak bases, and it therefore seemed best to re-examine the question of the exact form of the curves, using perchloric acid, which is free from this particular complication. A concentration was therefore selected (0.05 M) at which the peculiarities of individual substances should be less marked than at 0.2 M, while the buffer capacity of the solutions should still be adequate and the potentials definite and reproducible. Eight bases were then chosen which did not have insoluble perchlorates and which showed a regular gradation of base strength over the measurable range. These were titrated at the stated concentration with 1 M perchloric acid and the resulting potentials are reproduced in Fig. 6. The experimental values have not been corrected for the change in volume during titration because (a) the percentage volume change is the same in all the curves, (b) it is not yet clear just how great the correction should be in all cases and (*c*) as the volume change is only 5% at 100% neutralization, the correction is probably at most 0.06 log 1.05 = 0.001 volt, or within the experimental error.

The strongest of the bases, guanidine, is a diacid base, and was therefore studied in 0.025 M concentration. All the others were 0.05 *M*. In preparing the sodium acetate solution, the calculated amount of metallic sodium was quickly weighed out and added to the acetic acid. The top curve, marked "solvent," shows the potentials obtained when pure acetic acid is treated with amounts of the titrating acid corresponding to similar points on the curves below. The measured potentials, except those of the top curve, were steady and closely reproducible on successive trials. However, each curve records the results of a single titration only, except the top one where the potentials are mean values taken from a number of runs, with a mean deviation from the mean of about 0.01 volt. The curves show a clear gradation in character as one goes to progressively weaker bases and the break can be traced as far at least as to urea, even at this low concentration.

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[13] Ref. 2, p. 3053, Fig 2.

In order to save space, and because the uncertainty of the liquid junction potential throws doubt upon the absolute significance of the numerical results obtained, these will in general be reported only in the form of diagrams. It seems desirable, however, to give a clearer indication of the precision of the numerical values, and accordingly the titration data for some of the stronger bases are reproduced in Table I. These data with others are shown graphically in Figs. 2, 6, 7 and 8.

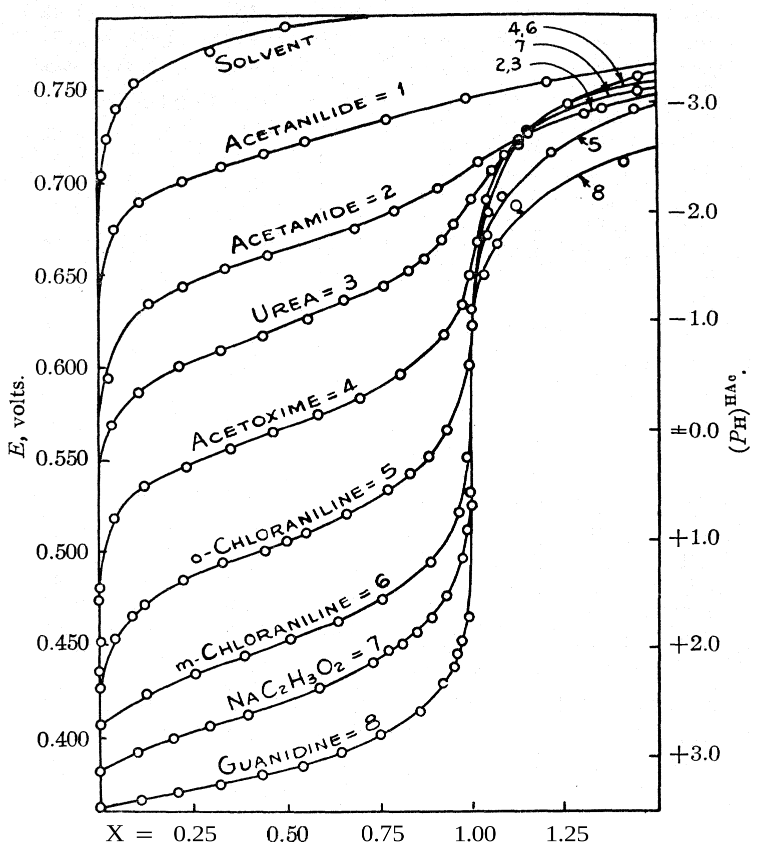

Fig. 6.—Titration of 0.05 N bases in glacial acetic acid with perchloric **acid.** Abscissas show fraction of base neutralized.

In Table I the first column (100X) gives the percentage neutralization. (The point where $\Delta E/\Delta V$ [the change of potential with volume of titrating acid] has a maximum value is taken in every case as the point of complete neutralization.) Col. 2 is the observed e.m.f. of the cell constructed as shown in Fig. **3** and described on p. 2369. The third column gives the negative logarithm of the fractional part of the original base remaining unneutralized. The fourth column is the $(P_H)^{HAc}$ value calculated accord-

Table I

Titration Data

100 X	E, volt	$-\log (1 - X)$	$(P_H)^{HAc}$	$(P_H)^{HAc} - \log (1 - X)$
Guanidine				
0	0.362	0	3.45	3.45
10.7	.366	0.05	3.39	3.44
21.4	.370	.10	3.32	3.42
32.1	.374	.17	3.25	3.42
42.8	.379	.24	3.16	3.40
53.6	.384	.33	3.08	3.41
64.2	.391	.45	2.96	3.41
75.0	.400	.60	2.81	3.41
85.7	.413	.84	2.59	3.43
92.2	.428	1.11	2.34	3.45
94.7	.437	1.28	2.18	3.46
96	.444	1.40	2.06	3.46
97.2	.451	1.55	1.95	(3.50)
98.6	.464	1.85	1.79	(3.64)
99.6	.525	2.40	0.70	(3.31)
			Mean	3.43 ± 0.02
Diethylaniline Run No. 1				
0	0.362	0	3.45	3.45
11.0	.365	0.05	3.40	3.45
22.0	.369	.11	3.33	3.44
33.0	.373	.17	3.26	3.43
44.0	.377	.25	3.20	3.45
55.0	.383	.35	3.10	3.45
66.0	.391	.47	2.96	3.43
76.9	.400	.64	2.81	3.45
87.9	.417	.82	2.52	3.34
99.0	.519	1.00	1.79	(2.79)
			Mean	3.43 ± .02
Diethylaniline Run No. 2				
0	0.366	0	3.38	3.38
11.0	.368	0.05	3.35	3.40
21.9	.370	.11	3.31	3.42
33.8	.374	.17	3.25	3.42
43.9	.376	.25	3.21	3.46
54.9	.383	.35	3.13	3.48
65.8	.390	.47	3.01	3.48
76.8	.400	.63	2.81	3.44
87.8	.415	.91	2.55	3.46
92.2	.427	1.11	2.35	3.46
96.6	.450	1.47	1.96	3.43
97.4	.460	1.58	1.79	3.37
98.8	.482	1.92	1.42	3.34
99.6	.612	2.40	−0.78	(1.62)
			Mean	3.43 ± .03
Ethylaniline				
0	0.375	0	3.23	3.23
11.1	.380	0.05	3.15	3.20
21.7	.385	.11	3.06	3.17
34.4	.391	.18	2.96	3.14
45.3	.396	.26	2.88	3.14
57.5	.404	.37	2.74	3.11
67.9	.412	.49	2.61	3.10
78.9	.423	.68	2.42	3.10
90.5	.444	1.02	2.06	3.08
95.0	.462	1.30	1.76	3.06
97.3	.477	1.57	1.50	3.07
98.2	.490	1.74	1.28	3.02
99.2	.514	2.10	0.88	2.98
Sodium Acetate				
0	0.382	0	3.12	3.12
9.7	.392	0.04	2.94	2.98
18.9	.399	.09	2.83	2.92
29.0	.406	.15	2.71	2.86
38.6	.412	.21	2.61	2.82
57.5	.426	.37	2.37	2.74
67.5	.435	.49	2.22	2.71
73.0	.440	.57	2.13	2.70
77.2	.446	.64	2.03	2.67
81.2	.450	.73	1.96	2.69
85.0	.456	.82	1.86	2.68
88.9	.464	.95	1.73	2.68
93.0	.476	1.15	1.52	2.67
97.0	.497	1.52	1.17	2.69
98.5	.512	1.82	0.91	2.73
99.4	.532	2.22	.58	2.80

ing to the convention stated on p. 2369. The fifth column gives the sum of the third and fourth. An idea of the precision of the measurements may be obtained from the constancy of this sum for diethylaniline and guanidine—two bases which are "strong" in their titration behavior that is, which act in this respect like sodium hydroxide in water. This is not true of the other bases, which are weaker, and for which the values in the fifth column of Table I show a definite trend. These points will be further discussed on p. 2380.

To test the approximation of the curves of Fig. 6 to theoretical forms, one may employ various types of logarithmic plotting. Thus if X is the fraction of the base neutralized, one may plot e.m.f. against log $X/(1 - X)$. On such a plot the titration curve of a base which obeys the mass law without correction is a straight line having a slope of 59 millivolts for a unit change in the logarithm of the ratio.

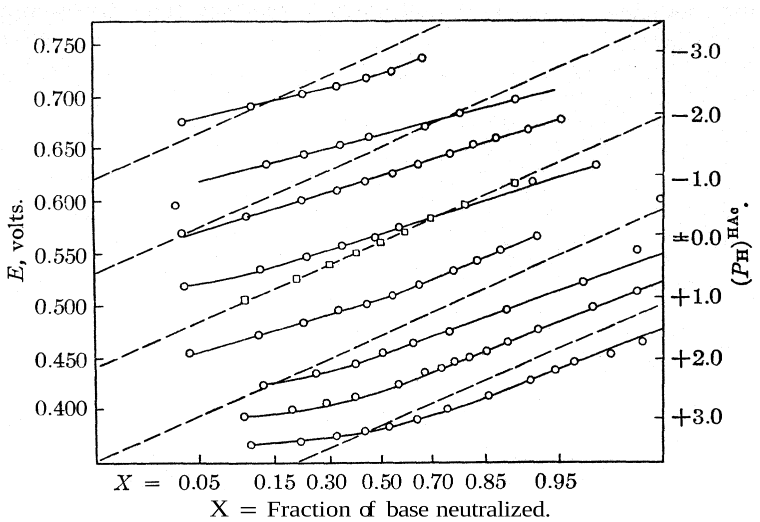

Fig. 7.—Logarithmic titration curves of bases in acetic acid titrated with perchloric acid. True abscissa = log $[X/(1 - X)]$.

In Fig. 7 this type of plotting is applied to the data of Fig. 6. The curves for the different substances lie in the same order and relative position as in that figure. The diagonal broken lines reproduce for comparison the slope which would be shown by bases which obeyed the mass law without correction. For comparison also we have taken the data of Cohn, Heyroth and Menkin[11] for acetic acid in water at the concentration 0.05 M, and arbitrarily placed the mid-point of this curve so that it falls upon the most centrally located broken line. The data at other points are then represented by squares. It is seen that in this case the deviations of the points from the theoretical slope are scarcely appreciable.

In the cases of all the substances dissolved in acetic acid, however, the deviations are considerable. The lines show a curvature which steadily increases with the strength of the base, and in all cases the slope is less than the theoretical.

It is thus evident that none of the bases act when titrated exactly as do weak electrolytes in water. On the other hand, the lowest curves in Fig. 6 are surprisingly similar to those given in water by *strong bases.*

In a further test of this point, a different type of logarithmic plotting may be employed. If the electromotive force is plotted against the logarithm of $1 - X$ (the unneutralized fraction), a curve of the strong base type will be a straight line. Thus in water the titration of sodium hydroxide with hydrochloric acid gives a straight line on such a plot. This is generally attributed to the essentially complete dissociation of NaOH and NaCl, the essentially constant value, within the range, of the activity coefficient of the hydroxyl ion and the fact that $a_{\mathrm{H}^+} \times a_{\mathrm{OH}^-} =$ Const. $= Kw$.

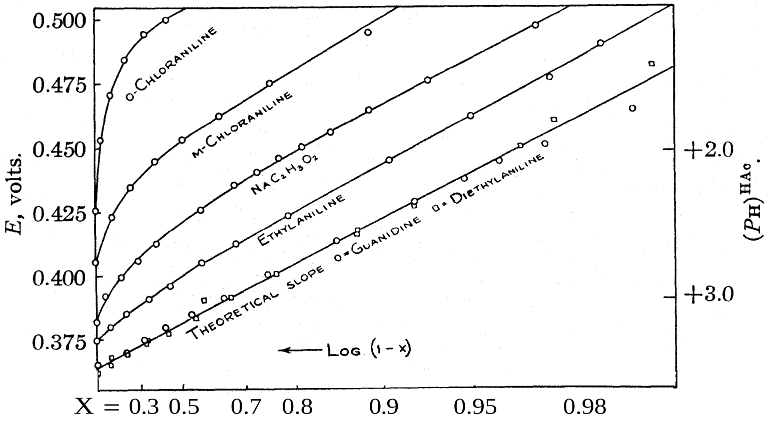

Fig. 8.—Logarithmic titration curves of bases in acetic acid. X = fraction of base neutralized. Abscissa = $-\log (1 - X)$.

If now this method of plotting is applied to the four lowest curves of Fig. 6, and to the titration of ethylaniline and diethylaniline under the same conditions (as shown, for example, in Fig. 2, 6A), Pig. 8 is obtained. Here the lowest line has the theoretical slope (for strong bases) of one PH unit (59 millivolts) per unit change of log $(1 - X)$, and has been adjusted vertically so as best to fit the points for the two bases diethylaniline and guanidine. The other lines are fitted as well as possible to the experimental points without regard to theory. All these latter exhibit a curvature which rapidly increases as the bases become weaker. This sort of plotting is a sensitive test for "strong base" behavior and shows that diethylaniline and guanidine have titration curves of the strong base type within the experimental error of 2 or 3 millivolts, as may also be seen from the constancy of the values in Col. 5 of Table I.

A possible inference from these results would be that the acetates of diethylaniline and guanidine are completely dissociated, while those of the other bases are incompletely dissociated. However, such a view encounters difficulties when one reflects that the dielectric constant of acetic acid is rather low (possibly about 10 at 25°)[14] and that, therefore, the attraction between univalent ions should be enormously greater than in water, so that there should be in this solvent no electrolytes which are strong in the sense in which this term is used in water; that is, in the sense that their ions at appreciable concentrations act like point charges almost unaffected by the surrounding ion atmosphere.

It seemed desirable, in seeking further light on this question, to abandon titration curves and to study the effect of dilution on solutions of the pure bases. This is, of course, the classical procedure followed by Ostwald and all his successors who have tested the applicability of the dilution law to electrolytic solutions—principally in water. These studies have nearly all been made with the aid of conductivity measurements. In non-aqueous solutions the conductivities are frequently very low and the effects of impurities proportionately great, so that significant results are only obtainable by this method at the price of extreme care and effort. There is available, however, another convenient method of following the course of electrolytic dissociation on dilution. If an electrode is available which is responsive to changes in the activity of one of the ions formed by the dissociating substance, and if the activity coefficient of this ion can be estimated at the various concentrations employed, dissociation can be studied by e.m.f. measurements as satisfactorily as by conductivity. Apparently this method has been surprisingly little used. On account of its many advantages, we decided to use the chloranil electrode in studying the form of the dilution curves of bases.

The Form of the Dilution Curves of Bases

If the hydrogen-ion activities of solutions of a base in water are measured over a large concentration range, and a plot is made of e.m.f. (or P_H) against the logarithm of the normal concentration of the base, the points for each substance should lie very nearly on a straight line with a slope of one (P_H) if the base is completely dissociated, while if its dissociation obeys the law of concentration effect, the slope should always be less than one, and there should be a considerable range where the points lie on a line with a slope of $^1/_2$.[15]

Fig. 9 shows theoretical curves for bases of varying strength in a solvent having an ion activity product of 10^{-14} (water at 25°). In drawing the

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[14] Landolt, Bornstein, "Tabellen," 5th ed., p. 1037, Suppl. 557.

[15] For a strong base, $a_{H^+} = \frac{K_w}{C_B}$ $\therefore P_H = P_w + \log C_B$, $\frac{\partial P_H}{\partial \log C_B} = 1$. For a weak base $K_B = \frac{a_{BH^+} \times a_{OH^-}}{a_B}$, $a_{BH^+} \cong a_{OH^-}$, $a_B \cong C_B$ and $a_{H^+} = \frac{K_w}{a_{OH^-}}$. $\therefore \frac{K_w^2}{a^2_{H^+}} \times \frac{1}{C_B} = K_B$, $2P_w - 2P_H + \log C_B = P_B$ and $\frac{\partial P_H}{\partial \log C_B} = {}^1/_2$.

curves account has been taken both of the dissociation of the solvent where that is appreciable and of the cases where the concentration of the undissociated base is not substantially equal to that of the total base. It is seen that the strong base curve has a unit slope while there is a range where each weak base curve has a slope of $^1/_2$. We could find no complete set of data to compare with these curves and, indeed, it would be difficult if not impossible to make the necessary measurements at the lower concentrations. A few measurements on a single strong base (NaOH) and a single weak base (NH_3) are reported by Michaelis[16] (for 18°) and these have been included. It is obvious that their behavior is typical of the classes to which they respectively belong.

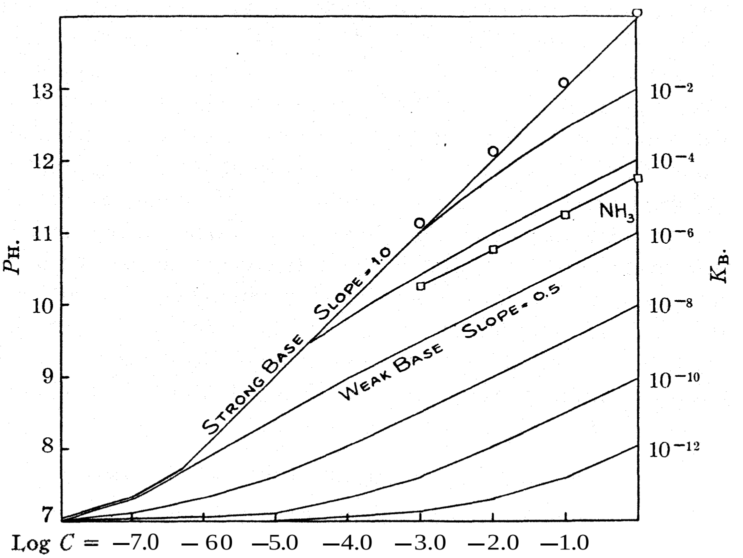

Fig. 9.—PH–Dilution curves of bases in H_2O. Theoretical curves drawn for t = 25°. Data from Michaelis at t = 18°. ○ = NaOH; □ = NH_3.

In applying this method to acetic acid solutions, we proceeded as follows: a rather concentrated solution of the base was first prepared (2 or 3 M) and from this two or three other solutions, each of which was one-tenth as concentrated as its predecessor. Fifty cc. of pure acetic acid was then measured out and its $(P\mathrm{H})^{\mathrm{HAc}}$ determined in the usual way. Then measured volumes of the most dilute solutions of the base (up to a volume of 5 cc.) were run into the acetic acid, and the new $(P\mathrm{H})^{\mathrm{HAc}}$ values determined. After 5 cc. had been added, the procedure was repeated with more concentrated solutions of the base. In this way the concentration

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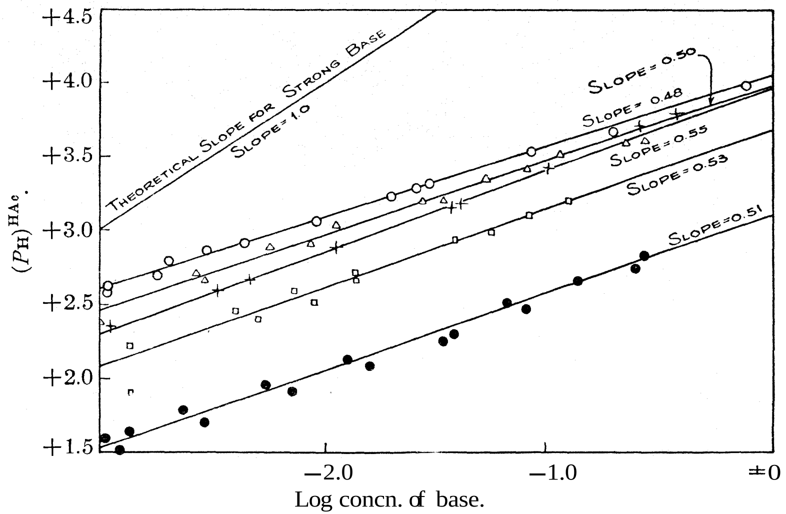
[16] Michaelis, "Hydrogen-Ion Concentration," Williams and Wilkins Co., Baltimore, Md., 1926, p. 24.

at each stage could be computed with sufficient accuracy on the assumption that the volumes were additive and it was therefore possible to plot $(P_{\rm H})^{\rm HAc}$ against the logarithm of the concentration. Fig. 10 is such a plot for two thoroughly "strong"[17] bases (diethylaniline and guanidine) and three that are appreciably "weaker" (pyridine, sodium acetate and *o*-chloroaniline). The potentials are less reproducible in these dilute solutions of pure bases than in the case of the titrations; nevertheless, most of the points fall on a straight line between concentrations of 1 *N* and 0.001 N, and these lines have very nearly the theoretical slope (for a weak base) of 0.5. At lower concentrations the measurements are not reproducible



○, Diethylaniline; +, pyridine; □, sodium acetate; △, guanidine; ●, *o*-chloro-aniline.

Fig. 10.—$(P_{\rm H})^{\rm HAc}$–Dilution curves of bases in acetic acid.

but seem to indicate an increase in the slope, as would be expected. At higher concentrations good measurements are very easy to make but their interpretation is obscure due to the individual peculiarities of concentrated solutions (see Fig. 11) and possibly to deviations of the volumes from additivity. A few measurements on still weaker bases indicated that their points fell on lines parallel to and below those given in Fig. 10. These data seem to constitute a convincing demonstration that in acetic acid bases which behave during titration like strong bases are nevertheless actually quite regular in their conformity to the requirements of the law of concentration effect, and are not to be regarded as completely dissociated in the sense in which this term is used of aqueous electrolytes.

It is evident that the electromotive force method constitutes a powerful

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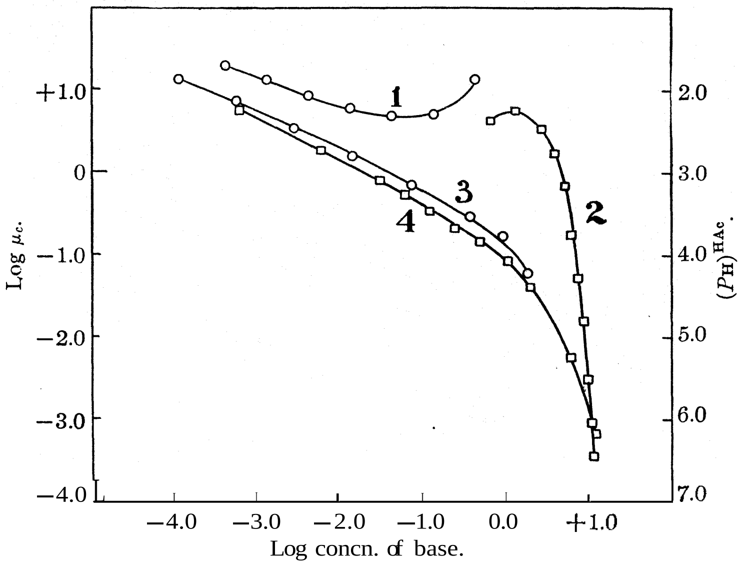
[17] As regards their titration curves.

tool for investigating the effect of concentration on the properties of solutions in non-aqueous solvents. This problem has been the subject of very numerous studies by the conductivity method but the results have been so complex and difficult to interpret that the interest of many investigators in this field has perhaps somewhat cooled in recent years. It is not too much to hope that this interest may be revived as the value of the electromotive force method becomes more widely appreciated. Thus it may be found that certain anomalies in the conductivity results, which make a considerable demand on auxiliary hypotheses such as those of association, solvation, etc., may not appear at all in the electromotive force measurements. A diagram (Fig. 11) will illustrate this idea. The molar conductances of solutions of potassium acetate and of pyridine in acetic acid have been determined over a considerable concentration range by Völmer[18] and by Patten.[19] When their values of μ_c are plotted against the concentration, both curves are anomalous, that for potassium acetate showing a minimum and that for pyridine a maximum value of the molar conductance. In Fig. 11 is given such a plot of their results except that logarithms of the molar conductance (μ_c) and of the concentration are



1, Potassium acetate—log μ_c; 2, pyridine—log μ_c; 3, potassium acetate—$(P_H)^{HAc}$; 4, pyridine—$(P_H)^{H*}$.

Fig. 11.—Comparison of effect of dilution on conductivity (Curves 1 and 2) and on hydrogen-ion activity (Curves 3 and 4) of bases dissolved in acetic acid.

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[18] B. Volmer, *Z. physik Chem.*, *29*, *187* (1899).

[19] H. E. Patten, *J. Phys. Chem.*, *6*, 554–600 (1902).

used as ordinates and abscissas, respectively (Curves 1 and 2). On the same diagram and with the same abscissa are plotted our values of log $a_{H^+} = -(P_H)^{HAc}$ (right-hand ordinate) ior the same substances over a much greater concentration range. The resulting curves (3 and 4) show no evidence whatever of the anomalies mentioned but steadily fall as the concentration of the base increases and are, of course, straight lines with a slope of $-{}^1/_2$ over a large part of the range, as stated above.

It is evident therefore that the form of the conductance functions is complicated in comparison to that of the activity functions, as a result of secondary effects of uncertain nature. Similar anomalies are shown by the conductance functions of sulfuric and hydrochloric acids in the same solvent, and again our (unpublished) activity data give no indication of their existence.

The Liquid Junction Potential

The significance of the results hitherto reported depends in large measure on the (assumed) constancy of the liquid junction potential when the concentration and composition of the solutions are varied, though not directly on the absolute value of this potential. Thus it might be supposed that the failure of the curves of Fig. 7 to approach more closely the theoretical form was due to systematic variations in the junction potential. It is perhaps impossible entirely to exclude this possibility. Nevertheless we feel that the following are strong arguments in favor of the essential constancy of this potential in all our measurements.

(1) The agreement of the individual points with the theory is so good in the case of the data of Table I and the lowest curve of Fig. 8 that there can hardly be any appreciable liquid junction error involved, yet these data cover much the same range of acid–base ratio and of acidity as the curves of Fig. 7.

(2) The similar consistency of the *dilution* curves of Fig. 10 seems to show that *concentration* changes from 1.0 N to 0.001 N are practically without effect on the liquid junction. We therefore feel that the effective constancy of this potential throughout all our measurements, while not definitely proved, is rendered very probable.

The following aspects of the data reported demand further elucidation: (I) the abnormally small effect of dilution on the "strong" base curves (Fig. 4B); (2) the abnormally large effect of dilution on the "weak" base curves (Fig. 5B); (3) the failure of the weak base curves to conform to the theory (Fig. 7); (4) the fact that bases which are clearly "weak" (Fig. 10) should nevertheless behave like "strong" bases when titrated (Fig. 8).

Among the factors which may be suggested as responsible for these anomalies are the following: (1) the low value of the dielectric constant of the solvent with the correspondingly large effect of interionic attractions on the activity coefficients of the ions, so that interionic association is always considerable; (2) large differences in the extent of solvation of the various ionic and molecular species present in the solutions. Thus it seems probable that association with the solvent is very complete in the case of the stronger bases but very incomplete in the pure solutions of the weaker bases.

In the absence of independent information concerning the colligative properties of such solutions as we have studied, it seems undesirable at present to elaborate further mechanical hypotheses to account for their observed peculiarities.

Summary

Diagrams and tables are given which show the effect of the following influences on the shape of the titration curves of bases dissolved in acetic acid: the nature of the titrating acid, the concentration and the strength of the base. It is shown that the weaker bases give anomalous titration curves while the curves of bases which act like strong bases in water conform to the theory of such titrations. The effect of dilution on the hydrogen-ion activity of solutions of bases is studied by the electromotive force method, and it is shown that even the "strongest" bases are truly weak electrolytes in this solvent. It is shown that these results practically demonstrate the effective constancy of the liquid junction potential between saturated aqueous potassium chloride and the various acetic acid solutions used. The value of the electromotive force method in studying the effect of dilution on dissociation is emphasized in the discussion.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE STATE UNIVERSITY OF IOWA AND THE EPPLEY LABORATORY]

A LEAD–MERCUROUS IODIDE VOLTAIC CELL

BY WARREN C. VOSBURGH

RECEIVED JUNE 4, 1928 PUBLISHED SEPTEMBER 5, 1928

The results of measurements of voltaic cells with mercurous iodide electrodes are not very concordant. Gerke[1] has calculated the electromotive force of the cell

$$\text{Hg} \mid \text{Hg}_2\text{I}_2 + \text{HI}\ (a = 1) \mid \text{HI}\ (a = 1) \mid \text{H}_2(\text{Pt}) \qquad (1)$$

from the results of Bugarsky[2] and from the results of Oeholm,[3] obtaining the values 0.0432 v. and 0.0414 v. at 25°, respectively. Cohen and Bruins[4]

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[1] Gerke, *Chem. Reviews*, 1, 385 (1925).

[2] Bugarsky, *Z. anorg. Chem.*, 14,145 (1897).

[3] Oeholm, *Acta Soc. Scientarum Fennicae*, 41, 1 (1913); *C. A.*, 7,2718 (1913).

[4] (a) Cohen and Bruins, *Z. physik. Chem.*, 93, 53 (1918); (b) see also, Yoshida, *J. Chem. Soc. Japan*, 48,435 (1927).

found for the cell

$$Cd(Hg) \mid CdI_2, \text{ sat.} \mid CdI_2, \text{ sat.} + Hg_2I_2 \mid Hg \qquad (2)$$

the value $E_{25} = 0.41712$ v.[5]

From this and the value calculated by Gerke[1] for the cell

$$Cd(Hg) \mid CdI_2 \text{ sat.} + HI\ (a = 1) \mid H_2\ (Pt) \qquad (3)$$

the value $E_{25} = 0.0403$ v. can be calculated for Cell 1. The electromotive force of Cell 3 was calculated from some results of Obata[6] with which some later results of the author[7] were in good agreement. A third value for Cell 1 given by Gerke, namely, $E_{25} = 0.0404$ v., was calculated from some results obtained in this investigation. It is in good agreement with the value calculated from the results of Cohen and Bruins. Ishikawa and Shibata[8] have determined the electromotive force of the cell

$$Zn(Hg) \mid ZnI_2 \mid ZnI_2 + Hg_2I_2 \mid Hg;\ E_{25} = 0.5243 \text{ v.} \qquad (4)$$

By combining their value with values for the cells

$$Ag \mid AgI + HI\ (a = 1) \mid HI\ (a = 1) \mid H_2\ (Pt);\ E_{25} = 0.1501 \text{ v.}^1 \qquad (5)$$

$$Zn(Hg) \mid ZnI_2 \mid ZnI_2 + AgI \mid Ag;\ E_{25} = 0.3987 \text{ v.}^9 \qquad (6)$$

the value $E_{25} = 0.0245$ v. is found for Cell 1, which is in poor agreement with the other values.

The purpose of this investigation was to measure accurately the electromotive force at various temperatures of the cell

$$Pb(Hg) \mid PbI_2 \mid PbI_2 + Hg_2I_2 \mid Hg \qquad (7)$$

Preparation of Materials

Mercury.—The mercury was purified by passing commercial redistilled mercury through a column of mercurous nitrate solution and redistilling at least once under reduced pressure in a current of air.

Lead Amalgam.—The lead amalgam was made electrolytically from purified mercury and either twice recrystallized lead nitrate or lead chloride made from recrystallized lead nitrate. Four different preparations were used. One contained 12.7% of lead and the other three contained 10% of lead.

Cadmium Amalgam.—The cadmium amalgam was prepared electrolytically from purified mercury and thrice recrystallized cadmium sulfate. It contained 10% of cadmium.

Lead Iodide.—The lead iodide was made by adding slowly a solution of recrystallized potassium iodide to a hot solution of twice recrystallized lead nitrate. The lead iodide so obtained was washed by decantation and preserved under water. Several different preparations were made in the course of the work, all by the same method.

Cadmium Iodide.—Two lots of cadmium iodide were prepared. No. 1 was prepared by recrystallizing C. P. cadmium iodide twice, the second time from redistilled water.

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[5] The measurements of Cohen and Bruins were made at temperatures between 16 and 24°. The value $E_{25} = 0.41712$ v. was obtained by an extrapolation which, however, introduces an uncertainty of less than 0.1 mv.

[6] Obata, *Proc. Phys. Math. Soc. Japan,* [3] **3,** 64, 136 (1921).

[7] Vosburgh, THIS JOURNAL, 49, 2228 (1927).

[8] Ishikawa and Shibata, *Bull. Chem. Soc. Japan,* 1, 169 (1926).

[9] Webb, *J. Phys. Chem.,* 27, 448 (1923).

No. 2 was prepared by allowing C. P. cadmium metal to react with a solution of C. P. iodine.[10] The solution was stirred continuously and iodine was added occasionally. The cadmium iodide so prepared was recrystallized twice, the second time from redistilled water.

The cadmium iodide to be introduced into the cells in the solid form was heated for five days at 150° to convert it into the stable form.[11]

Mercurous Iodide.—The mercurous iodide was prepared by precipitation. A solution of recrystallized potassium iodide was added slowly with mechanical stirring to a solution of twice or thrice recrystallized mercurous nitrate containing nitric acid. It was washed by decantation with either water or a very dilute potassium iodide solution and was preserved under water. Some of the preparations stood for several months under water before being used. The concentrations of the reacting substances varied in the different preparations but were of the order of **0.1** M.

Preparation **1** was made as described, redistilled water being used. It was digested on a hot-plate for two hours with water. Air was excluded during the precipitation by a current of nitrogen.

Preparation 2 was made similarly but without exclusion of air. Toward the end of the precipitation some orange-colored precipitate presumably containing mercuric iodide was formed. The addition of more mercurous nitrate converted it into the yellow mercurous iodide. In the subsequent preparations care was taken to keep the mercurous nitrate present in excess throughout the precipitation The mercurous iodide was washed by decantation, first with mercurous nitrate solution and then with very dilute potassium iodide solution.

Preparation **3** was a portion of No **2** which was digested on a hot-plate at nearly boiling temperature for about seven hours under a very dilute potassium iodide solution.

Preparations **4, 5** and **6** were precipitated in the cold, the first from solutions more concentrated than usual and the second from solutions more dilute. During the precipitation of No. **4** air was excluded and the solution was stirred with a current of carbon dioxide. Preparations 4, **5** and 6 were not digested

Preparation **7** was a portion of No. 6 which was digested for three days on a steam-bath in the dark.

Preparation 8 was prepared by the usual method but using redistilled water and with concentrations of about 0.2 M. It was digested for four days on a steam-bath in the dark.

Preparation of the Cells

The cells were set up in glass H-vessels. For the earlier cells[12] vessels of the type used by Vosburgh and Eppley[13] or that used by the author[14] for portable Weston cells were used. These vessels were hermetically sealed when the cells were made. For Cells **511–526**[15] vessels of the same type but of different dimensions were used. They were about **18** cm. long and **5.5** cm. wide. The inside diameter of the tubes was 12–**15** mm. The cells set up in these vessels were closed by means of paraffined corks.

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[10] See Ref. **4** a, p. **49.**

[11] Cohen, "Physico-Chemical Metamorphosis and Some Problems in Piezochemistry," McGraw-Hill Book Co., Inc., New York, 1926, p. 70; Cohen and Moesveld, *Z. physik. Chem.*, **94,471** (1920).

[12] Made at the Eppley Laboratory.

[13] Vosburgh and Eppley, THIS JOURNAL, **45, 2269 (1923).**

[14] Vosburgh, **J.** *Optical Soc. Am.*, **9, 66 (1924).**

[15] Made at the State University of Iowa.

A paraffined cork disk was pushed into the top of each leg of the vessel to a distance of 2 or 3 cm. and then covered with a layer of paraffin about 1 cm. thick. Finally, the openings of the tubes were closed by corks shellacked on the outside.

In setting up the mercurous iodide electrodes the procedure was that used by the author for setting up the mercurous sulfate electrodes of Weston Cells.[16] The mercurous iodide, with which was mixed lead iodide and in Cells 511–522 ground cadmium iodide crystals also, was washed first in a Gooch crucible and then by decantation in an atmosphere of nitrogen or carbon dioxide with the solution to be used in the cells. It was then transferred to the cell vessels out of contact with air. The mercurous iodide layer was at least 1 cm. deep. On top of it was placed some lead iodide and in Cells 511–522 some cadmium iodide crystals also.

The lead iodide electrodes were made by introducing first lead amalgam and then a paste of the electrolyte and either lead iodide or a mixture of lead iodide and cadmium iodide. In setting up Cells 511–522, in which the latter mixture was used, special precautions were taken to prevent oxidation of the lead amalgam.

In a number of cells a saturated solution of lead iodide in redistilled water was the electrolyte. This gave sufficient conductance so that the electromotive force could be measured accurately within a tenth of a millivolt. However, most of the cells so made were less constant and less reproducible than the others. In other cells a 0.01 *M* or 0.02 M potassium iodide solution was used as the electrolyte. An iodide solution has the advantage of dissolving mercuric iodide, so when the mercurous iodide mixture is washed with an iodide solution, any mercuric iodide present tends to be washed out The most reproducible cells were made with cadmium iodide solution as the electrolyte.

The cells were nearly always made in duplicate Duplicates usually agreed within a few hundredths of a millivolt. In the best cells made, Cells 517–522, the difference between duplicates was within 0.01 mv

The cells were mounted on wooden racks and the platinum wires leading from the cell electrodes were connected to copper terminals by means of fine copper wire which was soldered to both. Usually the negative electrodes were connected to a common terminal. while the positive electrodes were connected to separate terminals insulated from each other and from the wood by hard rubber or glass. In measuring the cells, copper lead wires from the potentiometer were clipped to the terminals of the rack by copper test clips. The racks of cells were immersed in an oil thermostat capable of being regulated to within 0.01° of the desired temperature.

Electromotive Force Measurements

Apparatus.—The electromotive forces were measured by means of a Leeds and Northrup Type K potentiometer. Two different potentiometers were used in the course of the work. The first was used only with the less reproducible cells with the very dilute solutions for electrolytes. The second, used for the measurement of the more reproducible cells with cadmium iodide electrolytes, was calibrated by the method described by the manufacturers.[17]

The standards used in the measurements recorded in Tables I and IV were those used in previous investigations.[16] The standards used in the measurements recorded in Tables II, III and V were nine others of equal quality, seven of which had been directly compared with the first stand-

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[16] Vosburgh, THIS JOURNAL, 47,1258 (1925).

[17] Leeds and Northrup Company, Bulletin No. 755, 1923, p. 22.

ards. Three saturated Weston Cells set up at the State University of Iowa agreed with these seven cells, which had been carefully carried from Newport to Iowa City, within 0.002%. Two years later a portable saturated Weston Cell obtained from the Eppley Laboratory agreed with the standards within 0.002%.

Measurements at 25°.—Measurements were made occasionally over a considerable period of time to show the constancy of the electromotive force before the values were accepted as final. Some of the cells had electromotive forces lower than the normal at first. Among these were Cells 511–522. The electromotive forces increased as time went on till finally a constant value was attained. Fig. 1 shows the change undergone by four of the cells. It is to be noted that constancy of electromotive force was not attained by Cells 511–512 until a month after they were set up. Thus, electromotive force measurements made soon after cells are set up cannot always be relied upon to give correct values.

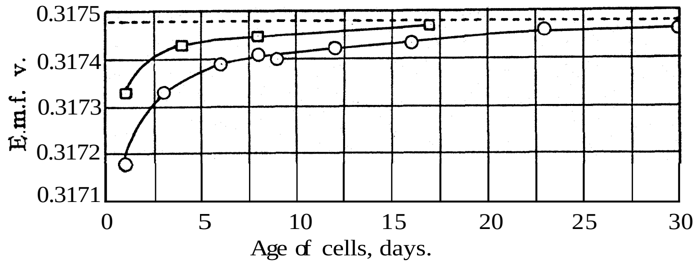

Fig. 1.

Tables I and II give the electromotive forces of the cells after constancy was attained. The time intervals are the periods of time which elapsed between the preparation of the cells and the measurements in question. Table I gives measurements of the cell

$$\mathrm{Pb(Hg)} \mid \mathrm{PbI_2,\ sat.} + x\,\mathrm{M\ KI} \mid x\,\mathrm{M\ KI} + \mathrm{PbI_2} + \mathrm{Hg_2I_2} \mid \mathrm{Hg} \qquad (8)$$

and Table II gives the results of measurements of the cell

$$\mathrm{Pb(Hg)} \mid \mathrm{PbI_2,\ sat.} + \mathrm{CdI_2,\ sat.} \mid \mathrm{CdI_2,\ sat.} + \mathrm{PbI_2\ sat.} + \mathrm{Hg_2I_2} \mid \mathrm{Hg} \qquad (9)$$

TABLE I

CELL: $\mathrm{Pb(Hg)} \mid \mathrm{PbI_2},$ SAT. + x M KI | x M KI + $\mathrm{PbI_2}$, SAT. + $\mathrm{Hg_2I_2} \mid \mathrm{Hg}$

Amalgam, cells	Concn % Pb	$\mathrm{Hg_2I_2}$ KI, M	No	Electromotive force at 25° 1 month, v.	2, v.	3, v.	4, v.
410–411	10	0.01	1	0.31765	0.31765	0.31765	0.31770
431432	10	.01	2	.31761	.31770	....	.31788
433–434	12.7	.02	3	.31761	.31786	.31778	....
436437	12.7	.02	1	.31748	....	,31760	....
439440	12.7	[a]	3	.31722	....	....	.31730

[a] The electrolyte for these cells was prepared by treating a 0.01 M sulfuric acid solution with an excess of solid lead iodide and filtering.

TABLE II

CELL: Pb(Hg) | PbI_2, SAT. + CdI_2, SAT. | CdI_2, SAT. + PbI_2, SAT. + Hg_2I_2 | Hg

Cells	Hg_2I_2 no	Electromotive force at 25° 1 month, v.	2, v.	3, v.	4, v.
511–512	4	0 31746	0.31748	0.31749	0.31740
513-514	5	.31768	,31769	.31768	.31766
515–516	6	.31754	.31755	.31756	....
517–518	7	.31746	.31747	.31748	.31748
519–520	8	.31747	,31747	.31748	.31748
521–522	8	.31748	.31748	.31748	.31749

It is quite evident that the cells with the cadmium iodide electrolyte (Table II) were superior to the other cells both in reproducibility and constancy. Of the former the best were Cells 517–522. These were all made with mercurous iodide which had been digested on a steam-bath under water with the object of bringing it to a stable physical condition. This practice has been shown[18] to be of value also in the preparation of mercurous sulfate for standard cells. The good agreement of Cells 517–522 makes it probable that the materials used were in a stable physical state. Most of the materials used for Cells 521–522 were different preparations from those used for the other four cells and if anything were better purified. Cells 513–514 were 0.2 mv. higher in electromotive force than most of the others, and it is to be concluded that the mercurous iodide preparation used was not in its most stable physical form.

To check the values of Cohen and Bruins[4"] and Yoshida[4b] for Cell 2 and to compare the mercurous iodide which the former authors prepared, from mercury and iodine with that prepared by precipitation, 4 cells like Cell 2 were set up. The procedure used was enough like that described above for the lead–mercurous iodide cells to need no further description. The electromotive forces are given in Table III. It is evident that the agreement with the cells of Cohen and Bruins and also those of Yoshida is very good.

TABLE III

CELL: Cd(Hg) | CdI_2, SAT. | CdI_2, SAT. + Hg_2I_2 | Hg

Cells	Hg_2I_2 no.	Electromotive force at 25° 1 month, v.	2, v.	3, v.	3.6, v.
520–524	7	0.41702	0.41701	0.41704	0.41704
525–526	8	.41701	.41698	.41700	.41700

Temperature Coefficients.—The cells of Table I were measured at 5° intervals of temperature between 15 and 40°. The measurements were made along with some measurements at the same temperatures of Weston standard cells and the details as to temperature regulation and general procedure have already been published.[19] The lead–lead iodide cells

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[18] Ref. 16, p. 1267.

[19] Vosburgh, J. Optical *Soc. Am.*, 12, 512 (1926).

did not show the hysteresis which the Weston cells showed, and so came to equilibrium more quickly, especially after a decrease in temperature. Table IV shows the differences between the electromotive forces at 25° and those at the other temperatures.

TABLE IV

VARIATION OF ELECTROMOTIVE FORCE WITH TEMPERATURE

		$E_t - E_{25}$				
Cells	E_{25}, v.	15°, mv.	20°, mv	30°, mv.	35°, mv.	40°, mv.
410411	031766	– 125	– 062	061	1.26	1.94
431–402	,31780	–1.22	–.57	.61	1.26	1.94
433434	,31783	–1.44	– 73	.67	1.36	2 07
436-437	,31764	–1 42	– 70	.63	1.30	1 96
439440	.31727	– 129	–.65	.63	1.29	1.93

The effect of temperature changes on Cells 517–522 and 523–526 was also determined. The temperature was changed successively from 25 to 20, 30, 35, 40, 35, 30 and 25°, while the standards were maintained at 25° in a separate thermostat. Temperatures were measured by a thermometer certified by the Bureau of Standards, and are probably accurate to ± 0.03'. The results are given in Table V.

TABLE V

VARIATION OF ELECTROMOTIVE FORCE WITH TEMPERATURE

		$E_t - E_{25}$						
Cells	E_{25}, v	20°, mv.	30°, mv.	35°, mv.	40°, mv.	35°, mv.	30°, mv.	25°, mv.
517–518	0.31748	–0.61	0.65	1.28	1.93	1.30	0.67	0.01
519–520	,31748	– .63	.66	1.28	1.93	1.29	.65	.00
521–522	.31749	– .66	.65	1.27	1.91	1.29	.64	.00
523–524	.41704	–1.93	1.79	3.60	5.41	3.57	1.74	–.10
525–526	.41700	–1.88	180	3.61	5.42	3.59	1.77	–.04

If $E_{25} = 0.31748$ v. is taken as the best value for Cell 7, the electromotive force between 15 and 40° is given by the equation

$$E_t = 0.31748 + 0.000129\ (t-25)$$

within the limits of error of measurement in the case of Cells 517–522 and within the limits of reproducibility in the case of the cells of Table IV.

A small lag in the attainment of equilibrium was noticed in the case of Cells 517–522. Usually two or three days were required for the attainment of constancy, although the electromotive force was usually within 0.04 mv. of its final value one day after an increase in temperature of 5°.

For Cell 2 the electromotive force between 25 and 40° is given by the equation

$$E_t = 0.41702 + 0.000360\ (t-25)$$

The agreement is not good at 20°, perhaps because sufficient time was not allowed for equilibrium. Equilibrium was attained rapidly after an increase in temperature, but rather slowly after a decrease, and the measurements made after a decrease in temperature are to be considered less reliable than those made after an increase.[20] Both Cohen and Bruins[4a] and Yoshida[4b] gave as the temperature formula for Cell 2 an equation for a curve instead of a straight line. However, the above formula agrees with the experimental values of Cohen and Bruins within 0.1 mv., and if the first term on the right-hand side of the equation (the value at 25°) were increased by 0.1 mv., the formula would agree with all but one of their experimental values within 0.01 mv.

Discussion

The difference between the electromotive forces of Cells 2 and 7 should give the electromotive force of the cell

$$\mathrm{Cd(Hg)} \mid \mathrm{CdI_2,\ sat.} \mid \mathrm{CdI_2,\ sat.} + \mathrm{PbI_2} \mid \mathrm{Pb(Hg)} \qquad (10)$$

Subtracting $E_{\text{Cell } 7} = 0.31748 + 0.000129\ (t - 25)$ from $E_{\text{Cell } 2} = 0.41702 + 0.000360\ (t - 25)$, the value

$$E_t = 0.09954 + 0.000231\ (t-25)$$

is obtained for Cell 10 as compared with

$$E_t = 0.0996 + 0.000235\ (t-25) - 0.0000002\ (t-25)^2$$

previously found by the author,[7] which is in good agreement with the results of Obata[6] for the same cell. The agreement between the two formulas is within the experimental error of the latter. Thus, the results for Cells 2, 7 and 10 are consistent among themselves, and as the values for Cells 2 and 10 agree with those of other observers, it is probable that the value given for Cell 7 is correct.

From the results for Cell 7 the free energy change, entropy change and heat of reaction can be calculated for the reaction

$$\mathrm{Pb(s)} + \mathrm{Hg_2I_2(s)} \longrightarrow \mathrm{PbI_2(s)} + \mathrm{2Hg(l)}$$

If the electromotive force of Cell 7 is added to that of the cell[21]

$$\mathrm{Pb} \mid \mathrm{Pb^{++}} \mid \mathrm{Pb(Hg)};\ E_t = 0.0057 + 0.000016\ (t-25) \qquad \mathbf{(11)}$$

the electromotive force of the cell

$$\mathrm{Pb} \mid \mathrm{PbI_2,\ sat.} \mid \mathrm{PbI_2,\ sat.} + \mathrm{Hg_2I_2} \mid \mathrm{Hg} \qquad \mathbf{(12)}$$

is found to be $E_t = 0.3232 + 0.000145\ (t - 25)$. Therefore, for the above reaction $\Delta F_{25} = -14{,}915$ cal., $AS = 6.69$ cal. per degree and $AH = -12{,}920$ cal.

For the heat of formation of lead iodide Braune and Koref[22] found thermochemically $\Delta H_{20} = -41{,}850$ cal., and Gerke[21] found electrochemically $\Delta H_{25} = -41{,}859$ cal. From the latter value and from the heat of reaction of lead and mercurous iodide, the heat of formation of mercurous iodide is found to be

$$\mathrm{2Hg(l)} + \mathrm{I_2(s)} \longrightarrow \mathrm{Hg_2I_2(s)};\quad \Delta H_{25} = -28{,}939 \text{ cal.}$$

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[20] In showing hysteresis only after a decrease in temperature these cells resemble Weston cells. The latter, however, have abnormally high values after a decrease in temperature while the former show abnormally low values.

[21] Gcrke, THIS JOURNAL, 44, 1703 (1922).

[22] Braune and Koref, *Z anorg Chem.*, 87, 180 (1914).

This agrees with the value of Varet,[23] A H = —28,850 cal., and less well with the value of Nernst,[24] *AH* = —28,400 cal., but does not agree with the value of Thomsen,[25] *AH* = —31,100 cal.

The electromotive force of Cell 2 (Table V) can be combined with the electromotive force of the cell[26]

$$Cd \mid Cd^{++} \mid Cd(Hg);\ E_t = 0.0505-0.000244\ (t-25) \qquad (13)$$

to give the electromotive force of the cell

$$Cd \mid CdI_2, \text{sat.} \mid CdI_2, \text{sat.} + Hg_2I_2 \mid Hg;\ E_t = 0.4675 + 0.000116\ (t-25) \qquad (14)$$

From this it can be calculated that for the reaction

$$Cd(s) + Hg_2I_2(s) \text{ --+ } CdI_2(s) + 2Hg(l)$$

$\Delta F_{25} = -21{,}575$ cal., $\Delta S_{25} = 5.35$ cal. per degree and $\Delta H_{25} = -19{,}979$ cal. If the above value for the heat of formation of mercurous iodide is taken as correct, the heat of formation of cadmium iodide is found to be

$$Cd(s) + I_2(s) \longrightarrow CdI_2(l);\ \Delta H_{25} = -48{,}918 \text{ cal.}$$

Thomsen[27] found *AH* = —48,830 cal.

Summary

The following cells were set up and their electromotive forces measured at 25° and at five degree intervals between 20 and 40°:

$$Pb(Hg) \mid PbI_2 + x\ M\ KI \mid x\ M\ KI + PbI_2 + Hg_2I_2 \mid Hg$$
$$Pb(Hg) \mid PbI_2 + CdI_2, \text{sat.} \mid CdI_2, \text{sat.} + PbI_2 + Hg_2I_2 \mid Hg$$
$$Cd(Hg) \mid CdI_2, \text{sat.} \mid CdI_2, \text{sat.} + Hg_2I_2 \mid Hg$$

The electromotive force of the first two was found to be $E_t = 0.31748 + 0.000129\ (t - 25)$ volts. The two cells agreed within the limits of reproducibility of the first, which was the less reproducible of the two.

The electromotive force of the third was found to be $E_t = 0.41702 + 0.000360\ (t - 25)$ volts, which is in good agreement with the results of Cohen and Bruins and Yoshida for the same cell.

From the electromotive forces of the cells the free energy and entropy changes and heats of reaction for the corresponding reactions were calculated. From the latter and a reliable value for the heat of formation of lead iodide the heats of formation of mercurous iodide and cadmium iodide were calculated to be

$$2Hg(l) + I_2(s) \longrightarrow Hg_2I_2(s);\ \Delta H_{25} = -28{,}939 \text{ cal.}$$
$$Cd(s) + I_2(s) \longrightarrow CdI_2(s);\ \Delta H_{25} = -48{,}918 \text{ cal.}$$

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[23] Varet, *Ann. chim. phys.*, [7] **8,** 91 (1896).

[24] Nernst, *Z. physik. Chem.*, **2,** 23 (1888).

[25] Thomsen, "Thermochemistry," Longmans, Green and Co., London, 1908, p. 283.

[26] Ref. 1, p. 382.

[27] **Ref.** 25, p. 268; see also ref. 7.

[CONTRIBUTION FROM THE DEPARTMENT OF MEDICAL RESEARCH AND THE DEPARTMENT OF PATHOLOGICAL CHEMISTRY, UNIVERSITY OF TORONTO]

THE USE OF PICRIC ACID AS AN ARTIFICIAL STANDARD IN THE COLORIMETRIC ESTIMATION OF SILICA

BY E. J. KING AND C. C LUCAS

RECEIVED JUNE 11, 1928 PUBLISHED SEPTEMBER 5, 1928

The determination of small amounts of silica in natural waters has been shown to be of industrial value as well as scientific interest. Diénert[1] has shown the importance of the silica content of ground waters in relation to their origin. In his studies of town water supplies, Thresh[2] noted an inverse relationship between the silica content of the water and the action of dissolved oxygen on lead pipes. The possible biological importance of silica was commented on by Richter,[3] who observed that artificial cultures of marine organisms thrived in glass vessels but that very poor development occurred in paraffined containers.

Atkins[4] investigated the possibility of a lack of silica being a limiting factor in the multiplication of phytoplankton.

Since the gravimetric determination of traces of silica in water is both long and tedious, Diénert and Wandenbulcke[5] proposed a colorimetric method based on the production of a highly colored yellow silico-molybdic acid. When dilute silica solutions are treated with an acid and ammonium molybdate, a color develops which exactly matches that of dilute picric acid solutions. Diénert and Wandenbulcke proposed an artificial standard of 36.9 mg. of picric acid per liter as being equivalent to 50 mg. of silica per liter. The permanence of the picric acid solution renders it a more desirable standard than the relatively unstable silicate solutions which might be used. The procedure consists in adding 2 cc. of a 10% solution of ammonium molybdate and 4 drops of 50% (by volume) sulfuric acid to 50 cc. of solution. The yellow color which develops reaches its maximum in less than ten minutes and remains constant for some time. Appropriate dilutions of the picric acid standard are made and the solutions are compared in a colorimeter or in Hehner tubes.

Atkins[4] followed the above procedure in his studies of the silica content of natural waters and used the 36.9 mg. picric acid standard. Thresh and Beale[6] regard the colorimetric method as being as accurate as the

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[1] F. Diénert, *Compt. rend*, 155, 797 (1912).

[2] Thresh, "The Action of Natural Waters on Lead," *Analyst*, 47, 459, *500* (1922).

[3] O. Richter, *Verh. Gesell. deut. Naturf. Arete Breslau*, 2,249 (1904).

[4] W. R. G Atkins, *J. Marine Biol Assocn., United Kingdom*, 13, 151–159 (1923).

[5] F. Diénert and F. Wandenbulcke, *Compt. rend.*, 175, 1226–1229 (1923); Bull. *soc. chim.*, 33, 1131–1140 (1923).

[6] J. C. Thresh and J. F. Beale, "The Examination of Waters and Water **Supplies,**" 1925, London.

gravimetric, but recommended the use of 40 mg. of picric acid per liter as a standard equal to 50 mg. of silica per liter.

As a result of a series of colorimetric determinations of the silica content of marine waters on the west coast of Canada, in which unusually high values were obtained, the picric acid standards used were suspected of being at fault. This led to a careful comparison of the color intensities given by picric acid and silicate solutions. For this purpose a standard solution was made containing 40 mg. of vacuum dried, C. P., picric acid per liter. This solution was found to have considerably more color than that developed in a solution containing 50 mg. of silica per liter when treated with ammonium molybdate and sulfuric acid.

Standard picric acid solutions containing 40 mg. per liter were prepared from various makes of C. P. picric acid, all of which were dried to constant weight in a vacuum desiccator. Solutions made from picric acid recrystallized from water, from ethyl alcohol and from benzene had the same depth of color as the other standard solutions. This seemed satisfactory evidence that the picric acid solutions used had a definite and constant color value.

Merck's pure silica was dried in a muffle furnace at red heat to constant weight. The material was cooled in a desiccator and weighed rapidly to avoid any possible adsorption of moisture. An excess of anhydrous sodium carbonate (Kahlbaum) was mixed in a platinum crucible with 0.2000 g. of silica and cautiously heated to fusion. The melt was cooled, dissolved in distilled water and made up to 200 cc. Five cc. of this solution when diluted to 100 cc. gave a concentration of silica of 50 mg. per liter. When treated with ammonium molybdate and sulfuric acid, a color was again obtained which was much less intense than that of the 40 mg. picric acid standard.

Pure silica was prepared by treating washed sea sand with calcium fluoride and concentrated sulfuric acid. The silicon tetrafluoride which was produced was passed into distilled water and the hydrated silica formed by hydrolysis was collected on a filter, washed and dehydrated in a muffle furnace. A silicate solution made from this material developed the same intensity of color as the former solution.

The color values of these silicate solutions when read against the 40 mg. picric acid standard in a Duboscq colorimeter are given in the accompanying table.

TABLE I

COLOR VALUES OF 50MG. SILICATE SOLUTIONS AGAINST 40MG. PICRIC ACID STANDARD

	Silicate solns. prepared from	Reading of test, mm.	Reading of standard, mm.
(1)	Commercial silica dust	10.0	6.3
(2)	Powdered quartz	10.0	6.3
(3)	Commercial silica dust	10.0	6.4
(4)	Merck's pure silica	10.0	6.4
(5)	Silica from silicon tetrafluoride	10.0	6.4

A stock solution (containing approximately 1 mg. of silica per cc.) made from Baker's C. P. $Na_2SiO_3 \cdot 9H_2O$ was tested colorimetrically. Five cc. of this solution, diluted to 100 cc., when treated with acid and molybdate developed a color of such intensity that with the test set at 10.0 mm. the standard read 6.0 mm.

Two hundred-cc. portions of the stock solution were analyzed gravimetrically with the following results: silica from 200 cc. of stock solution, (1), 0.1874 g.; (2), 0.1867 g.

Since by analysis the stock solution was only 93.6% of its stated concentration, the dilute solution prepared from it was also under strength to the same degree. Consequently, a solution containing 50 mg. of silica per liter when set at 10.0 in the colorimeter would give a standard reading of 6.0 mm. X 100/93.6 = 6.4 mm.

From the foregoing figures it would appear that a picric acid solution, to show equal color to that given by a 50 mg. per liter silica solution treated with the reagents, should contain 0.64 X 40 = 25.6 mg. of picric acid per liter. A solution of this concentration was prepared and found to have the same intensity of color as that given by the silica solution when matched in a Duboscq colorimeter or in Hehner tubes.

It was thought that the discrepancy between our results and those of other workers might lie in their having used commercial picric acids. Since considerable amounts of water are added to picric acid by the manufacturers to eliminate the possibility of explosion in transit, care must be taken to dry the material thoroughly before attempting to use it in quantitative work. Possibly the earlier workers neglected to take this precaution. To test this point crystals were taken from the top of a freshly opened bottle of Baker's picric acid. A solution of the proper color value required 36 mg. per liter of these crystals, but when dried to constant weight in a vacuum desiccator over calcium chloride only 26 mg. per liter was necessary. Samples of picric acid from different bottles had widely varying moisture contents and even in the same bottle the moisture content at different levels varied considerably. While most reputable brands of picric acid when dried to constant weight give solutions of maximum color value, recrystallization from benzene according to the method of Benedict[7] may be resorted to if the purity of the sample is in doubt.

Summary

The intensity of the yellow color given by a silicate solution containing 50 mg. of silica per liter when treated with the reagents of Diénert and Wandenbulcke is equivalent to that of a solution of picric acid containing 25.6 mg. of vacuum-dried, C. P. picric acid per liter.

TORONTO, CANADA

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[7] S. R. Benedict, *J. Biol. Chem.*, **54**, 239–241 (1922)

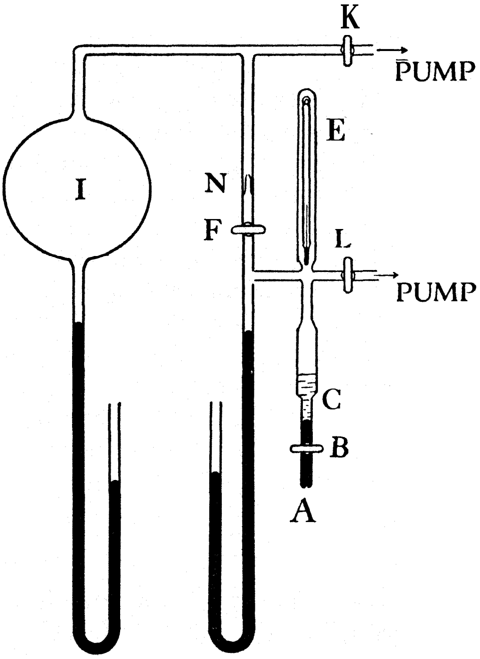
[CONTRIBUTION FROM THE PHYSICAL CHEMISTRY LABORATORY OF THE UNIVERSITY OF WISCONSIN]

MOLECULAR WEIGHTS OF SATURATED VAPORS BY THE EFFUSION METHOD

BY HENRY EYRING

RECEIVED JUNE 25, 1928 PUBLISHED SEPTEMBER 6, 1928

The application of the method of effusion in measuring the molecular weights of gases has been carefully studied by a number of investigators[1] since Graham first announced it. The success of the procedure depends upon accurate time and pressure measurements and upon the selection of an orifice of dimensions which reduce viscosity effects to a minimum. Under such circumstances molecular weights having an accuracy of 1% for gases of rather different properties are attainable.



Pig. 1.

It seemed desirable to devise a rapid method of estimating the molecular weight of organic vapors if certain obvious difficulties could be overcome. The final all-glass apparatus which satisfactorily accomplishes this purpose was constructed as shown in Fig. 1.

The operations consist simply in evacuating the whole apparatus with a Hyvac pump, then admitting liquid into the vessel at B. The stopcock is then opened and the time taken with a stopwatch for the pressure in the receiving chamber to rise to some predetermined pressure. The same operations are repeated with air, care being taken to adjust stopcock B so that the pressure of air remains constantly equal to the vapor pressure of the liquid whose molecular weight is to be determined. The following data were obtained using purified isopropyl alcohol: time for air, 140 seconds; time for isopropyl alcohol, 202 seconds. Then the molecular weight of isopropyl alcohol = $(202/140)^2$ 28.8 = 60. The

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[1] Bunsen, "Gasometry," p. 198; J. N. Edwards, "Technologic Papers of the Bureau of Standards," No. 94.

whole determination can be conducted in less than a half-hour and involves no weighings. The apparatus is simple, involves no washing and can be permanently attached to the wall. The method can be applied to gases and to all vapors with vapor pressures greater than that of water without using a cathetometer. This range of course can he extended to lower vapor pressures by making more accurate pressure measurements or by raising the temperature.

If the pressure in the receiving chamber is permitted each time to rise to one-half the vapor pressure (pressure on side containing liquid) exactly the same calculation as was used to compare it with air can be used to intercompare liquids of different vapor pressures without the calibration run. In Table I this method has been styled Method 2 to distinguish it from the procedure in which the time for each vapor is compared directly with the time for air called Method 1. Thus it took **227** seconds for benzene to build up a pressure equal to half its vapor pressure while it took **317** seconds for carbon tetrachloride. Assuming a molecular weight of benzene of **78** we have for carbon tetrachloride $(317/227)^2\ 78 = 152$. The advantage of Method No. 2 is the elimination of the comparison run with air effectually cutting the time of a determination in two. The disadvantage is that the vapor pressure must be accurately measured and exactly one-half the vapor pressure (or some other convenient fraction) be taken as the pressure rise in the receiving chamber. If a large number of determinations are to be made, undoubtedly the second method, using a cathetometer or mounted telescope, is most satisfactory. Under such circumstances successive determinations can be made in about fifteen minutes.

The following times obtained for air to reach a pressure in the receiving chamber of one-half the constant pressure maintained on the sending side show this time to be independent of the sending pressure.

Pressure in cm..................	73.35	57.35	44.00	24.80
Time of half press. incr., sec.......	163.0	164.3	163.3	165.5

The independence of time of this "half pressure increase" follows from kinetic theory. Equation (315) of Jeans, "The Dynamical Theory of Gases," may be slightly modified to give

$$dn = \frac{(p_0 - p)}{\sqrt{2\pi MRT}} A\,dt = \frac{V_r dp}{RT}$$

where dn is the number of moles effusing through an orifice of A square centimeters per dt seconds; $p_0 - p$ is the vapor pressure minus the pressure in the receiving chamber, that is, the effective pressure; M is the molecular weight; R is the gas constant in ergs per degree; T is the absolute temperature and V_r is the volume of the receiving chamber.

Whence

$$dt = \frac{V_r}{A}\sqrt{\frac{2\pi M}{RT}}\,\frac{dp}{p_0 - p}$$

and

$$t = 2.303\,\frac{V_r}{A}\sqrt{\frac{2\pi M}{RT}}\,\log\frac{p_0}{p_0 - p} = \frac{V_r}{A}\,6.37 \times 10^{-4}\sqrt{\frac{M}{T}}\,\log\frac{p_0}{p_0 - p}$$

For $p = p_0/2$, we have

$$M = T\,t_0^2\left(\frac{A}{V_r}\right)^2 1572^2\left(\frac{1}{0.310}\right)^2$$

From this it is seen that the time for the pressure in the receiving chamber to reach one-half the sending pressure (or any other fraction) is independent of the sending pressure. The formulas for the preceding calculations of molecular weights follow immediately from the deduction above, since when the temperature T is constant, $M = Kt_0^2$. The cross sectional area of the orifice was calculated by taking $V_r = 2656$ cc.; $T = 296°$; $t_0 = 164$; whence A was found to equal 0.00097 sq. cm. or 0.097 sq. mm.

Orifices of platinum were found unsatisfactory, presumably because of flaps which changed the sizes of the openings. Glass orifices considerably smaller in cross section introduced errors due to viscosity. One orifice prepared by sending a large spark through the glass gave satisfactory results for the molecular diameter of hydrogen assuming viscous flow but entirely unsatisfactory results for its molecular weight using the relationship above. Apparently the leak was through a large number of small cracks.

The orifice shown in Fig. 1 at *N* was made by blowing a thin round bulb on 6 mm. glass tubing. A hot glass rod was then used to pull a small capillary out from the bulb which was then broken off flush with the bulb surface, giving an opening of 0.1 sq. mm., approximately. With an orifice of this size the receiving chamber should have a volume of about two and one-half liters to give a convenient time of efflux

Certain details of operation seem necessary for the success of a determination. After evacuating the system, F and K are closed and a weighing bottle containing mercury and the liquid is placed at **A** and mercury drawn up until it reaches the stopcock B. The apparatus is re-evacuated, I, being then closed. The weighing bottle is then lowered slightly and B opened until sufficient liquid is drawn into the apparatus. The weighing bottle is raised, mercury again being drawn up until any liquid in the neighborhood of the stopcock B has been displaced. In this wav there was no difficulty in keeping a stopcock, lubricated with ordinary stopcock grease, from leaking with any organic liquids. Using either a pinch clamp on rubber tubing or a stopcock lubricated with phosphorus pentoxide proved unsatisfactory.

After introducing the liquid the stopcock F was turned at the same time a stop watch was started. The vapor pressure was kept at the desired pressure by occasionally warming the liquid C with the hand. When air is being run it can be kept very accurately at the desired pressure by occasionally partially closing **A** with the finger.

Some typical results are given below.

In addition to these experiments Mr. P. B. Tuttle made determinations on a number of substances not listed here, obtaining satisfactory results. The vapor from the constant boiling mixture of hydrochloric acid at 73.8

TABLE I

Vapor	Mol. wt.	Mol. wt., Method 1	Mol. wt., Method 2
CH_3OH	32	32.8	32[a]
C_2H_5OH	46	46.2, 46.9	45.4
C_6H_6	78	77.6	77.3
CCl_4	154	....	152
	18	16.8, 18.4	18.54
$(CH_3)_2CHOH$	60	56.2, 60	...
$CHCl_3$	119	116.5	...

[a] Assumed in determining constant.

cm. pressure gave a molecular weight of 22, showing the absence of association.

It has been customary to explain the high specific heat of saturated (wet) steam by assuming it to be due to the presence of large molecular aggregates.[2] Such aggregates might be due to a mechanical suspension of water or to associated molecules. The values obtained for saturated water vapor at room temperature give no indication of association. This seems consistent with results obtained by others using different methods.

The investigation of any supposedly associated vapors should yield interesting results. The simultaneous determination of successive vapor pressures and molecular weights of mixtures of organic liquids as the mixed vapors pass through the orifice N should be of value in analysis.

Summary

A method for the rapid determination of molecular weights of saturated vapors has been outlined. No appreciable association of saturated water vapor, of the vapor from constant boiling hydrochloric acid nor of organic vapors was observed.

MADISON, WISCONSIN

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[2] Lewis, "A System of Physical Chemistry," Longmans, Green and Co., New York, **1916**, Vol. III, p. 8; Jeans, "The Dynamical Theory of Gases," Cambridge University Press, Cambridge, England, **1916**, p. 265.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

THE MECHANISM OF HOMOGENEOUS GAS REACTIONS. I. THE EFFECT OF BLACK BODY RADIATION ON A MOLECULAR BEAM OF NITROGEN PENTOXIDE[1]

BY F. O. RICE, H. C. UREY AND R. N. WASHBURNE[2]

RECEIVED JUNE 27, 1928 PUBLISHED SEPTEMBER 5, 1928

The homogeneous unimolecular character of the decomposition of nitrogen pentoxide first studied by Daniels and Johnston[3] has now been thoroughly established by a large number of investigations.[4] However, in spite of a large amount of theoretical work,[5] the mechanism of the reaction cannot be regarded as well understood. The attempts to explain the mechanism of the nitrogen pentoxide decomposition in common with other reactions are based upon the Arrhenius hypothesis of active and inactive molecules. There is only one exception to this, namely, the form of the radiation hypothesis in which it is assumed that the molecule absorbs a quantum of light and decomposes in a single act. The velocity of the reaction would therefore be proportional to the density of radiation capable of decomposing the molecule. Since the density of this radiation increases exponentially with the reciprocal of the absolute temperature, the temperature coefficient of the reaction is satisfactorily explained. On the basis of all other hypotheses it seems necessary to assume a process of activation in order to account for the temperature coefficient. Our difficulties arise when we attempt to devise a process of activation, for this must be much more rapid than the observed chemical reaction. We may conveniently summarize the various proposals that have been made, as follows.

1. The Simple Radiation Hypothesis.—This can be represented by

$$AB + h\nu \longrightarrow A + B$$

Or we may have a process of activation of the type

$$AB + h\nu \longrightarrow AB'$$

followed by the reaction

$$AB' \longrightarrow A + B$$

$$AB' + AB \longrightarrow A + B + AB$$

$$AB' + AB \longrightarrow 2A + 2B$$

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[1] This paper is an abstract of the thesis of R. N. Washburne submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Du Pont Fellow in Chemistry.

[3] Daniels and Johnston, THIS JOURNAL, **43,** 53 (1921).

[4] A summary of these is given by Rice and Getz, *J. Phys. Chem.*, **31,** 1572 (1927).

[5] Most of these references are included in a review of the radiation hypothesis, Daniels, *Chem. Reviews*, **5,** 39 (1928).

In the last two examples the velocity of the reaction will fall with decreasing pressure.

It should be pointed out, however, that nitrogen pentoxide does not absorb in the region such that $Nh\nu$ is equal to the heat of activation as calculated from the temperature coefficient of the reaction.

2. The Elaborated Radiation Hypothesis.—On the basis of this hypothesis nitrogen pentoxide for example is supposed to absorb successive quanta such that the total is equal to the heat of activation. Nitrogen pentoxide has a very strong absorption band at 5.81 μ such that absorption of five of these quanta would give the heat of activation. It should be pointed out, however, that the coefficient of absorption of compounds (including nitrogen pentoxide) would have to be many orders higher than ever observed to account for the observed rates of chemical reactions. It must also be noted that infra-red radiation does not increase the rate of chemical reactions.[6]

3. Radiation Hypothesis with a Chain Mechanism.—On the basis of this hypothesis it is assumed that the molecule of nitrogen pentoxide activated by radiation starts a chain of successive reactions which results in the final decomposition of many molecules. This suggestion will not explain the decomposition of nitrogen pentoxide for reasons given under (2) and in addition any chain mechanism appears to be improbable because the energy change for the entire reaction is very small; it would be necessary to assume that one of the products of a decomposing nitrogen pentoxide molecule carried all the energy of activation and others none and farther that this energy would be completely transferred to another nitrogen pentoxide molecule and not to any other molecules. This appears to be very improbable.

4. Sir J. J. Thomson Hypothesis.—On the basis of this hypothesis[7] it is assumed that a molecule of nitrogen pentoxide may acquire energy of activation from the surrounding medium by some other means than radiation or collisions with other molecules. He postulates that the amount of energy possessed by a molecule may fluctuate with the time and that only on the average is energy conserved. He assumes that the probability that a molecule will acquire a certain energy is an exponential function of its internal energy. Our experiment throws no light on this hypothesis.

5. Activation by Molecular Collisions.—On the basis of this hypothesis, a molecule of nitrogen pentoxide is assumed to obtain its energy of activation by collision with another molecule. In this case the rate of activation is proportional to the number of collisions and should therefore

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[6] Hibben, THIS JOURNAL, 50, 937 (1928) The paper contains the references to previous work.

[7] Thomson, *Phil.* Mag., [7] 3,241 (1927).

be proportional to the square of the concentration. In order that the reaction may be experimentally unimolecular it is necessary to assume that the rates of activation and deactivation are very rapid compared to the rate of the reaction and further that the rate of decomposition of the activated molecules is a truly unimolecular process which is independent of collisions of the activated molecules; thus the probability of decomposition of an activated molecule per unit time is no greater during collision than during the time between collisions. This last condition seems to be supported by the fact that nitrogen pentoxide decomposes at the normal rate when dissolved in liquids, with the exception of nitric acid.4 This exception is due probably to the formation of a complex compound.

Attempts have been made to test this hypothesis by conducting experiments at low pressures which should at sufficiently low pressures change the order of the reaction from unimolecular to bimolecular and decrease the absolute rate. The experiments that have been published so far are contradictory.[8] We are unwilling to discuss these papers because some work in this Laboratory by Miss E. Wilson has yielded results differing from both these papers. Preliminary measurements show that the rate falls off even at pressures of several mm.

The difficulty of deciding the mechanism of the decomposition of nitrogen pentoxide or any other reaction lies perhaps in the fact there are three processes occuring simultaneously in reactions as ordinarily studied. These three processes are *(a)* absorption and emission of radiation, (b) intermolecular collisions and (c) collisions with the walls of the vessel. It is the purpose of this series of papers to separate these three effects and study them independently. The first effect may be isolated from the other two by allowing a molecular beam of nitrogen pentoxide to pass through a furnace, within which approximately black body radiation is maintained. Similar work has been done by Kröger[9] using iodine and by Lewis and Mayer, and Mayer[10] using pinene. They report no reaction in either case. The results of our investigation are in accord with these results; no detectable decomposition occurred.

The second effect may be isolated by allowing two beams to impinge as was done by Kroger for cadmium and iodine and cadmium and sulfur. Undoubtedly this is impractical in the case of nitrogen pentoxide because in the first place the total number of collisions is small and only a very minute fraction of these would result in active molecules.

The third factor may be isolated by allowing the beam to impinge

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[8] Hirst and Rideal, *Proc. Roy. Soc.* (London), **109A, 526 (1925);** Hibben, THIS JOURNAL, **50,940** (1928).

[9] Kröger, *Z. physik.* Chem., **117,387 (1925).**

[10] Lewis and Mayer, *Proc. Nat. Acad. Sci.,* **13, 623 (1927)**; Mayer, THIS JOURNAL, **49,3033 (1927).**

on a heated surface from which it is reflected to a surface cooled to liquid air temperatures. Mr. I,. A. Staib has undertaken experiments of this character in this Laboratory. Such experiments offer the possibility of determining the life of excited molecules providing it happens to be of the order of magnitude of the time of flight from the activating to the collecting surfaces. This point, however, will be discussed in greater detail in a following paper.

Apparatus and Methods

Molecular **Beam** Apparatus.—The apparatus with which the final experimental work was done (see Fig. 1) was made of Pyrex glass. The nitrogen pentoxide evaporates from the storage reservoir (not shown) and enters the beam chamber, C, through the 3 mm. hole, a, in the end of the delivery tube, B; 9 millimeters above a is the rough defining hole, b, which is 4 mm. in diameter. The final defining hole, c, 1 mm. in diameter, is 10 millimeters above b. The holes b and c are in the center of glass disks which were sealed into the apparatus when it was constructed. This eliminates the possibility of any nitrogen pentoxide entering the furnace chamber other than through c. The beam of nitrogen pentoside issuing from the chamber C passes through the furnace, D (described in detail below), and is condensed on the liquid-air cooled surface E. This surface is the base of the cylindrical tube, F, which is introduced into the apparatus by means of a ground-glass joint at G. This facilitates the removal of the sample for analysis at the completion of an experiment. The surface, E, which is 2.6 cm. in diameter, is surrounded by a collar 1.3 cm. high which serves as an auxiliary condenser to reduce losses that would occur if the molecules did not condense upon the first collision with E.

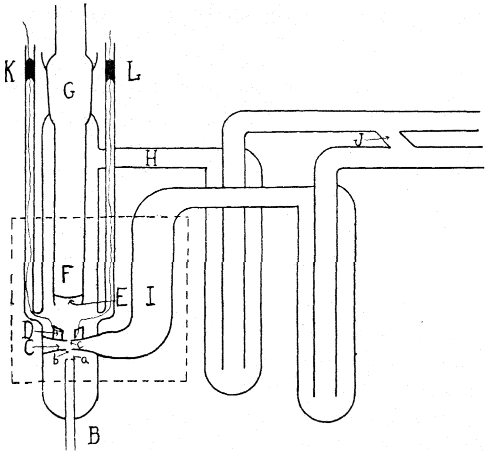

Fig 1.—Molecular beam apparatus.

The apparatus is evacuated through H and I, which lead to separate liquid-air traps and Stimson two-stage diffusion pumps. The two branches are connected at J to eliminate any circulation of gases through the region C should the diffusion pumps not be working with equal efficiency. A single Nelson oil pump was used as a fore pump. Pressures were measured with a McLeod gage with which pressures of 10^{-5} mm. of mercury could be read accurately, and those in the 10^{-6} order were estimated within 10%.

Furnace.—The furnace D used as a source of black body radiation (see Fig. 2) was made from a piece of Pyrex tubing 1.2 cm. long with an inside diameter of 8.8 mm. It is suspended by three glass prongs, a, from platinum stirrups, b, fused in the glass collar D which rests upon the plate containing the final defining hole. The furnace is heated electrically with a platinum wire (0.14 mm. dia.) wound spirally about it in a groove made for that purpose. Electrical current is supplied through heavy platinum leads and tungsten seals at K and L (Fig. 1). The groove, which encircles the furnace ten times, was etched into the glass with hydrofluoric acid. The distance between successive spirals is 1 mm. The furnace was firmly mounted on a spool-like core which could be fitted into the chuck of a lathe. The glass was coated with a thin layer of wax in which a spiral was cut with a needle-like tool mounted in the tool carrier. By adjusting the latter for a screw pitch of 24 turns to the inch, a very uniform spiral was obtained. The furnace was then immersed in hydrofluoric acid for five minutes. Longer immersions were found to widen the groove too much. By repeating the above process five times a sharply defined groove about 0.2–0.3 mm. deep was obtained, a depth sufficient to prevent the wire from slipping off the furnace when heated. The furnace was then wired and in the finished furnace 8 complete winds (*23.2* cm.) were effective in heating. Current input was measured by a milliammeter and voltmeter.

The portions of the apparatus which had to be at liquid-air temperatures are included within the dotted lines in Fig. 1. This cooling was finally effected by covering the glass with lead foil to increase thermal conduction and circulating liquid air from a container above the apparatus through a ten foot length of rubber tubing, which had been wound snugly about the two branches of the apparatus. The whole region was heavily insulated with asbestos and cotton to make the cooling more efficient. To maintain circulation of the liquid air through the rubber tubing a gentle suction was applied at the free end. If suction is not applied moisture condensing from the air soon plugs the tube with the result that the temperature of the apparatus rises. Tests made with a large test-tube wound with rubber tubing in this way showed that temperatures of about −170° could be maintained. The reservoir is heavily insulated with felt, the liquid air level being indicated by a wire attached to a cork float. A very fine wire gauze in the bottom of the reservoir prevents ice crystals from entering the rubber tube and plugging it. This method of cooling was found entirely satisfactory aside from the fact that about *700* cubic centimeters of liquid air was required per hour.

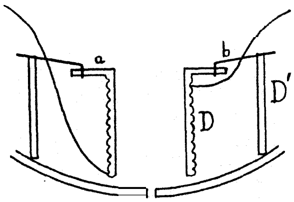

Fig 2.—Furnace.

The final experiments were made with the supply of nitrogen pentoxide at a temperature of −60 ± 1°. This temperature was maintained by surrounding the reservoir with toluene contained in a Dewar flask. The Dewar flask was likewise surrounded by a larger one containing carbon dioxide snow and ether. As the inner Dewar was not very highly evacuated, heat was conducted from it nearly as fast as absorbed from the apparatus. The temperature of the toluene was measured with a pentane thermometer and controlled by the addition of small pieces of carbon dioxide snow or with a nichrome heating wire. Aside from frequent stirring, little attention was needed to maintain the desired temperature.

In experiments in which the crystals were kept at the temperature of carbon dioxide snow and ether or liquid ammonia, the nitrogen pentoxide reservoir was merely immersed in a Dewar flask containing the desired substance. When liquid ammonia was used, the gas was kept from entering the room by bringing a metal funnel-like cap down over the flask. The funnel was connected to a suction pump and such a rapid flow of air maintained that no odor of ammonia could be detected.

The nitrogen pentoxide was prepared in the same manner as described by Rice and Getz.[4] Before distilling the crystals into the reservoir of the molecular beam apparatus they were raised to room temperature and all visible traces of nitrogen tetroxide removed by passing dried air over them. The use of ozone for purification of the nitrogen pentoxide was omitted to preclude the possibility that traces of it might be collected with the sample and subsequently oxidize the alkaline nitrite solution. The traces of nitrogen dioxide which were always present could be corrected for by the blank runs, that is, experiments in which the furnace was not heated.

Experimental Procedure

The experimental procedure can best be described by a brief outline of the steps involved in an actual determination. A phosphorus pentoxide tube is sealed to the projection of the storage bulb of the molecular beam apparatus. The main supply of nitrogen pentoxide is then connected to this tube and a third drying tube is sealed in at this junction and air drawn through it over the crystals, which are at room temperature, until visible traces of nitrogen dioxide are removed. The lower end of the reservoir is now surrounded with carbon dioxide snow and ether and about 3–4 g. of nitrogen pentoxide condensed by evacuating the system. The lower ends of the liquid-air traps are immersed in liquid air to prevent mercury vapor from distilling back into the reservoir during the process. The main supply of crystals and the drying tubes are then removed and the reservoir is immersed in the toluene bath described above. To remove the greater portion of the nitrogen dioxide formed in the above transfer the diffusion pumps are started and the toluene is kept at $-35°$ for about one and one-half hours. During this time the furnace is heated to 300–400° to drive off adsorbed gases. Finally the tolurne is cooled to $-60°$ and liquid air is then introduced into the liquid-air reservoir and the collecting tube F. In about one and one-half hours the molecular beam apparatus comes to liquid-air temperature. The burners under the diffusion pumps are turned down and air, which passes through soda lime, calcium chloride and phosphorus pentoxide is admitted. The collecting tube is removed while a current of air is forced through the apparatus to prevent the diffusion of moisture into it. The opening is immediately closed with an inverted beaker having a rubber collar which fits tightly about G. The collecting tube is washed off and dried, by warming in a flame and wiping with a linen cloth before putting it back into the apparatus. The burners under the diffusion pumps are lighted, liquid air is poured into the collecting tube and the fore pump started. In four minutes the pressure in the apparatus drops to 1×10^{-5} mm. of mercury and in six minutes to less than 1×10^{-6}. Readings of the current input and the pressure are taken frequently during the runs. At the end of the desired time the sample is removed and dissolved in dilute potassium hydroxide (1 cc. of 0.001 *N* KOH made up to 20 cc.). The collecting surface and collar are thoroughly rinsed into the solution and the tube is dried as above before returning to the apparatus. The experiments were carried out in series of from five to nine runs each.

Analytical Methods.—The nitrite content was determined by a method described in a bulletin of the American Public Health Association[11] and the nitrate content by the method of Chamot, Pratt and Redfield.[12] These methods make it possible to determine 0.001 mg. of nitrite nitrogen and 0.1 mg. of nitrate nitrogen to within 2–3%.

Calculations

Before the experiments which have been described were undertaken, it was necessary to make preliminary calculations on the amounts of nitrogen pentoxide which would pass through the defining holes of our molecular beam apparatus, the time the molecules are in the furnace and the furnace temperature required to secure measurable decomposition.

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[11] "Standard Methods of Examination of Water and Sewage," American Public Health Association, 1920.

[12] Chamot, Pratt and Redfield, THIS JOURNAL, 33, 366, 381 (1911).

Stern[13] in his work on molecular beams has used pressures in the high pressure chamber such that the mean free path of the molecules is of the same order of magnitude as the width of his slit. Kroger and Lewis and Mayer have used much more intense beams and Johnson[14] has studied the intensities and sharpness of such beams as functions of the pressure. We found in this work that higher pressures than those used by Stern resulted in the freezing up of the defining holes. Since nitrogen pentoxide and nitrogen dioxide can be determined quantitatively in very small amounts, it was unnecessary to use beams of high intensity. It was found empirically that when the nitrogen pentoxide chamber was held at a temperature of −60°, a satisfactory beam was secured. The calculated vapor pressure at this temperature is 0.042 mm. using the formula of Russ and Pokorny;[15] assuming that the nitrogen pentoxide molecule has the same diameter as the benzene molecule, the mean free path would be 0.3 mm., which is only one-tenth of the diameter of the first defining hole. The amount of nitrogen pentoxide passing through the last defining hole can easily be shown to be

$$p\sqrt{\frac{M}{2\pi RT}} \times \frac{2A_1A_2}{d^2} \qquad (1)$$

where A_1 and A_2 are the areas of the defining holes, d is the distance between the holes and p is the pressure in dynes per sq. cm. The calculated amounts of nitrogen pentoxide passing the slit system per hour is 1–2 mg., which is about ten times the amount actually secured. This discrepancy may be due to a considerable error in calculating the vapor pressure of nitrogen pentoxide, to the fall in pressure along the tube leading from the storage chamber to the first defining hole and to a considerable time lag in the warming up of this tube from liquid air temperature to −60°.

We shall now calculate the fraction of the nitrogen pentoxide molecules which should decompose during their flight through the furnace, assuming that the probability of decomposition per unit time is the same in the beam as that observed when the gas decomposes in bulk. In making this calculation we shall use the following symbols: T = temperature of furnace; T' = temperature of N_2O_5 chamber; $K(T)$ = probability of decomposition per unit time at temperature T, that is, the velocity constant of the reaction; n_v = number of molecules having velocities lying between v and $v + dv$; n = total number of molecules of all velocities; x = coordinate along the axis of the furnace.

The number of molecules having velocities lying between v and $v + dv$ which decompose during the time dt is

$$K(T)\, n_v\, dt \qquad (2)$$

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[13] Stern, *Z. Physik*, 39, 761 (1926).

[14] Johnson, *Phys. Rev.*, 31, 103 (1928).

[15] Russ and Pokorny, *Monatsh.*, 34, 1027 (1913).

Now

$$n_v = 4\pi\left(\frac{M}{2KT'\pi}\right)^{3/2} e^{-\frac{mv^2}{2KT'}} v^2\, \mathrm{d}v \tag{3}$$

and changing to the variable x instead of t by the relation $\mathrm{d}x = v\mathrm{d}t$ we have

$$\mathrm{d}n = -K(T)n4\pi\left(\frac{M}{2KT'\pi}\right)^{3/2} e^{-\frac{mv^2}{2KT'}} v^2\, \mathrm{d}v\, \frac{\mathrm{d}x}{v} \tag{4}$$

Integrating and remembering that $K(T)$ is a function of x, the position in the furnace, we have

$$\int\frac{\mathrm{d}n}{n} = 4\pi\left(\frac{m}{2KT'\pi}\right)^{3/2}\int e^{-\frac{mv^2}{2KT'}} v\, \mathrm{d}v \int -K(T)\mathrm{d}x \tag{5}$$

This gives

$$\ln\frac{n}{n_0} = \frac{\sqrt{2m}}{\sqrt{KT'\pi}}\int_0^l -K(T)\mathrm{d}x \tag{6}$$

Since we have taken x to be the coordinate along the axis of the furnace, this calculation applies only to those molecules passing directly along the axis. Molecules passing at an angle traverse a longer path and pass through a part of the furnace having a higher temperature. Since the results are negative, we shall assume that all the molecules pass along the axis; this approximation would merely reduce somewhat the theoretical decomposition. The last integration has been made graphically by calculating temperatures along the axis of the furnace; the velocity constants corresponding to these temperatures were then calculated from the formula $k = 4.98 \times 10^{13}\, e^{-\frac{24{,}700}{RT}}$ and plotted against corresponding values of x.

The temperature of the furnace was determined by placing a thermocouple against its inner wall. This gave a temperature of 793°K., which is a minimum value since heat was conducted away from the wall through the lead wires. We also suspended the thermocouple in the center of the furnace. It registered a temperature of 523°K., but a calculation of the amount of radiant energy falling on the thermocouple and that conducted away through the lead wires shows that this temperature must be far too low. In calculating the temperatures along the axis we assume that Pyrex glass radiates 0.9 as much energy per second as a black body. This makes the effective wall temperature of the furnace $793 \times 0.9^{1/4} = 771$°K. The temperature of a point on the axis distant x cm. from one end of the furnace is equal to the effective temperature of the furnace wall multiplied by the fourth root of the fraction of the solid angle subtended by the furnace at this point, divided by 4π. This is

$$771\left[\frac{l-x}{2\{(l-x)^2+r^2\}^{1/2}} + \frac{x}{2(x^2+r^2)^{1/2}}\right]^{1/4} \tag{7}$$

This gives a temperature of 718°K. and 634°K. for the center and ends of the furnace, respectively, and 10^6 for $\int_0^l K(T)\mathrm{d}x$; substituting the numerical values in Equation (6) we find for n/n_0 the value 10^{-27}, which means that only one molecule in 10^{27} should remain undecomposed. We performed additional experiments at higher temperatures which we estimated roughly from the relative power input; the effective wall temperatures were 806°K. and 846°K., that is, **35** and 75° higher than the temperature at which the detailed calculations have been made. We attempted to use the change of resistance with temperature of the furnace winding as a measure of its temperature but found this to be erratic. We attribute this to the conductivity of the Pyrex glass furnace, which was heated to its softening point.

In all these calculations we have used the least favorable assumptions and approximations so that the calculated decomposition should be less than if these assumptions and approximations were not made.

Experimental Results

The greater portion of this research was done with the furnace walls at 793°K. as determined by the thermocouple; this temperature is that used in the calculations given in the preceding section. Three runs were made at 806°K. and one at 846°K. as determined by the increased power input. These results are summarized in Table I. The percentages of nitrogen peroxide obtained are the same as in the original material, as shown by separate analysis. There is no indication of any decomposition whatsoever in the beam.

TABLE I

BLACK BODY RADIATION ON NITROGEN PENTOXIDE

Time of each expt. = 1.5 *hours*

Expt no.	N_2O_5, mg.	NO_2 (as N_2O_5), mg.	NO_2 (as N_2O_5), %	*T*, °K
1a	0.0639	0.0088	13.8	*Cold*
1b	.0713	.0086	12.1	793
1c	.0668	.0086	12.8	*Cold*
1d	.0631	.0102	16.0	793
1f	.0744	.0084	11.3	*Cold*
1g	.0697	.0096	13.7	793
1h	.0709	.0054	7.6	*Cold*
1k	.0634	.0068	10.7	793
1m	.0702	.0063	9 0	*Cold*
2a	.0995	.0034	3.4	*Cold*
2b	.0803	.0028	3.5	806
2c	.0631	.0029	4 6	*Cold*
2d	.0818	.0027	3.3	806
2e	.0665	.0026	3.9	*Cold*
2f	.0748	.0026	3.5	806
2g	.0670	.0023	3.4	*Cold*
3a	.0796	.0027	3.4	846

Discussion of Results

We have passed a beam of nitrogen pentoxide molecules through a furnace containing approximately black body radiation under such conditions that there was no intermolecular collision or collisions with the walls. The temperature of the furnace was such as to give practically complete decomposition if nitrogen pentoxide reacted at the rate secured by extrapolating the known experimental values obtained in the bulk decomposition to these higher temperatures. Since no decomposition occurred we have proved that infra-red radiation does not decompose nitrogen pentoxide molecules and there appears to be no special mechanism of absorption alone that can explain away this experiment. It may be pointed out that chains cannot occur in a molecular beam; consequently this experiment does not disprove the hypothesis which assumes a chain mechanism started by absorption of radiation.

It is convenient at this point to consider the probability of absorption of a quantum of light by a molecule passing through the furnace. This calculation is not essentially different from previous considerations showing that the coefficient of absorption of nitrogen pentoxide or other molecules would have to be very much larger than the observed values in order to account for the observed rate of decomposition. An approximate value for this coefficient for nitrogen pentoxide may be calculated from observations made by Warburg and Leithäuser;[16] for the region of the strongest absorption band, namely, 5.81μ, they find that the intensity is decreased to 0.7 of its initial value by passing through a column 30 cm. long containing nitrogen pentoxide at 0.5 mm. of mercury. This gives approximately 6.7×10^{-19} for the coefficient of absorption per molecule, *a*,. This is related to the Einstein probability coefficient, $B_{i \longrightarrow j}$, for a transition from a state i of lower energy to a state j of higher energy by the absorption of light of frequency v under the influence of unit energy density lying between the frequencies v and v + dv by the approximate formula,[17] $B_{i \longrightarrow j} = c/h\nu \int \alpha_\nu d\nu$, where the integral is to be extended over the whole range of absorption. As a further approximation we take the coefficient *a*, as constant over the region of the half width of the line; from Warburg's curve this half width is about 0.3μ. The $\int \alpha_\nu d\nu$ then becomes $c\alpha_\nu$ AX/X^2 and $B_{i \longrightarrow j}$ is 1.6×10^{17}. We have then for the rate of absorption of energy $dN/dt = -Nu_\nu B_{i \longrightarrow j}$; now assuming that each absorption results in decomposition we have $\ln (N_0/N) = u_\nu B_{i \longrightarrow j} t$. The mean life of the molecules is, therefore, $1/B_{i \longrightarrow j} u_\nu$; substituting the numerical value for $B_{i \longrightarrow j}$ and for u_ν the density of black body radiation of frequency v at a temperature of 900°K., we secure the value 9 seconds for the mean life. Since the molecules in this experiment are in the furnace for about 4×10^{-5} secs., only a negligible fraction could even absorb radiation of this strongest absorption band. Similar calculations

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[16] Warburg and Leithauser, Ann. *Physik*, 28, 313 (1909).

[17] See Tolman, "Statistical Mechanics," The Chemical Catalog Co., Inc., New York, 1927, p. 175.

using the absorption coefficients where an electron transition is involved, such as in the dissociation of bromine into a normal and an excited bromine atom, show that such dissociations could not be effected in a molecular beam using the most intense sources of light available. Thus the experiments of Kröger, Lewis and Mayer, Mayer and the present investigation are in entire agreement with the theoretical expectations.

Summary

1. In reactions as ordinarily studied there are three factors influencing the decomposition, namely, the absorption and emission of radiation, intermolecular collisions and collisions with the walls. Methods have been discussed for separating these three factors and studying them independently.

2. We have completed experiments on the effect of radiation alone on nitrogen pentoxide by passing a molecular beam of this substance through a furnace containing approximately black body radiation. Even at the lowest temperature only one molecule in 10^{27} should have escaped decomposition if black body radiation alone caused the decomposition under ordinary conditions. We could detect no decomposition in any experiment.

3. We have calculated the probability of absorption of radiation by the nitrogen pentoxide molecule and find the experimental result in agreement with theory.

BALTIMORE, MARYLAND

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

TRANSFERENCE NUMBERS OF IONS IN SOLID SODIUM CHLORIDE AT HIGH TEMPERATURES

BY T. E. PHIPPS AND R. T. LESLIE

RECEIVED JUNE 30, 1928 PUBLISHED SEPTEMBER 5, 1928

For a large number of solid salts it has been shown that the relation between the electrical conductance and the absolute temperature may be represented by an equation of the form:

$$\ln k = A/RT + C \tag{1}$$

where k is the specific conductance, A is a heat quantity designated as the heat of liberation of the ions from the lattice, and R is the gas constant. It has been found, however, that this relation is not linear over the whole temperature range for sodium and potassium chlorides, bromides and iodides. Ussataja and Hochberg[1] have observed this deviation for sodium chloride above 500° and have attempted to apply an equation of the form

$$\ln k = AT + C \tag{2}$$

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[1] Ussataja and Hochberg, *Z. Physik*, **46,** 88 (1927).

above this temperature. Phipps, Lansing and Cooke[2] and Phipps and Partridge[3] have investigated the above salts and have found that the relation between log k and $1/T$ is linear but that the curve shows two slopes. The upper is slightly greater than twice the lower slope for the halides of sodium and potassium mentioned above. The curve for sodium chloride is shown in Fig. 1. On account of the difficulty of measurement in the transition range, due probably to polarization effects, it is not certain whether the change in slope is gradual or abrupt.

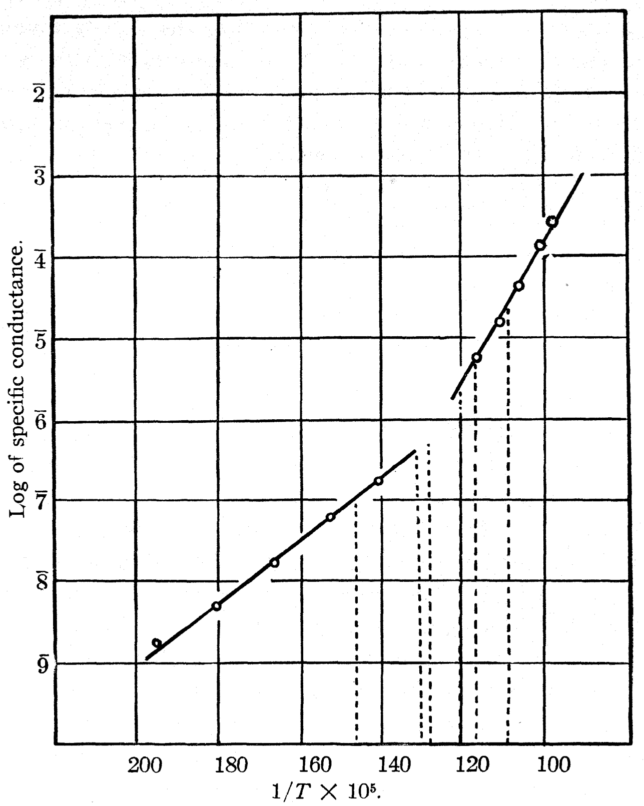

Fig. 1.—Temperature-conductance curve of solid sodium chloride. Dotted lines mark temperatures at which transference experiments were run.

Tubandt's[4] transference experiments upon salts of the less polar type such as the halides of silver and lead have indicated uni-ionic conduction in practically all cases. For these same halides a single slope is observed

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[2] Phipps, Lansing and Cooke, This Journal, 48,112 (1926).

[3] Phipps and Partridge, *Thesis,* University of Illinois, 1927 (to be published).

[4] Tubandt, *Z.* anorg. *allgem. Chem.,* 115,105 (1921).

when log k is plotted against $1/T$. The existence of two slopes in the conductance curves for the more polar halides of sodium and potassium led Phipps, Lansing and Cooke[2] to make the suggestion that there may be a change in the mechanism of conduction in the latter case as the temperature is raised, perhaps from uni-ionic to bi-ionic conduction. Smekal[5] interpreted the two-slope behavior just mentioned as supporting the "imperfect lattice" theory, the lower slope being determined by the heat of liberation of "Lockerionen" (that is, ions freer to move due to their position on the "inner surfaces" of the imperfect lattice) while the upper slope is determined by the heat of liberation of the "Gitterionen" (that is, the ions on the interior of units which are small enough to be considered as perfect). Smekal's conclusion rests upon the transference experiment of von Seelen[6] in which it was found that only the sodium ion moved in sodium chloride at 400°. This, however, is below the temperature at which the conductance curve changes slope.

Transference experiments were undertaken to determine if possible whether or not uni-ionic conduction persists at high temperatures in solid sodium chloride. The results may be briefly stated as follows. Transference by the chloride ion is negligible up to approximately 510°. At higher temperatures the chloride ion assumes an important part in the conduction.

Experimental

It has been suggested that the nature of the electrodes determines the mechanism of conduction. Thus Le Blanc and Kroger[7] have attributed the transference number of unity for silver in silver iodide, as observed by Tubandt,[4] to the fact that Tubandt used silver electrodes which provided a "follow-up" ion for the silver but not for the iodide ions of the lattice. In the present investigation it did not seem possible to design an electrode reversible for the chloride ion for use with sodium chloride at high temperatures. A metallic sodium anode and a nickel cathode were used. If Le Blanc and Kroger are correct in their surmise, the movement of the sodium ion would be favored by this choice of electrodes. In spite of the fact that the conditions might be considered adverse to the movement of the chloride ion, the results showed conclusively that the chloride ion took part in the conduction at high temperatures.

The chief difficulty encountered in the work was in the devising of a satisfactory sodium electrode. The final form of the apparatus which **was** used is shown in Fig. 2. The transference cell proper consisted of a block of rock salt, G, into which a hole was drilled to form a cup for the sodium, and three or four thin plates of salt upon which this cup rested. The cup constituted the anode portion and the plates the cathode portion. Attempts were made at first to use open cups, but the sodium spattered while

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[5] Smekal, *Z. Physik*, 44,869 (1927).

[6] v. Seelen, *ibid*, 29, 125 (1924).

[7] Le Blanc and Kroger, *Z. Electrochem.*, 30,253 (1924).

being introduced and evaporated too rapidly during the run. To obviate these difficulties a salt cover having two small holes, one for the introduction of the sodium and the other for the nickel electrode wire, was finally used. The nickel electrode rested on the cover of the anode cup as may be seen in Fig. 2 (detail). This formed a direct path through the salt to the nickel cathode. However, calculation showed that not more than 3% of the current could have passed by this path instead of through the sodium in the cup. Even if the nickel electrode should force movement of the chloride ion at the expense of the sodium ion, an uncertainty of at most 0.03 in the transference number of either ion would result from this shunt around the sodium. It is thought that the actual error introduced here is much less than 0.03.

The cups were about a centimeter in cross section and two centimeters high, while the plates were from a quarter to a half a square centimeter in area and a tenth of a centimeter thick. The parts were smoothed with fine emery paper. It was found in this connection that fitting together of raw cleaved surfaces resulted in excessive sticking and faulty cleavage at the end of the experiment. All parts were given a preliminary heating to about 400°, cooled in a desiccator and weighed before the experiments.

The lower part of the frame, E, in which the crystals were held was constructed entirely of nickel in order to withstand the sodium vapor. The nickel plate cathode, H, was removable so that it could be washed separately from the rest of the frame, and the washings analyzed for salt in case the crystals stuck to it. This frame was suspended from the negative terminal in such a way that it could be removed to facilitate mounting the crystals before the run.

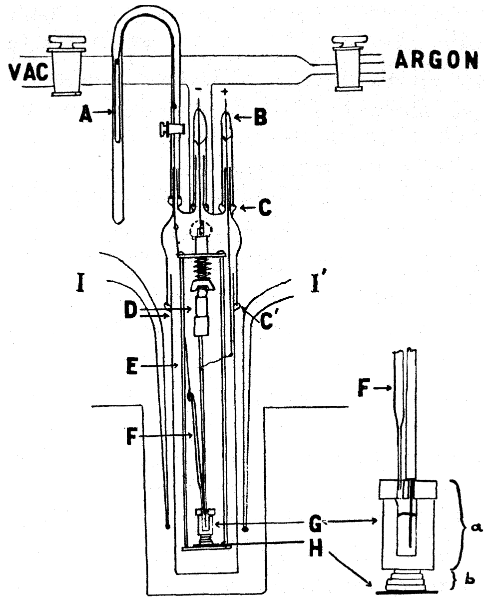

Fig. 2.—Apparatus used in determining transference numbers. A, brass counterpoise; B, tungsten-to-glass seals; C, C′, sealing wax seals; D, quartz; E, nickel frame; F, pyrex capsule filled with sodium; G, rock salt transference cell; H, removable nickel; I, I′, thermocouples; a, anode portion; b, cathode portion.

The tube inclosing the whole apparatus was of quartz to allow visibility during the introduction of the sodium into the anode cup and to withstand the high temperatures. The tube was considerably attacked by the sodium vapor at the high temperatures and became coated with the usual brown deposit of silicon together with a layer of soda glass, which had to be removed by treatment with hydrofluoric acid after each run. Failure to do this led to cracking of the tube when it was next heated. The quartz tube was joined at C′ with a sealing wax seal to the Pyrex cap shown in Fig. 2.

The glass capsule, F, was filled with sodium by the method described by Gibson and Phipps[8] and was suspended in the position shown in the figure with the brass counterpoise, A, drawn up and clamped by means of the stopcock.

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[8] Gibson and Phipps. This Journal, **48,312** (1926).

To start the run the apparatus was evacuated to 10^{-5} or 10^{-6} mm. of mercury, and the temperature of the furnace surrounding the quartz tube was raised to about 150°. This caused the sodium to melt and run out of the capsule into the cup. The stopcock holding the counterpoise was then opened so that the capsule was drawn up into the cool part of the tube where it was not attacked by the sodium vapor. The stopcock to the vacuum pump was then closed and the apparatus filled with argon to about two atmospheres' pressure. This decreased the rate of evaporation of the sodium. Before the argon entered the apparatus it was passed through an alloy of sodium and potassium and through forty centimeters of magnesium perchlorate trihydrate in a vacuum-tight, all-glass train which was joined to the argon tank by a copper-to-glass seal.

The temperature was then brought up to the desired point and regulated automatically by a potentiometer, contact galvanometer and stick-relay system which was actuated by the thermocouples, I, I′, shown in the figure. This regulator had been previously calibrated in a blank run by inserting a Pt, Pt-Rh thermocouple in the position occupied by the crystals in an actual run. Regulation was found to be within a degree.

The total current through the crystals was measured by a silver coulometer and was kept below a milliampere to prevent heating. At high temperatures the sodium evaporated rapidly from the cup and it was necessary to determine by trial how long the run could be continued without losing all of the sodium.

The cathode crystals were colored blue in all of the runs above 410° except in the experiments where artificially grown sodium chloride plates were used, in which case a brown color resulted. All of the other parts remained colorless. The amount of sodium which diffused into the cathode plate was doubtless negligible, as shown by the work of Phipps and Mason.[9] Its presence could not have given rise to metallic conductance since only the end crystal was colored. A layer of metallic sodium was generally found between the cathode crystal and the nickel plate. Much of the sodium liberated at this interface distilled to the cooler parts of the apparatus.

Immediately after the apparatus was opened the cup and the cover were separated from the salt plates. The two parts were dropped as quickly as possible into separate portions of absolute alcohol and the sodium allowed to dissolve. The crystals were then rinsed with alcohol, the rinsings being added to the proper washings, and dried at 130° for several hours. The cup and cover were weighed together as anode portion. The plates remained stuck together and were weighed as cathode portion.

The possibility of serious error due to faulty cleavage made necessary the following rather elaborate procedure. To determine the cleavage

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[9] Phipps and Mason, *Ill. Acad. of Science*, **18,304 (1925).**

error in the weight of the anode and cathode crystals, the plate next to the cathode was first split off and the remaining block of crystals again weighed. The change in weight due to transference should have occurred in this first plate. The next plate in order was then split off and the remainder weighed. This was continued until all the plates had been separated. The group of plates which included the plate next to the anode cup and which changed weight the least is shown in Table I as "middle section." In some experiments this middle section showed a change in weight and in such cases it was assumed that the change was entirely due to faulty cleavage between the middle section block and the cathode plate. Accordingly, such change was included in the change in weight of the cathode plate. However, part or all of this change of weight might have arisen from faulty cleavage between the anode cup and the middle section. The change in the transference number which would result if the change in weight of the middle portion were ascribed entirely to faulty cleavage between the anode cup and the middle section is shown in parentheses after each transference number in Table I.

The alcohol washings from the anode and cathode portions were analyzed separately and the weights of these portions were corrected for the salt which had dissolved. This correction was not apportioned among the plates in finding the change in the middle section because it was suspected that most of the salt in the alcohol washings came from the plate next to the cathode as a result of the rather violent reaction between the layer of sodium and the alcohol at this surface. In fact the alcohol washings from the cathode crystal and the nickel cathode nearly always showed small chips of undissolved salt at the bottom in amount considerably exceeding the solubility of the salt in absolute alcohol. These chips undoubtedly came from the cathode–cathode crystal interface and comprised by far the greater part of the sodium chloride in the washings. This will explain the very large correction of the cathode crystals for weight lost in washings, which in an extreme case (No. 14, Table I) amounted to 5 mg. That the middle plates contributed practically nothing to the alcohol washings was proved by the fact that in nearly every run at least one plate in the middle section was found after the washing to check to a tenth of a milligram with its original weight. The error in imputing the solubility losses of the middle plates to the cathode plate affects the transference numbers indirectly if at all by affecting the magnitude of the possible cleavage errors (the values in parentheses, Table I). The weight of the cathode portion was further corrected for the salt which stuck to the nickel cathode. The nickel frame and the inside of the quartz tube were also washed and the salt found was added to the weight of the cup and cover. This was justified by the fact that the exposed area of the anode cup and cover was about ten times that of the cathode portion so that the error caused by attributing all of this salt to evaporation from the anode is less than the uncertainty due to cleavage. At the highest temperature, 655°, the error in the transference number which might have resulted from this approximation was 0.01 unit.

Results

The pole reactions may be written

$$\mathrm{Na} \longrightarrow \mathrm{Na}^+ + \ominus \text{ anode}$$
$$\mathrm{Na}^+ + \ominus \longrightarrow \mathrm{Na} \text{ cathode}$$

On the passage of C equivalents of current through the cell there is a net loss of $C(1 - t_+)$ equivalents of sodium and $C\,t_-$ equivalents of chlorine, that is to say, $C\,t_-$ equivalents of sodium chloride from the cathode portion.

TABLE IA

DATA FROM TRANSFERENCE EXPERIMENTS IN DETAIL

Expt.	Sample No.	Temp., °C.	Voltage	Time, hours	Weight of crystals, g. (1) Cathode Before	(1) Cathode After	(2) "Middle" Before	(2) "Middle" After	(3) Anode Before	(3) Anode After
14	1	580	110	15	1.7851	1.7746	0.7944	0.7941	3.4706	3.4728
24	3	580	110	19	1.4741	1.4642	.2850	.2855	....	....
25	3	580	110	20	1 8727	1.8576	.8719	.8713	4.1312	4.1379
26	2	510	310	46	1.6539	1.6506	.7192	.7197	....	....
29	2	490	220	59	0.6231	0.6306	.3292	.3298	....	....
33	[a]	490	220	38	.2764	.2746	.0934	.0934	....	....
34	2	410	220	161	.1879	.1873	.0800	.0801	....	....
36	3	655	70	10	.5772	.5690	.1107	.1100	6.6489	6.6453
38	3	558	220	46	.3163	.3068	.0684	.0684	....	....
39	3	655	70	16	.5174	.5100	.0669	.0664	....	....

[a] Artificial plates.

TABLE IB

DATA FROM TRANSFERENCE EXPERIMENTS IN DETAIL

Expt.	Curr. approx. M.A.	Equivs. of curr	NaCl in washings, g (4) Cathode portion	(5) Anode portion	(6) Frame and tube	Loss by cathode portion[a]	Gain by anode portion[b]	t_- from cathode[c]	t_- from anode[d]
14	0.75	0.000233	0.0055	0.0024[d]	...	0.0049	0.0046	0.36(−0.02)	0 34(+0.02)
24	.75	.000421	.0020	...	...	.0079	...	.32(+.02)	....
26	.75	.000554	.0026	.0037	0.0036	.0125	.0140	.38(−.02)	.43(+.02)
26	.1	.000386	.0027	...	...	.0005	...	.03(+.02)	....
29	.1	.000115	.0023	...	...	.0002	...	.03(+.09)	....
33	.1	.00054	.0020	...	...	−.0002	...	−.06(.00)	....
34	.1	.000137	.0007	...	...	.0	...	.00(+.01)	....
36	1.2	.000476	.0003	.0055	.0055	.0079	.0074	.28(−.025)	.27(+.025)
38	.5	.000375	.0001	..	...	.0094	...	.43(.O)	....
39	1.0	.000407	.0007	...	...	.0067	...	.28(−.02)	....

[a] (Loss in 1) − (4).

[b] (Gain in 3) + (5) + (6).

[c] Figures in parentheses are corrections which would result in t_- if changes in weight of middle section were calculated as due to sticking of the cup to the middle section rather than as a change due to transference.

[d] + Frame and tube.

An equal gain should be observed at the anode. To obtain the value of the transference number, the net loss in weight of the cathode portion or the net gain of the anode portion is reduced to equivalents and divided by the total number of equivalents of current passed.

The results of ten out of thirty-nine runs are given in detail in Table I and summarized in Table II. The missing runs suffered mishaps chiefly from the following causes: (1) poor temperature control, (3) leaks or breaks in the vacuum line causing oxidation of the sodium and serious contamination of the crystals, *(3)* failure of the sodium to run out of the capsule into the anode cup in sufficient quantity, (4) complete evaporation of the sodium from the cup, (5) faulty cleavage after the runs, (6) failure to take complete data (thus in the earlier runs the loss of sodium chloride in the alcohol washings was not determined), (7) cracking of the crystals on heating up the apparatus at the beginning of the run, (8) the use of too high a potential across the cell, causing arcing.

TABLE II

SUMMARY OF TRANSFERENCE NUMBERS

Temp., °C.	No.	Transference number of chloride ion From anode	From cathode	Average
410	34	...	0.00	0.00
490	29	...	.03	−.01
	33	...	−.06[a]	
510	26	...	.03	.03
558	38	...	.43	.43
580	14	0.34	.36	.36
	24	...	.32	
	25	.43	.38	
655	36	.27	.28	.28
	39	...	.28	

[a] In this case the negative value is probably due to the fact that small errors in manipulation and weighing were of great importance on account of the small amount of current transferred.

Best results were obtained from the cathode portions. In three cases satisfactory checks were obtained from analysis of both anode and cathode portions. The complete removal of the sodium from the anode cup was difficult, and even with the best vacuum conditions and the purest argon the anode cover showed a small amount of black contamination, presumably from the interaction of oxidized sodium with the nickel. This made it impossible in most cases to get a satisfactory determination of transference numbers from the weight of the anode cup.

Material from four sources was used. Sample 1, which was the same material used by Phipps, Lansing and Cooke in the determination of the conductance curves, was natural halite from Navarre, Michigan. Sample 2 was a second specimen from Navarre, Michigan. Sample **3** came from Heilbronn, Germany. In run No. **33** (Table I) the anode cup was made from Sample 3, while the plates were grown from a melt. The material of the melt was Mallinckrodt's "Reagent Quality" sodium chloride, thrice recrystallized from conductivity water. It is apparent from the data that the source of the sodium chloride had no appreciable effect upon the transference numbers.

Discussion

From a consideration of all the sources of error it is concluded that the transference numbers summarized in the last column of Table II are accurate to ±0.05 unit. At 580°, where the greatest number of determinations was made, the mean value of five determinations is 0.36 for the chloride ion. It appears certain that there is a change in the mechanism of electrolytic conduction through the salt very near to the temperature at which the extrapolated slopes of the conductivity curve shown in Fig. 1 intersect.

The decrease in the value of t_- with increasing temperature in the upper range was unexpected. It might have been due to leakage of the current through the sodium vapor at the high temperature, which increased with the temperature. Saha and Sur[10] have stated that the specific resistance of sodium vapor at 900° is about 13,000 ohms. At 600" calculation shows that conduction through the vapor would be insignificant compared with conduction through the salt. It seems more probable that the direct current produces a polarization of the crystal, which reacts upon the mechanism of conduction so as to affect unequally the mobilities of the two ions of the lattice. It is perhaps predictable from the behavior of the transference numbers that with very small currents passing for long periods of time the transference number of the chloride ion would approach 0.50. If this is correct, the absolute values of the transference numbers given in Table II have little significance except as an indication of the degree of polarization of the crystal under the stated conditions, From the point of view of the lattice theory the significant fact appears to be that at sufficiently high temperatures both ions of the sodium chloride lattice acquire the freedom which only the sodium ion possessed at lower temperatures. Similarity between the conductance curves (log k vs. $1/T$) of the chlorides, bromides and iodides of sodium and potassium indicates that this phenomenon is general among uni-univalent polar salts. The fluorides may prove exceptional.

Summary

Transference experiments were performed on sodium chloride at temperatures varying from 410 to 655", using a reversible sodium anode and a nickel cathode.

The fraction of the current carried by the chloride ion is practically zero between 410 and 510°. Between 558 and 655° chloride ion carries a

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[10] Saha and Sur, *Quart. J Indian Chem. Soc.*, **1**, 10 (1924).

considerable part of the current. It is significant that the temperature region in which the change from uni-ionic to bi-ionic conduction occurs is the same as the temperature region in which the slope of the conductance curve (log k vs. $1/T$) doubles its value.

In the temperature range 558 to 655° the fraction carried by the chloride ion appears to decrease with increasing temperature. This is thought to be a polarization effect.

[CONTRIBUTION FROM THE MISSOURI SCHOOL OF MINES AND METALLURGY]

THE SOLUBILITY OF ALUMINUM BROMIDE IN CARBON DISULFIDE

BY H. H. KAVELER AND C. J. MONROE

RECEIVED JULY 11, 1928 PUBLISHED SEPTEMBER 5, 1928

Carbon disulfide as a solvent of inorganic salts was first studied by Arctowski,[1] who found the mercury halides slightly soluble, but the common inorganic salts insoluble. Kohler[2] found that aluminum bromide and iodide are rather soluble. Qualitative data of various investigators on the solubilities of various salts in this solvent have been compiled by Walden.[3]

As aluminum bromide dissolves in carbon disulfide to the extent that various inorganic salts dissolve in water, quantitative determinations of its solubilities at various temperatures were made.

Preparation of the Reagents

The carbon disulfide was purified by the method of Sidot,[4] with modifications of Arctowski, as follows. Commercial carbon disulfide was shaken with mercury until the surface of the metal was no longer tarnished and was then distilled from anhydrous calcium chloride. It was kept in contact with phosphorus pentoxide until ready for use, when it was decanted into a dry flask containing a little paraffin, from which it was distilled out of contact with air. The product, which had a sweet, pleasant odor, was used immediately.

Aluminum bromide was prepared from the purest commercial aluminum and C. P. bromine purified by distilling from chromic acid and from potassium hydroxide and potassium bromide.

As the extreme solubility of the salt made it desirable to prepare as much as 700 g. at one time, a somewhat different apparatus than that of Kohler, Richards,[5] and others was used, as shown in Fig. 1.

A combustion tube (*c*), of 12 mm. diameter and 1 meter length, resting in an electric furnace (E), was fused onto a train of three 750cc. distilling flasks. It was charged

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[1] Arctowski, *Z. anorg. Chem.*, 6, 267, 404 (1894).

[2] Kohler, THIS JOURNAL, 22, 387 (1900).

[3] Walden, "Electrochemie Nichtwassrigen Lösungen," 1924, p. 480–481.

[4] Sidot, *Compt. rend.*, 69, 1303 (1869).

[5] Richards, THIS JOURNAL, 42, 2222 (1920).

with 100 g. of the metal, cut into small strips, and was heated to 400°, at which temperature a stream of dry hydrogen saturated with bromine was passed over the hot aluminum. The product was most rapidly formed when a reaction between the hydrogen and bromine to form hydrogen bromide proceeded with the production of flashes of light, the hot metal being a good catalyst for this reaction, which normally proceeds at a higher temperature.

When about 80% of the metal was used up, the introduction of bromine was stopped. The salt, carried by the escaping gas into the first flask, was then refluxed in a slow stream of hydrogen and distilled, at a pressure of about 15 mm., into the second, and then the third flask. The product is a white, highly crystalline compound. Its melting point has been reported to be 97.1°.[6]

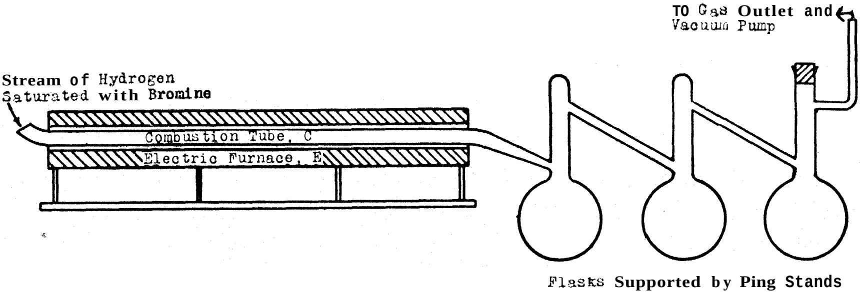

Fig. 1.—Arrangement for preparing quantities of aluminum bromide.

Determination of the Solubility

After sealing off the third distilling flask from the others, the desired amount of disulfide was added to the bromide while dry hydrogen was passed into the side neck. The sample tube was inserted and the flask shaken in a thermostat. At temperatures below 70°, an hour was found to be sufficient time for equilibrium to be attained. At higher temperatures, more than twelve hours was allowed for establishment of equilibrium, due to a polymorphic transformation of the solute.

Below 30°, an ordinary glass tube served as a delivery tube for taking samples. Since at higher temperatures the highly concentrated solutions would deposit crystals when forced into a sampling tube cooler than the bath, a delivery tube had to be used which could be kept at the temperature of the thermostat. A glass sampling tube was wound with nichrome wire and sealed inside of a larger tube to prevent the wire from coming in contact with the solution (see Fig. 2). This was calibrated, under the conditions at which it was to be used, with the aid of a small thermometer suspended inside the delivery tube, a temperature–current curve being obtained. With this device samples at the high temperatures could be taken with the same accuracy as at the low temperatures.

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[6] The melting point of aluminum bromide has been reported (a) as 97.1° by Kendall, Crittenden and Miller, THIS JOURNAL, 45, 963 (1923), and (b) as 90.5° by Biltz and Voigt, *Z. anorg. Chem.*, 126, 39 (1922).

A convenient aspirator was made from two 500cc. leveling bottles, filled with mercury, the raising or lowering of one causing pressure to be applied or withdrawn quickly, while the same dry air is kept in contact with the solutions.

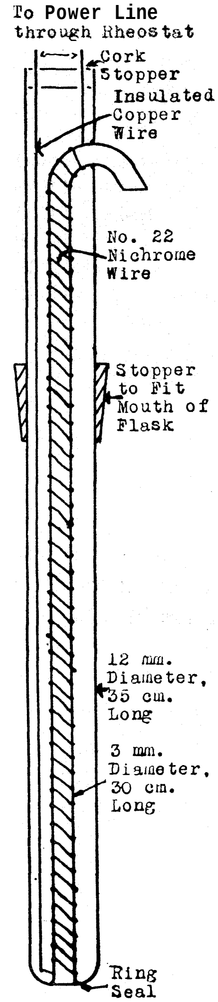

Fig. 2.—Device for sampling saturated solutions at constant temperatures.

The end of the delivery tube was placed in a bell jar filled with dry air to prevent fuming during the taking of a sample.

As aluminum bromide dissolves in carbon disulfide with the absorption of heat, and in water with the evolution of a large quantity of heat, addition of water to a sample, preliminary to analysis for bromide by the Volhard method, resulted in local, violent reaction, even when the temperature was far below zero. Addition of a third liquid, as ethyl alcohol, which forms with the first two a one-phase region, resulted in the violence of the reaction being reduced to such an extent that the method could have been used, although a small amount of hydrogen bromide was still lost. It was found that the complex $AlBr_3 \cdot 2C_6H_5NO_2$ was readily formed below 20°,[7] and that it reacted with water very quietly, with no loss of hydrogen bromide, so the following method of analysis was adopted.

(1) The weighing bottle containing the weighed sample was set into 100 cc. of water in a 600cc. beaker and 15–25 cc. of pure, anhydrous nitrobenzene added to the sample. (2) Pour hundred cc. of water, cooled to about 10°, was poured into the beaker. (3) With the weighing bottle covered with water, the mixture in it was stirred until all the aluminum bromide had reacted to form the complex. (4) The bottle was tipped, allowing water to run in slowly, the white, gummy complex going into solution with a hissing noise. (5) After stirring, the aqueous solution was decanted into a volumetric flask. (6) The residual emulsion of nitrobenzene, carbon disulfide and water, which retains some of the salt, was washed with water until the emulsion broke, when no detectable amount of bromide remained with the organic liquids. (7) The volume of the combined aqueous solution was made up to a standard liter, an aliquot part taken and titrated for bromide

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[7] This compound, along with others of the benzene series, was reported by Menschutkin; see Seidell, "Solubilities of Inorganic and Organic Compounds," D. Van Nostrand Co., New York, 1919, pp. 21–24.

by the Volhard method, and the percentage of aluminum bromide in the original sample calculated.

Using this method of analysis, as much as 80 **g.** of the anhydrous salt were put into solution without difficulty.

TABLE I

RESULTS OF ANALYSES (SEE FIG. 3)

Temp., °C.	Wt. of sample, g.	Wt. % of $AlBr_3$	Mole % (av.) of $AlBr_3$	Temp., °C.	Wt. of sample, g.	Wt. % of $AlBr_3$	Mole % (av.) of $AlBr_3$
0.1	25.943	41.8		50.1	10.687	80.9	54.5
	14.238	41.5	17.0	60.0	13.257	86.5	
8.4	14 374	49.1			15.536	86.2	644
	17.895	49.0	21.6	70.0	18.955	90.5	73.1
15.0	12.105	55.4		71.0	6.915	91.0	
	17.720	54.7	25.8		29.569	91.1	742
20.0	14.979	58.7		76.0	10.363	93.5	79.1
	15.545	58.9	28.9	81.0	7.717	94.5	83.3
25.0	10.309	62.8		85.0	81.639	96.2	87.8
	16.165	62.5	32.3				
30.0	23.615	66.6					
	12.874	66.7	36.2				

Discussion of Results

The exceptionally high solubility of this salt in carbon disulfide is in accordance with several rules[8] derived from a study of solutions of electrolytes in other solvents.

TABLE II

SOLUBILITIES IN CARBON DISULPIDE

Salt	M. p., °C.	Heat of fusion, cal./mole[a]	Soly. in CS_2 in mole % at 25
KCl	772	6450	Insoluble (0 002)
KBr	748	(3040)	Insoluble
KI	(about 748)	(3820)	Insoluble
AgCl	455	3500	Insoluble
AgBr	430	2370	Insoluble
$HgCl_2$	265	5490	0.0147
$HgBr_2$	235	5010	0.0489
HgI_2	250	3280	0.0638
$AlCl_3$	195	(3450)	Slightly soluble
AlI_3	191	(4280)	Rather soluble
SnI_4	145.3	4180	Rather soluble
$AlBr_3$	97.1	2790	32 3

[a] The heats of fusion in parentheses were calculated, the others and the melting points were taken from standard tables. The salts are arranged in the order of their solubilities.

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[8] Hildebrand, "Solubility," The Chemical Catalog Company, Inc., New York, 1924, p. 166.

(a) Aluminum bromide is unique in that it has a melting point and a heat of fusion much lower than the same values for almost any inorganic salt. (Some salts have lower melting points, but much higher heats of fusion; others have lower heats of fusion but much higher melting points.) Table II shows that the solubilities of salts in carbon disulfide are in accordance with the rule of greater molal solubility the lower the melting point and heat of fusion.

(b) Solvation tends to increase solubility. The color of the saturated solutions varied from a red at low temperature to an almost opaque black at 85°, possibly due to molecules of $x\mathrm{AlBr_3}y\mathrm{CS_2}$ being formed.

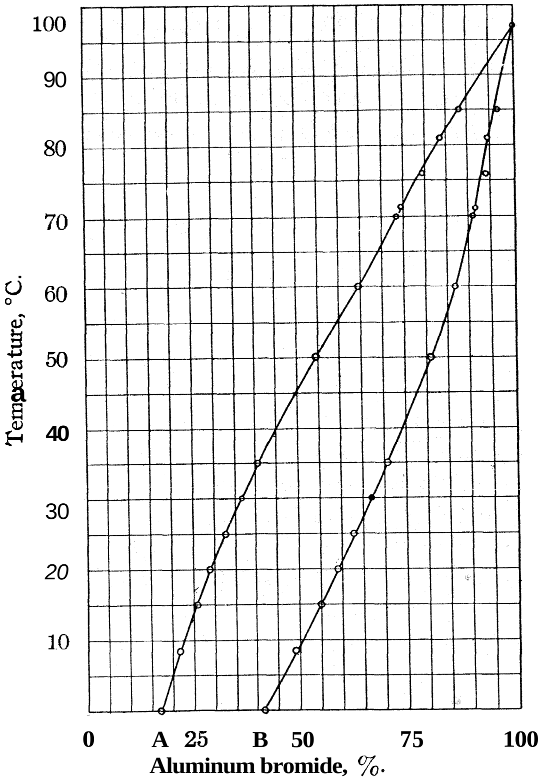
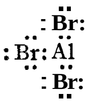


Fig. 3.—Curve A, mole %; curve B, weight %.

(c) The solubilities of the various salts in Table II are roughly in accordance with the rule that equal polarity of solvent and solute tends to increase solubility, although aluminum chloride, which has about the same polarity as aluminum bromide, is insoluble in carbon disulfide.

(d) On the basis of the Lewis theory,[9] the electronic structure of aluminum bromide is



$$\begin{array}{c} \ddot{\mathrm{:Br:}} \\ \mathrm{:\ddot{Br}:\ddot{Al}} \\ \mathrm{:\underset{..}{Br}:} \end{array}$$

The Al atom, not having the maximum number of electrons, may obtain a pair from a bromine atom of another molecule, with resultant polymerization and increased solubility (Kohler,[2] by the boiling point rise method, found the salt had the formula Al_2Br_6 in carbon disulfide), or may obtain the desired electrons from an atom of sulfur, with resultant solvation and increased solubility (see rule b), in accordance with the rule that the existence, in one of the components, of an atom without the maximum number of surrounding electrons or atoms promotes the solubility.

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[9] Lewis, This Journal, 38, 762 (1916).

The ideal solubility[10] of aluminum bromide is 38 mole % at 20°, and 88 mole % at 85°, calculated using the approximate Raoult's law equation

$$\log N = -(L_f/4.58)\,(1/T - 1/T_m)$$

The experimental data show a negative deviation from this law at low temperature and almost perfect agreement at high temperature, typical of the behavior of many binary systems.[11]

The solubility–temperature curve shows a change of slope between 70 and 71°, indicating the existence of two crystalline modifications of the solute, confirming the thermal method report[6]'' on a polymorphic transformation at 70.1'.

The Conductivity of CS_2–$AlBr_3$ Solutions

Dilute solutions were found to have conductivities more than a thousand times that of pure carbon disulfide, although the solvent, due to its low dielectric constant, is a poor ionizing agent.

Summary

1. A method for the synthesis of quantities of aluminum bromide is described.

2. A method for sampling saturated solutions at constant temperature is described.

3. A new method for the analysis of anhydrous aluminum bromide has been found.

4. Quantitative data on the solubility of the salt in carbon disulfide have been obtained.

5. Solutions of aluminum bromide in carbon disulfide have been found to be appreciably conducting.

6. The existence of polymorphic forms of aluminum bromide has been confirmed by the solubility method.

ROLLA, MISSOURI

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[10] Ref. 8, p. 158.

[11] Ref. 8, p. 40–58.

NOTES

Note on the Formation of Ammonia from Active Nitrogen and Active Hydrogen.—Professor A. Koenig and E. Elod have called my attention to experiments in which they mixed hydrogen and nitrogen, after each gas had been activated separately in a discharge.[1] They did not find ammonia, contrary to results obtained by me.[2] This apparent discrepancy can be explained easily by the conditions of their experiments. One explanation is suggested by Koenig and Elod themselves, namely, that at the much higher pressures employed by them (10–15 mm. compared to 0.04–0.1 mm. in my experiments) the atomic hydrogen had recombined before reaching the mixing point. This explanation is supported by recent work.[3] Another effect contributing to the discrepancy is that ammonia is decomposed by active hydrogen.[4] At the high pressures of active nitrogen and due to the comparatively long gas exit tube, all of the ammonia (if a trace did form) must have been destroyed. In my experiments more favorable conditions obtained, the condensable gases being frozen out at liquid air temperature immediately following and in close proximity to the mixing chamber. Even so, the ammonia yields were undoubtedly somewhat reduced in the passage of this short space.

BERNARD LEWIS[5]

RECEIVED JUNE 6, 1928
PUBLISHED SEPTEMBER 5, 1028

A Modified Confirmatory Test for Aluminum.—The confirmatory test for aluminum given by Noyes[1] is not quite satisfactory for class exercise, for the test requires much practice and great dexterity on the part of the students. For this reason, Otto[2] sought to improve this cobalt aluminate test.

Noyes' procedure[1] is as follows. The ammonium hydroxide precipitate is dissolved in nitric acid and to the solution a few cc. of water and drops of cobalt nitrate solution are added, in addition to the ammonium hydroxide solution to reprecipitate the aluminum. The precipitate is washed free from sodium salt as completely as possible. The filter paper is then rolled with the precipitate, a platinum wire wound around it and the

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[1] A. Koenig and E. Elod, *Z. Elektrochem.*, 21, 285 (1915).

[2] Lewis, THIS JOURNAL, 50, 27 (1928).

[3] J. Kaplan, *Phys. Rev.*, 30, 640 (1927).

[4] Strutt, *Proc. Roy. Soc. London*, *85*, 219 (1911); Willey and Rideal, *J. Chem. Soc.*, 1927, 677.

[5] National Research Fellow.

[1] A. A. Noyes, "Quantitative Chemical Analysis," The Macmillan Company, New York, 1923, p. 190.

[2] C. Otto, THIS JOURNAL, 48, 1604–1605 (1926).

filter heated until the carbon is burned off. A blue residue shows the presence of aluminum.

The modification introduced in the test by the authors is that the precipitate produced in the reprecipitation is filtered through a filter paper with a few asbestos fibers at the cone of the filter. Instead of the filter paper, the asbestos fibers which hold the precipitate are burned, hooked in a platinum wire. Blue beads over the asbestos indicate the presence of aluminum.

In this proposed modification, several advantages are obtained. The presence of 0.2 mg. of aluminum is easily detected. The presence of sodium salt with the precipitate does not interfere in the test; thus, complete removal of sodium salt by washing is not necessary. Washing is necessary when a filter is used, for sodium salt will fuse with the filter and lessen the delicacy of the test. The modified test is satisfactory even when the aluminum precipitate is not washed at all. The ignition to produce the blue cobalt aluminate takes a shorter time. A longer ignition does not interfere with the result, as in the case of filter paper, which drops to pieces if ignited too long.

CONTRIBUTION FROM THE
COLLEGE OF AGRICULTURE
UNIVERSITY OF THE PHILIPPINES
PHILIPPINE ISLANDS

ELIAS H. PAÑGANIBAN
FLORENCIO A. SOLIVEN

RECEIVED JUNE 25, 1928
PUBLISHED SEPTEMBER 5, 1928

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, PRESIDENCY COLLEGE]

6-ALDEHYDO-COUMARIN AND DYES DERIVED FROM IT

BY RAJENDRANATH SEN AND DUKHAHARAN CHAKRAVARTY

RECEIVED JUNE 6, 1927 PUBLISHED SEPTEMBER 5, 1928

Richard Stoermer and Ed. Oetker[1] first obtained 6-aldehydo-coumarin (melting at 189°) as an intermediate product in the synthesis of coumarin-6-carboxylic acid from 6-acetoxymethylcoumarin, but it was never prepared in quantity and no work appears to have been done with it. In the present case *p*-coumaric aldehyde or 6-aldehydo-coumarin has been prepared in quantity by the application of Reimer and Tiemann's reaction on coumarin (the yield being about 3.5 g. of the aldehyde from 16 g. of coumarin).

The application of Reimer and Tiemann's reaction on coumarin may be expected to lead to the formation of two aldehydes, the aldehyde group occupying the ortho position in one (I) and para position in the other (II) with reference to the lactonic oxygen atom; but it has been possible to isolate only one aldehyde in the pure condition, which is found to be identical with 6-aldehydo-coumarin, melting at 187–189°.

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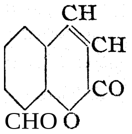
[1] Stoermer and Oetker, ***Ber.***, 37, 192–203 (1904).



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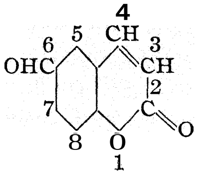

II

In every preparation it has been found that in addition to the p-coumaric aldehyde, which is rather sparingly soluble in alcohol, another by-product is obtained instead of the expected o-aldehyde or 8-aldehydo-coumarin, in fairly large yield, which is readily soluble in alcohol but which, on account of its ready transformation into the resinous state, is extremely difficult to purify. After going through a long and laborious process of purification, which necessarily involves much loss of the substance, a small quantity of a solid product has been isolated from this resinous by-product, which softens at 174° with decomposition. It is soluble in alkalies, forming a deep red solution, and the lactonic ring in the substance seems to be rather unstable, as it is broken up when kept for some time in contact with cold sodium bicarbonate solution. It does not respond to the ordinary tests of an aldehyde. It appears to be very probable that the o-aldehyde is actually formed and subsequently undergoes some sort of transformation in the presence of the caustic alkali. This substance is still under investigation.

The introduction of an aldehyde group into the benzene nucleus of coumarin seems to affect the stability of the lactonic ring as is shown by the comparatively ready solubility of 6-aldehydo-coumarin in caustic alkalies. The aldehyde also differs from coumarin in the following respects. While coumarin forms a greenish-yellow solution in caustic alkalies, the aldehyde gives a slightly reddish solution. The solubility in water and organic solvents in general is also diminished.

The only derivatives of p-coumaric aldehyde prepared by Richard Stoermer and Ed. Oetker[1] were an oxime and a semicarbazone. The aldehyde, prepared by the present method, gives the identical oxime (melting at 223°) and semicarbazone (sintering at 305°) and also a hydrazone with phenylhydrazine (melting at 207°), which was not prepared before. The aldehyde alsp undergoes benzoin condensation in the usual manner, giving a product which may be called coumaroin. The aldehyde readily responds to Claisen's reaction and dicoumaral[2] acetone ($C_9H_5O_2\text{-}CH{=}CHCOCH{=}CHC_9H_5O_2$) and coumaral acetophenone ($C_9H_5O_2CH{=}CHCOC_6H_5$) have been obtained by its condensation with acetone and acetophenone, respectively. Dicoumaral acetone is yellow and coumaral acetophenone is colorless; this is probably due to the presence of a larger number of ethylene linkages and C=O groups in the former.

[2] The radical [$C_9H_5O_2CH{=}$] of 6-aldehydo-coumarin may be called "Coumaral."

Several interesting azo-methine dyes have been obtained by the condensation of 6-aldehydo-coumarin with (1) mono-amines such as *p*-toluidine, *β*-naphthylamine, *p*-nitraniline and amino-azobenzene, (2) diamines such as benzidine, o-, *m*- and p-phenylenediamines and **(3)** such dyes as rosaniline, chrysoidine and safranine, which contain free amino groups. These azo-methine dyes are usually hydrolyzed by warming with dilute acids.

One molecule of a mono-amine ordinarily reacts with one molecule of the aldehyde. One molecule of o-, *m*- or p-phenylenediamine reacts with two molecules of the aldehyde; but with benzidine and chrysoidine only one molecule of aldehyde condenses, the presence of the free amino groups being proved by diazotization. With rosaniline and safranine the reaction goes normally, one molecule of the former reacting with three molecules of the aldehyde and one molecule of the latter reacting with two molecules of the aldehyde. It is interesting to note that the replacement of the NH_2 groups in p-nitraniline, amino-azobenzene and the dyes rosaniline and safranine markedly diminishes the intensity of color, owing perhaps to the elimination of the auxochromic effect of the NH_2 groups. It is curious that although coumaral-chrysoidine, $C_6H_5N{=}NC_6H_3(NH_2)$-$N{=}CHC_9H_5O_2$, contains chromophoric groups, $N{=}N$, $CH{=}N$ and the auxochromic group NH_2, yet it produces a much yellower shade on silk and wool than chrysoidine.

By the condensation of the aldehyde with dimethylaniline in the presence of zinc chloride or hydrochloric acid as the condensing agent, tetramethyldiaminodiphenylcoumarylmethane, $C_9H_5O_2CH(C_6H_4N(CH_3)_2)_2$, has been obtained, This leuco-base, on oxidation with lead dioxide in the usual manner, gives a fine deep bluish-green dye (coumaral green), which is of much interest on account of the presence of the lactone ring associated with the basic group $N(CH_3)_2$, the compound being soluble both in acids and alkalies.

Pyronine dyes have been obtained by condensing the aldehyde with diethyl-*m*-aminophenol and also with such hydroxy compounds as resorcinol, hydroquinone and gallic acid in the presence of sulfuric acid (sp. gr. 1.84) at a temperature of 120–130° in the manner described by Sen and Sinha.[3] a- and @-naphtholsgive colorless, phthalein-like compounds under similar conditions.

It has been noticed, however, in the course of these condensations, that the $C{=}O$ group in the lactone ring of coumarin, which was observed to react in the presence of zinc chloride by Sri Krishna[4] and also by Sen and Guha Sarkar,[5] reacts with the hydroxy compounds in the presence of concd.

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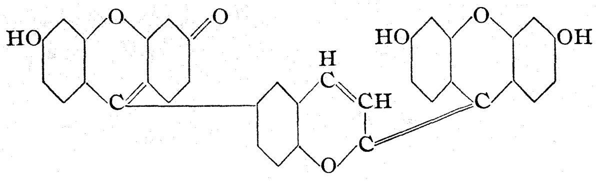
[3] Sen and Sinha, THIS JOURNAL, 45,2984 (1923).

[4] Krishna, J. *Chem. Soc.*. 119, 1420 (1921).

[5] Sen and Sarkar, THIS JOURNAL, 47, 1079 (1925).

sulfuric acid also in many cases at much lower temperature than when zinc chloride is used as the condensing agent.

Thus resorcinol-coumarein[4] is found to be readily obtained by condensing coumarin with resorcinol in the presence of sulfuric acid (sp. gr. 1.84) at a temperature of 120–130° on the oil-bath. Hence in the condensation of 6-aldehydo-coumarin with the aromatic hydroxy compounds like resorcinol under similar conditions the C=O group in the lactone ring as well as the aldehyde group reacts. Therefore the compound with resorcinol is given the structure of tetraresorcinol-coumarein (III).

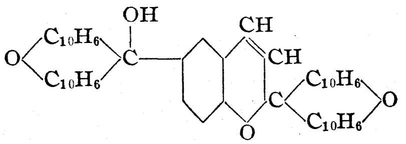


III

Silk and wool are dyed bright orange shades by the potassium salt of this compound.

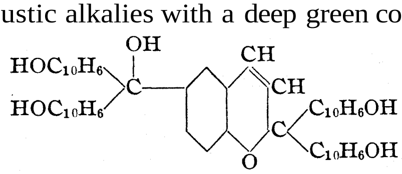
The condensation products with hydroquinone and resorcinol can be very readily brominated in an alcoholic medium; the former giving a tetrabromo and the latter a hexabromo derivative; silk and wool are dyed dark brown shades by the former and beautiful dark red shades by the latter.

a- and β-naphthol condense with the aldehyde, giving rise to phthalein-like bodies. The β-naphthol compound is completely insoluble in alkali and the analytical result corresponds to the following formula (tetranaphthol-coumarein): (IV)



IV

but in the case of a-naphthol, two different compounds are obtained;[5] one (IV) insoluble in caustic alkali (ortho condensation) and the other (V) soluble in caustic alkalies with a deep green color (para condensation)



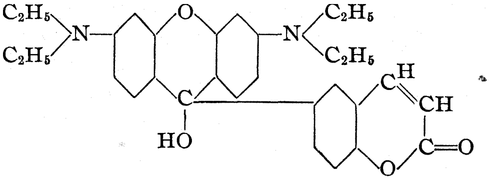
V

but the second product has not been obtained in a sufficiently pure condition for analysis.

The condensation product of 6-aldehyde-coumarin and gallic acid is, as expected, tetragallic acid coumarein, which is a polygenetic dye, wool being dyed a dark brown shade on chrome mordant, a reddish-brown shade on aluminum mordant and a dark olive shade on iron mordant.

Qualitative experiments show that the compound with o-cresotinic acid also exhibits polygenetic character, wool being dyed a pink shade on aluminum mordant and a light blue shade on chromium mordant.

The condensation product of the aldehyde with diethyl-*m*-aminophenol, which may be called coumaral-rhodamine (VI) is a fine bluish-violet dye, soluble both in acids and alkalies. It is interesting to note that unlike the other hydroxy compounds already mentioned, only 2 moles of diethyl-*m*-aminophenol condense with 1 mole of the aldehyde; the C=O group of coumarin itself failing to react with diethyl-m-aminophenol under these conditions.



VI

A comparative study of the colors of coumaral green and coumaral rhodamine and the analogous compounds from benzaldehyde is interesting. Thus while malachite green and benzaldehyde-rhodamine (rosamine) produce green and bluish-red shades, respectively, on silk and wool, the analogous compounds with 6-aldehydo-coumarin produce beautiful bluish-green and bluish-violet shades. The latter compounds differ from the former in the presence of an additional lactonic ring, which is perhaps responsible for this marked change in color.

Experimental

Preparation of **6-Aldehydo-Coumarin.**—Sixteen grams of coumarin is dissolved with 27 g. of caustic soda in 40 cc. of water and heated on the boiling water-bath with a reflux condenser for eight to nine hours with frequent addition of chloroform (20 cc. in all), keeping the temperature at 80° initially for three hours. The deep red solution is heated on the water-bath to drive away the excess of chloroform and when cooled is filtered and acidified with concentrated hydrochloric acid. A liquid separates out which solidifies on keeping.

The precipitate is filtered off, washed with water and extracted with a mixture of alcohol and ether (8:1) after slight warming. The insoluble white residue is filtered off rapidly at the pump and washed with alcohol. This is the 6-aldehydo-coumarin. It is finally crystallized from 80% alcohol; yield about 3.5 g.; a white, needle-shaped crystalline solid, slightly soluble in cold water and in cold alcohol, moderately soluble in cold benzene and practically insoluble in ether, readily soluble in chloroform, acetone and glacial acetic acid, m. p. 187–189°.

The alcoholic solution, which remains after the separation of the aldehyde, is evaporated to drive away the alcohol and ether, when a pasty semi-solid substance remains. This is then washed with benzene and ether in order to remove coumarin and a certain portion of the tarry matter produced. The residue is again dissolved in alcohol and gradually poured with constant stirring into water acidified with hydrochloric acid. After repeated treatment in this manner (at least ten or twelve times), a product is isolated which is a pale yellow solid and decomposes at 174–175°, the decomposed product melting at 205–207°. It is sparingly soluble in cold water, ether and benzene, fairly soluble in chloroform and readily soluble in alcohol, acetone and glacial acetic acid.

Anal. Calcd. for $C_{10}H_6O_3$: C, 68.96; H, 3.44. Found C, 68.8, 68.7; H, 3.9, 3.8.

Coumaral-phenylhydrazone.—The hydrazone is prepared in glacial acetic acid medium; yellow, microcrystalline substance, moderately soluble in alcohol, readily soluble in acetone and glacial acetic acid; m. p. 205–207°.

Anal. Calcd. for $C_{16}H_{12}O_2N_2$: N, 10.6. Found: N, 10.67, 10.8.

Coumaroin.—Coumaroin is prepared in the usual manner like benzoin and crystallized from water; microcrystalline, reddish-yellow substance, moderately soluble in water and alcohol. It reduces Fehling's solution and softens at 178–180°.

Anal. Calcd. for $C_{20}H_{12}O_6$: C, 68.96; H, 3.44. Found: C, 69.1, 68.8; H, 3.7, 3.9.

Dicoumaral-acetone.—Two grams of 6-aldehyde-coumarin is dissolved in 2 g. of caustic soda in 10 cc. of water and warmed with 5 cc. of acetone on the water-bath at 70–80° for two to three hours with a reflux condenser. The solution is then cooled and filtered and the filtrate acidified with dilute acetic acid. The yellow precipitate thus obtained is thoroughly washed with water and crystallized from absolute alcohol, giving yellow, needle-shaped crystals, insoluble in water and moderately soluble in alcohol and acetone; m. p. 159°.

Anal. Calcd. for $C_{23}H_{16}O_5$: C, 74.6; H, 3.78. Found: C, 74.2, 74.3; H, 4.1, 4.

Coumaral-acetophenone.—The method of preparation is the same as with acetone; colorless micro crystals from absolute alcohol, insoluble in water and fairly soluble in alcohol; m. p. above 250°.

Anal. Calcd. for $C_{18}H_{12}O_3$: C, 78.26; H, 4.34. Found: C, 77.9, 77.7; H, 4.6, 4.7.

Dyes Derived from 6-Aldehydo-coumarin. Azo-methine Dyes

Coumaral-*p*-toluidine.—The preparation of coumaral-toluidine is typical: 2 g. of 6-aldehydo-coumarin (dissolved in boiling alcohol) and 2 g. of *p*-toluidine (dissolved in glacial acetic acid) are boiled on the water-bath with a reflux condenser for four to five hours. The alcohol is then evaporated on the water-bath, when needle-shaped crystals of the compound separate. These are filtered off, washed with water acidified with hydrochloric acid and finally crystallized from a mixture of absolute alcohol and glacial acetic acid (6:1); yellow, needle-shaped crystals, insoluble in water, sparingly soluble in alcohol, readily soluble in glacial acetic acid; m. p. 145–147".

Anal. Calcd. for $C_{17}H_{13}O_2N$: N, 5.3. Found: N, 5.45, 5.3.

Other azo-methine dyes prepared are listed in Table 1.

Triphenylmethane Dyes

Tetramethyldiaminodiphenylcoumarylmethane.—Two grams of 6-aldehydo-coumarin and 10 cc. of dimethylaniline are heated on the boiling water-bath for thirty hours with an air condenser with frequent additions of concentrated hydrochloric acid (10 cc. in all). The solution is then made alkaline with caustic soda, distilled in steam, filtered and acidified with hydrochloric acid. The green solution is filtered and ammonia is added to the filtrate, when a greenish-white precipitate is obtained. The precipitate is filtered off, washed with water, and finally crystallized from acetone; yield, 90% of

TABLE IA

AZO-METHINE DYES FROM 6-ALDEHYDO-COUMARIN

No.	Coumaral-	Formula	Prepared in alcohol +	M. p., °C.	Analyses, N, % Calcd.	Found	
1	-β-Naphthylamine	$C_{20}H_{13}O_2N$	HCl^a	173	4.7	4.99	4 8
2	-*p*-Nitraniline	$C_{16}H_{10}O_4N_2$	HCl^n	<250	9 5	9.99	9.9
3	-Amino-azobenzene	$C_{22}H_{15}O_2N_3$	HCl^a	169	11 9	12.05	12.2
4	Di-()-*p*-phenylenediamine	$C_{26}H_{16}O_4N_2$	HAc	<250	6.66	6.5	6 6
5	Di-()-*m*-phenylenediamine	$C_{26}H_{16}O_4N_2$	HAc	<250	6.66	6.45	6.5
6	Di-()-*o*-phenylenediamine	$C_{26}H_{16}O_4N_2$	HCl	<250	6.66	7.1	7.0
7	-Benzidine	$C_{22}H_{16}O_2N_2$	HCl	<250	8 2	7.8	7.7
8	Tri-()-rosaniline	$C_{50}H_{33}O_7N_3$	NaAc^b	142	5 33	4.95	4.9
9	Di-()-safranine	$C_{40}H_{28}O_5N_4$	HCl	...	8.7	8.29	8 4
10	-Chrysoidine	$C_{22}H_{16}O_2N_4$	HAc	210–212	15.2	15.68	15 6

[a] On water-bath.

[b] Rosaniline hydrochloride used.

TABLE IB

PROPERTIES OF AZO-METHINE DYES FROM 6-ALDEHYDO-COUMARIN

No.	Color	Crystal form	Cryst. solvent	Sol. in	Color on silk and wool
1	Pale yellow	Micro	Alc. + acetone (4:1)	...	...
2	Yellow	...	...	Alc.^{a} (sp.)	...
3	Red-yellow	Needles	Alc. + HAc (4:1)	...	Yellow
4	Brown	...	...	...	Gray-yellow
5	Brown	Micro	Boiling alc.	...	Red-yellow
6	Yellow	...	...	Alc.^{a}	...
7	Yellow	Needles	Boiling alc.	...	Pale yellow
8	Red-violet	Powder	...	$CHCl_3$	Pink
9	Red-violet	Needles	Boiling alc.	...	Bright pink
10	Orange	Powder	...	$CHCl_3$^{a,b}	Yellow

[a] Insoluble in ether.

[b] Insoluble in benzene and carbon tetrachloride.

the theoretical; colorless, needle-shaped crystals, insoluble in water, sparingly soluble in alcohol, moderately soluble in acetone, soluble in hot caustic alkalies and also in acids; m. p. 220°.

Anal. Calcd. for $C_{26}H_{26}O_2N_2$: N, 7. Found: N, 7.2, 7.1.

Tetramethyldiaminodiphenylcoumarylcarbinol (**Coumaral** Green).—The leuco-base is oxidized with lead dioxide in the usual manner. The hydrochloride is a deep bluish-green substance, producing a bluish-green shade on silk, wool and tannined cotton.

Pyronine Dyes

Tetraresorcinol-coumarein (III).—The preparation of this compound is typical. A mixture of 1 mole (2 g.) of dried 6-aldehydo-coumarin, 4 moles (5 g.) of dried resorcinol and 2 cc. of concentrated sulfuric acid (sp. gr. 1.84) is heated on an oil-bath for four to five hours at 120–130° with an air condenser. Copious evolution of sulfur dioxide takes place, as detected by its pungent odor and the development of a blue color on starch-iodate paper. The product is washed with water, dissolved in caustic soda solution and the original compound is precipitated with dilute hydrochloric acid. It is then dissolved in alcohol and the alcoholic solution is poured into water till a turbidity is produced. The solution is then filtered and the filtrate allowed to stand overnight with more water. The precipitate thus obtained is dried at 110° in an air oven. Pyronine dyes prepared, together with their derivatives, are listed in Table II.

TABLE IIA

PYRONINE DYES FROM COUMARIN

Prepared by condensing one mole of coumarin with four moles of combining compound in the presence of sulfuric acid (sp. gr. 1.84) at 120–130°

			Yield,	Carbon, %		I-Iydrogen, %	
	-Coumarin	Formula	%	Calcd.	Pound	Calcd.	Found
1	Tetraresorcinol-(III)	$C_{34}H_{20}O_7$	80[a]	75.55	75.5 75.44	3.7	3.9 3.93
2	Tripotassium salt	$C_{34}H_{17}O_7K_3$	..	K, calcd., 17.9		Found, 18.26	
3	Hexabromo deriv.	$C_{34}H_{14}O_7Br_6$	..	Br, calcd. 47.3		Found, 46.9	
4	Tetrahydroquinone	$C_{34}H_{22}O_8$	75	73.12	72.76 72.9	3 94	4.1 4.2
5	Tetrapotassium salt	$C_{34}H_{18}O_8K_4$	..	K, calcd., 22		Found, 22 5	
6	Tetrabromo deriv.	$C_{34}H_{18}O_8Br_4$	..	Br, calcd., 36.6		Found, 36.2	
7	Tetra-β-naphthol-(IV)	$C_{50}H_{30}O_4$	60	86.45	85.9	4.32	4.6
8	Tetra-α-naphthol-(IV)	$C_{50}H_{30}O_4$	40	86.45	86.1 86.3	4.32	4.4 4.2
9	Tetragallic acid-	$C_{38}H_{20}O_{19}$	70	58 46	58.3 58.34	2.56	2.8 2.7
10	Coumaral-rhodamine (VI)[b]	$C_{30}H_{32}O_4N_2$	75	N, calcd., 5.8.		Found, 5.7 5.4	

[a] Pour to five hours.

[b] Prepared by same procedure from coumarin and two moles of diethyl-*m*-aminophenol.

TABLE IIB

PROPERTIES OF PYRONINE DYES

No.	Color of powder	Color on silk and wool	Remarks
1	Red	Bright orange	Red-green fluores, alk. or alc. solns. Softens, 225°
2	...	...	...
3	Deep red	Deep red	...
4	Red-violet	Chocolate	Sol. in alc. and acetone. Insol. ether and $CHCl_3$
5	...	...	...
6	Yellow	Dark brown	...
7	Almost none	...	Sol. alc., $CHCl_3$, C_6H_6. Insol. acetone, boiling caustic alk.
8	Almost none[a]	...	Sol. $CHCl_3$. Insol. ether, acetone, boiling caustic alk.
9	Black	Polygenetic on mordanted wool: chrome, dark brown; aluminum, red-brown; iron, dark olive	
10	Blue-violet[b]	Blue-violet[e]	Sol. $CHCl_3$. Insol. CCl_4, CS_2

[a] Micro-crystals from boiling alcohol.

[b] Purified by dissolving in acetic acid and precipitating with ammonia, finally recrystallizing from alcohol.

[c] Acetate used; softens at 140°, m. p. 155°.

Summary

1. 6-Aldehydo-coumarin or *p*-coumaric aldehyde, melting at 189°, has been prepared by the application of Reimer and Tiemann's reaction on coumarin; it gives a hydrazone, an oxime and a semicarbazone, responds to Claisen's reaction and undergoes benzoin condensation in the usual manner.

2. Interesting azo-methine dyes have been obtained by the condensation of 6-aldehydo-coumarin with (1) mono-amines such as *p*-toluidine, β-naphthylamine, *p*-nitraniline and amino-azobenzene; (2) diamines such as benzidine, *o*-, *m*- and *p*-phenylenediamines; (3) dyes such as rosaniline, safranine and chrysoidine which contain free NH_2 groups.

3. Beautiful triphenylmethane dyes have been obtained by condensing the aldehyde with dimethylaniline and o-cresotinic acid.

4. Pyronine dyes have been obtained by condensing the aldehyde with diethyl-m-aminophenol and also with such hydroxy compounds as resorcinol, hydroquinone and gallic acid in the presence of sulfuric acid. The C=O group in the lactone ring as well as the aldehyde group reacts in these condensations except in the case of diethyl-m-aminophenol.

CALCUTTA, INDIA

[CONTRIBUTION FROM THE DEPARTMENT OF AGRICULTURAL CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

EFFECTS OF LIGHT UPON NITRATE ASSIMILATION IN WHEAT[1]

BY W. E. TOTTINGHAM AND HENRY LOWSMA

RECEIVED FEBRUARY 2, 1928 PUBLISHED SEPTEMBER 5, 1928

In a previous article[1a] on temperature effects in the metabolism of wheat the senior writer stressed the need of determining the adequacy of spectral balance when the illumination is wholly from an artificial source. The present paper deals with the assimilation of nitrate by young wheat plants, as affected by differences in spectral distribution and total intensity of light. As grown in our climatic chambers under water cells, the Marquis variety of spring wheat, which we have employed solely, requires between 1200 and 2000 foot candles of illumination at about 18° in a twelve-hour day, from Mazda C electric lamps. This estimate is based upon the maximum yield of dry matter. It is not clear, however, that this is the most significant index of optimal illumination, as will appear in a test to be presented presently. In this case more nitrate was assimilated, but at the expense of tissue production, when the Mazda lamps were supplemented by the visible and long ultraviolet rays from a carbon arc.

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[1] Published with permission of the Director of the Wisconsin Agricultural Experiment Station.

[1a] W. E. Tottingham, *Plant Physiol.*, **1**, 307 (1926).

While it is well known that short ultraviolet light is generally injurious to plants, little is known concerning specific effects of blue-violet and long ultraviolet rays. Plant physiologists have long known that the tropic effects of light are due primarily to the shorter wave lengths of the visible spectrum, but these is little, if any, published work showing the metabolic response of the organism to this particular factor.

Experimental Part

Our preliminary experience dealt with selective effects of greenhouse glass upon irradiation of maize (Zea *mais*) by sunlight. Seedlings of the Golden Glow variety from ordinary field stock were reared in sand in a greenhouse without permitting direct access of the sun's rays. Uniform selection as to appearance and size was then made for transference to water cultures of one plant to each jar of about 0.9 liter (1.0 quart) capacity. The nutrient solution was one designed to supply a high proportion of nitrate, containing 0.2% of sodium nitrate in 0.3% of total salts. A modification of this formula contained 0.2 as much nitrate. At intervals of three to four days the residual solutions were replaced by fresh portions. On sufficiently clear days a chosen section of the cultures was placed outside the greenhouse for direct exposure to solar radiation during about one and five-tenths hours at midday, taking care that the temperature change was gradual and similar for all cultures. Each section included eight plants. A second test was made in cooler weather, when the difference in irradiation was possible only on warmer days. The temperature was 6.0 to 12.0° warmer in the house than out of doors during periods of exposure in both tests, and the vapor pressure deficit of the atmosphere was 80 to 70% greater in the former location in the second test. In so short a period of exposure 'temperature would hardly be a critical factor in metabolism and, furthermore, maize appears to be relatively stable in composition with varying environment.[2] Moreover, general experience has shown a conservation of carbohydrates at lower temperatures, with decreased percentage of nitrogen. It might be expected that increased transpiration would favor the absorption of nitrate in the cultures continuously housed, but the work of Muenscher[3] indicates that these functions are independent of each other. There are thus small grounds for anticipating increase of nitrate assimilation in the exposed plants.

At the expiration of each culture period the fresh tissues were extracted with water and analyzed by methods which are specified elsewhere.[4]

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[2] W. E. Tottingham, Science, 59, 69 (1924); W. E. Tottingham and H. W. Kerr, *Plant Physiol., 1,* 415 (1926).

[3] Muenscher, *Am. J. Botany, 9,* 311 (1922).

[4] Committee on Methods of Chemical Analysis, Recommendations, *Plant Physiol.,* 1,397 (1926); **2,** 91, 195,205 (1927).

The residual nutrient solutions were restored to their original volumes for the determination of nitrate, Strowd's modification of DeVarda's method[6] being employed here for both extracts and nutrient solutions. In view of the large variability in physiological behavior of maize, it was deemed inexpedient to deal with smaller units than the total mixed tissue and solution of each section of cultures. Hence, one can hardly express variability of the results. It should be noted that the radiation in the second test was only 40% of that in the first and the average daily maximum temperature out of doors was 13.9° lower in the former case. The results with maize are assembled in Table I.

TABLE I

RELATION BETWEEN SOLAR ILLUMINATION AND NITRATE ASSIMILATION IN MAIZE AS AFFECTED BY GREENHOUSE GLASS

Exposure to direct sunshine	Radiation outside greenhouse, cal.	Nitrate supply, mg. per liter	Nitrate absorption, %	Dry matter, %	Composition of dry matter					
					Glucose, %	Sucrose, %	Protein Insol., %	N Sol., %	Basic N, %	Nitrate N, %
Aug. 10–25	1237[a]	63	86	9.8	1.8	16.4	2.1	0.8	0.08	0.9
None	1237	63	79	10.0	2.6	16.6	2.0	.6	.06	.8
Aug. 10–25	1237	299	18	9.3	1.5	15.8	1.8	.9	.09	.6
None	1237	299	14	11.6	4.9	9.4	2.0	.6	.05	.3
Oct. 5–17	506	207	2	6.3	...	5.8[c]	2.6	.9	.05	.9
None	506	207	−8[b]	8.9	...	2.3[c]	2.5	.6	.11	.8

[a] Calories for two and three days' exposure after last change of nutrient solution, 221 and 194, respectively.

[b] Excretion from the plant.

[c] Total sugars after hydrolysis.

Other tests were made with spring wheat (*Triticum sativum*) of the Marquis variety, using the same form of nutrient solution as before. A preliminary trial shows the range of variability which may be expected in results of this character. The seed used was a pure line selection provided by Dr. J. G. Dickson of the Department of Plant Pathology in this institution. Seedlings four days old were irradiated for sixteen hours per day by tungsten incandescent lamps at an intensity of 200 foot-candles, with the use of a blower to reduce heat effects. The temperature at the surface of the culture jars ranged from 17 to 18°. After twenty-one days' exposure, the entire plant was dried at 70° for analysis. These results are given in Table II. In all of the tests on wheat it has been impracticable to report variability, because of the limited repetition of culture treatment. With water cultures generally, forty plants were supported in a 3.5-liter jar and with soil cultures reared to maturity, ten or twelve plants per pot of 3.5 kg. of soil. Even with duplicate culture treatment the yield was insufficient for more than single analyses of immature plants.

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[6] Strowd, *Soil Science*, 10, 333 (1920).

TABLE 11

VARIABILITY OF YIELD AND COMPOSITION IN WATER CULTURES OF WHEAT ILLUMINATED AT 200 FOOT CANDLES BY TUNGSTEN LAMPS

Series	Dry matter, g.	Protein N, %	Protein, g.	Other sol. N, %	NO_3 absorption, mg. per liter	Total sugars %	Total sugars g.
A	11.40	1.95	1.39	1.33	52	1.72	0.20
B	11.35	1.88	1.32	1.29	58	1.53	.17

In test 2 upon wheat, a 500-watt Mazda lamp was supplemented by a carbon arc for increasing the proportions of shorter visible wave lengths and the long ultraviolet. The latter was a Thomsen inclosed lamp of 7.5 amp. capacity, operating on 110 volts A.C. Its globe was replaced by a conical tin reflector similar to those used with the tungsten lamps. Measurements with a Sharp-Millar photometer employing a selective screen for the red rays showed the intensity of illumination from the arc to be about 0.25 that from the filament lamp. Comparative measurements at various wave lengths were made by means of a spectrophotometer and the results are quoted hereafter.

This test covered a period of ten days with seedlings which had attained an age of one week. By daily use of the arc lamp for one to one and one-half hours the intensity of red rays was increased about 2.0%, corresponding to about 150% increase in the long ultraviolet. The interposing of common window glass between lamps and plants eliminated effectiveness of rays shorter than about 3000 Å. At the termination of irradiation the tissues of the plant tops only were well ground and extracted with water in the fresh state, determining nitrate (as hereafter) by the colorimetric method of Burrell and Phillips.[6] The data of this series are in Table III, with graphic presentation in Fig. 1.

TABLE III

INFLUENCE UPON THE METABOLISM OF WHEAT OF INCREASING THE SHORTER WAVE LENGTHS OF LIGHT ABOVE 3000 Å. ILLUMINATION OF 200 FOOT CANDLES. INCREASE OF ULTRAVIOLET BY THE CARBON ARC, 200%

Source of illum.	Yield of dry matter, g	Glucose, %	Sucrose, %	Total sugar, g.	Insol. prot. N, %	Sol. prot. N, %	Total prot., g.	Basic N, %	Amino N, %	Nitrate N, %	NO_3 abs., mg. per liter
Mazda C	13.0	1.4	2.7	0.53	1.9	0.6	2.04	0.2	0.2	1.0	6
Mazda +arc	10.3	1.3	1.8	0.32	1.9	.7	1.75	.2	.5	0.8	16

The radiation curves in our figures were derived from the following sources: spectral energy distribution of the 1000-watt gas filled tungsten lamp, from data supplied through correspondence by Dr. W. E. Forsythe of the Nela Research Laboratories, whose data were derived from color temperatures; the graphs of Coblentz, Dorcas and Hughes[7] for the

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[6] Burrell and Phillips, *J. Biol. Chem.*, 65,229 (1925).

[7] Coblentz, Dorcas and Hughes, *Sci. Paper Bur. Stds.* No. 539, 1926.

emission spectrum of the carbon arc, as determined by a spectrometer and thermopile. Our own measurements of relative intensity of visible radiations from the tungsten lamp and carbon arc between 4060 and 6720 Å. were made by means of a Konig-Martens spectrophotometer. This instrument was made available through the kindness of Professor J. R. Roebuck of the Department of Physics, this institution. As a base of comparison we have employed our measurements of light intensity from the two sources by means of a Sharp-Millar photometer, with a screen of potassium dichromate, assuming that the observed difference was valid for wave length 6000 Å.

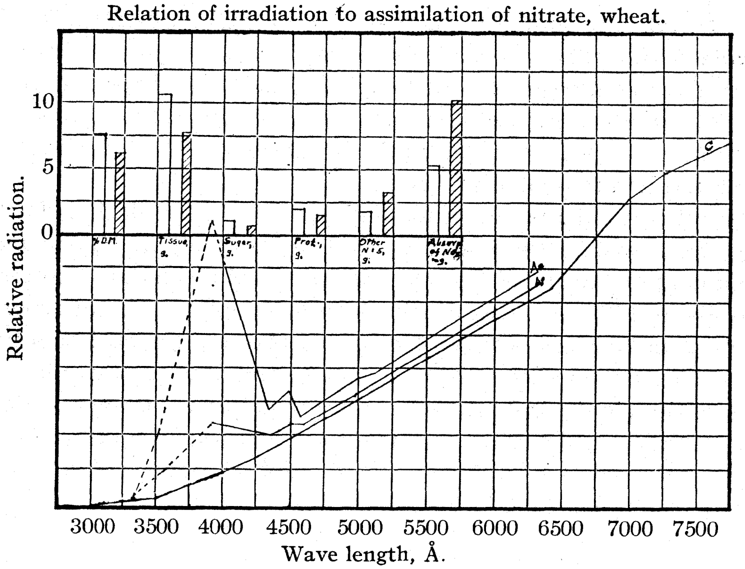

Fig. 1.—Cobstructed from the data of Table III. Line C shows the spectral distribution of radiation from the Mazda lamps. The radiation supplied by the additional use of the carbon arc is shown by line Ae. Curve Af shows the effective radiation based upon relative times of operation of the two types of lamps. In the altitudinal graphs clear areas represent responses to Mazda lamps, hatched areas those to the combined lamps.

The comparison in the long ultraviolet region is determined from Table 2 and Fig. 2 of Coblentz and associates. It is apparent from our Fig. 1 that the arc added about 3% to the intensity of visible radiations from the filament lamp and from 0 to about 300% in the long ultraviolet, with a maximum at about 3900 Å.

A further test was made of the effects of long ultraviolet radiation. In this case rays shorter than 3000 Å. were eliminated as before, while in a parallel group of cultures rays shorter than 4000 Å. were withheld by a special glass.[8] It was necessary, of coarse, to compensate for inequalities in light transmission by the different glasses, as given in the publication cited and by our own measurements with a Sharp-Millar photometer. The distances between the light filters and plants were adjusted accordingly. Water cultures reared in the greenhouse for seventeen days were irradiated for sixteen days. The intensity of 200 foot candles from the tungsten lamp was increased about 4.0% in the red rays by the arc and about 400% in the long ultraviolet. Without the use of special means to dispose of heat it was not possible to irradiate at higher intensities, but the temperature was here maintained at 16.0 to 17.0°. The leaves receiving the more restricted radiation were wider than the others but turned yellow toward the close of exposure. Table IV shows the data obtained from analysis of the tops only.

Relation of irradiation to assimilation of nitrate, wheat.

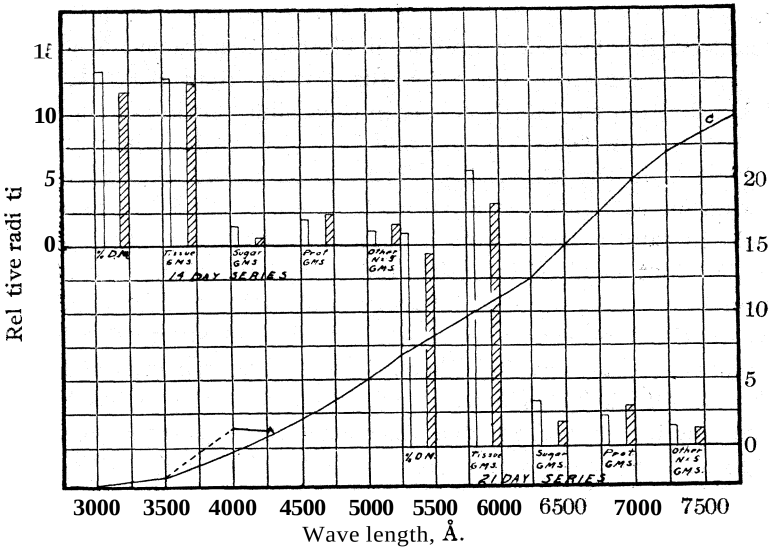

Fig. 2.—Constructed from the data of Table VI. Curve C shows the spectral distribution of radiation from the Mazda lamp. Curve A shows part of the additional radiation when the arc lamp was used. The latter increased the red rays about 0.5%, the long ultraviolet 50%. In the altitudinal graphs clear areas represent responses to the Mazda lamp, hatched areas those to the combined lamps.

It should be noted that for such tests as this, in which only a part of the plants is considered and the nutrient solution is renewed, one is not justified in expecting the plant analysis to conform to variations in the nutrient solution. In other words, the data do not permit the striking of balances between absorption from the solution and accumulation in

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[8] Noviol, Bur. Standards, *Tech. Paper*, **119**, Fig. 24, **1919.**

TABLE IV

INFLUENCE OF LONG ULTRAVIOLET RAYS ON THE METABOLISM OF WHEAT AT 200 FOOT CANDLES, THESE RAYS FROM THE TUNGSTEN LAMP BEING INCREASED 400% BY THE CARBON ARC

Quality of light, Å.	Yield of dry matter, g.	Yield of dry matter, %	Glucose %	Sucrose, %	Total sugar. g.	Insol. prot. N, %	Sol. prot. N, %	Total prot. g.	Other org. N, %	Nitrate N, %	NO_3 absorption, mg. per liter
Above 4000	*11.8*	*11.8*	*1.0*	*1.7*	*0.32*	*2.2*	*1.0*	*2.33*	*1.0*	*1.5*	*29*
Above 3000	*11.3*	*11.5*	*0.9*	*1.7*	*.30*	*2.3*	*1.1*	*2.36*	*0.9*	*1.3*	*52*

the plant. A more complete check on this issue will be desirable in future work.

In a succeeding test the variability in illumination was made still greater, glass G34Y eliminating wave lengths shorter than 6000 Å. (orange), Noviol A limiting the effects chiefly to the visible portion of the spectrum, or to rays greater than 4000 Å., and Noviol O withholding rays shorter than 3700 Å. in the ultraviolet. The further use of Celo glass extended the radiation well into the ultraviolet, to about 2800 Å. Seedlings five days old in sand cultures were irradiated for nineteen days by lamps at about 300 foot candles' intensity and nine days further by sunlight in addition to a total estimated intensity of about 1200 foot candles. The plants deprived of yellow to violet light developed broader leaves but were more flaccid than the others. They were also etiolated and susceptible to attack by mildew. Under Celo glass the plants were erect, with narrow leaves, while in the other cases they appeared to be normal. The temperature here ranged from 17.0 to 20.0° and the tissues were analyzed from the fresh state. Data of this series appear in Table V.

TABLE V

INFLUENCE OF SPECTRAL PORTIONS UPON THE METABOLISM OF WHEAT AT AN AVERAGE INTENSITY OF ABOUT 300 FOOT CANDLES, TUNGSTEN AND ARC LAMPS SUPPLEMENTED BY SUNLIGHT

Quality of light, Å.	Yield of dry matter, g.	Yield of dry matter, %	Glucose, %	Sucrose, %	Total sugar, g.	Protein N, %	Protein g.	Other organic N, %	Nitrate N. %
Above 2800	8.2	13.5	2.2	3.9	0.50	2.4	1.23	2.2	0.2
Above 3700	11.4	11.9	2.7	2.6	.60	2.4	1.70	1.7	.3
Above 4000	11.1	11.8	1.9	3.6	.61	2.4	1.64	2.0	.3
Above 6000	9.5	12.1	3.0	4.4	.70	2.1	1.33	1.6	.8

It appeared that the planes of illumination thus far employed were probably deficient for full photosynthetic activity by the wheat plant, and that it would therefore be desirable to test the effect of spectral balance at much higher planes of light intensity. The adequacy of illumination was tested by the yields of dry matter in the climatic chambers already described,"' with the modification of covering the water cell by a sheet-iron dome adapted to forced ventilation and installing reflectored lamps therein. Differences in light intensity were secured by changing the elevation of culture jars on the rotating table. The cultures were irradiated for sixteen hours daily and the temperature was maintained at about 15.0°. With the further control of relative humidity at a uniform value of about 70.0%, the only markedly variable environmental factor was light intensity. Three tests with water cultures in periods of irradiation from 9.0 to 17.0 days showed, both by yields and sugar content, that 600 foot candles was much inferior to 1200 foot candles from this source of illumination. Other cultures on soil were continued for twenty-one and thirty-one days, at 13.0 to 14.0°, and with the light intensity ranging from about 2000 to 7000 foot candles in one case, and 2250 to 8000 foot candles in the other. In this case arc lamps were used at a constant distance through glass with an increase of about 0.4 to 0.1% in the red rays and about 40 to 50% in the long ultraviolet. The shorter test gave slight indication of deficiency of the lower plane of illumination but the longer one showed no difference either in yields of dry matter or percentage of nitrogen therein. These results indicate that the optimal range of this form of radiation for wheat, at the temperature here effective, lies between 1200 and 2000 foot candles and probably nearer to the latter value, as measured by yield of tissue.

On the basis of the preceding results a final test was made of the effect of supplementary radiation in the shorter wave lengths at total intensities ranging from about 1200 to 5000 foot candles as the plants increased in height. Sand cultures reared for twenty-one days in the greenhouse were subjected to controlled illumination in the chambers at about 18.0' for periods of fourteen and nineteen days. The increase of radiation due to the arc was about 0.5 to 0.8% in the red rays and 50 to 80% in the ultraviolet. In this case the tissues were dried at 98° before analysis. The data are given in Table VI, supplemented by Fig. 2.

TABLE VI

INFLUENCE UPON THE COMPOSITION OF WHEAT OF SUPPLEMENTING THE TUNGSTEN LAMP BY THE CARBON ARC ABOVE 3000 Å. TOTAL ILLUMINATION 1200 TO 5000 FOOT CANDLES. INCREASE OF ULTRAVIOLET BY THE ARC, ABOUT 50%

Source of illum.	Dry matter, %	g.	Glucose, %	Sucrose, %	Total sugar, g.	Protein, g.	Protein N, %	Other org. N. %	Nitrate N, %
Tung. lamp, 14 days	13.1	12.9	8.2	0.3	1.10	1.75	2.2	1.2	0.3
Tung. + arc, 14 days	11.7	12.3	0.8	0.3	0.14	2.32	3.0	1.5	.4
Tung. lamp, 21 days	16.2	20.5	6.8	6.4	2.71	2.07	1.8	0.9	.3
Tung. + arc, 21 days	14.2	18.7	4.5	2.4	1.29	2.73	2.3	2.4	.2

Discussion

The data with maize show reduction of efficiency in the assimilation of nitrate and synthesis of soluble protein, and partly also of basic forms of nitrogen, by passage of sunlight through greenhouse glass. In the first test, at least, the sugar content did not vary sufficiently to account for the above difference. It seems probable that the results were due to deficiency of the shorter wave lengths of light under glass, for, as is well known, these are highly absorbed. Some authorities, such as Hovestadt,[9] give as the transparency of ordinary crown glass 10.0 cm. thick 90 to 95% for red to yellow, 70 to 80% for blue to violet and 60% or less for long ultraviolet. Stone[10] made tests on the diminution of chemical activity of light in passing through greenhouse glass. We understand that he followed the degree of oxidation in exposed solutions of ferric oxalate. The decrease was 14% in July and 43% in December.

From the test of variability with wheat it would seem that one could attach significance to variations of 10.0% and more in the composition of the plants and of twice this extent in the absorption of nitrate.

From the results of the second test with wheat it is apparent that the increase in proportion of long ultraviolet and visible blue-violet above that in the spectrum of the Mazda C lamp markedly increased the absorption of nitrate, and to a less extent enhanced the synthesis of amino forms of nitrogen. This activity is reflected in decreased content of nitrate and sugars in the plants receiving the more complete radiation. It will be noted that the differences in the absorption of nitrate are not accounted for by differences in the composition of plant tissue. This apparent discrepancy can well be explained by the fact that we have no data on nitrate absorption from the previous portions of nutrient solution, and the added fact that the root tissue was not analyzed. Computations based on the data of Coblentz, Dorcas and Hughes[7] and our own tests of spectral distribution indicate that the energy of wave lengths 3500 to 4500 Å., as related to those from 4500 to 7500 Å., or from the region of long ultraviolet to short blue waves to that from short blue to short infra-red, had a ratio of about 1:6 with our combined lamps as compared with 1:3 in sunlight. Thus a considerable increase in the proportion of shorter wave lengths of light produced a significant increase in protein synthesis.

From the third test (Table IV) it appears that the long ultraviolet rays as here effective were conducive to increased absorption of nitrate without promoting its assimilation. Final conclusions on this matter must await further trials. In the succeeding test the rays from 3700 to 4000 Å., or just below the range of the visible spectrum, were not found to be effective in this manner from the data on tissue. On the other hand, light extending into the middle ultraviolet considerably reduced the yields of tissue and of protein therein without sensibly affecting the composition.

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[9] Hovestadt, "Jena Glass and its Scientific and Industrial Applications," transl. by J. D. and A. Everett, London, **1902**, pp. 47, **50.**

[10] Stone, Mass. Agric. Expt. Station, Bull. 144, **1913.**

This effect should probably be ascribed to the well-known injurious action of shorter ultraviolet rays upon living matter. Absence of rays shorter than orange led to reduced yields of tissue and protein. The relative accumulation of nitrate and sugars in this case indicates inefficiency in protein synthesis.

While the foregoing tests might be criticized as inconclusive, due to the relatively low planes of total light intensity, this cannot apply to the final trials. The illumination here exceeded the intensity already reported as producing a maximum yield of plant tissue. Although the effect of the arc upon total intensity was here very small (about 0.5% increase in the red rays, and 50% in the ultraviolet), a considerable increase of protein at the expense of sugars is evident. Again, this process was accompanied by a decline in the production of tissue. It was deemed impracticable to follow the absorption of nitrate from sand cultures. Attention is called to the increased percentage of water in plant tissue subjected to increase of the shorter wave lengths of light, excepting the effect of shorter ultraviolet.

Summary

1. Data are presented from the growth of maize in water cultures during late summer. These indicate that the absorption of nitrate and synthesis of protein are promoted by light rays which are absorbed by greenhouse glass under the conditions here effective.

2. Data are presented from the growth of wheat in sand and water cultures which were irradiated by electric lamps for periods of ten to twenty-one days. With total intensities of 200 to 1200 foot candles and upward the long ultraviolet region was increased about 50 to 400% by use of carbon arcs. The concomitant increase in red-orange rays was about 0.5 to 4.0%, with unmeasured increases in the shorter wave lengths of the visible spectrum.

3. In the early growth phases of wheat, relatively limited increases in the proportion of shorter visible light rays greatly enhance the absorption of nitrate and significantly increase the synthesis of protein. These effects are accompanied by small increments of the percentage of water in the tissue and declines in the yields of sugars and total dry matter. Long ultraviolet rays seem to be effective in the absorption of nitrate, but the present results do not establish any further role.

4. The proportion of blue-violet rays in our artificial light was considerably smaller than in sunlight. Further study is desirable with sunlight or a similarly balanced spectrum,

MADISON, WISCONSIN

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE RICE INSTITUTE]

THE EFFECT OF STRUCTURE OF ORGANIC HALIDES ON THEIR RATE OF REACTION WITH INORGANIC HALIDES. II. THE EFFECT OF THE METHYLTHIO GROUP. A NEW VESICANT[1]

BY W. R. KIRNER

RECEIVED FEBRUARY 27, 1928 PUBLISHED SEPTEMBER 5, 1928

A study of the effect of a sulfur atom on the reactivity of an ω-chlorine atom which is in the same molecule and separated by one, two or three methylene groups should be of interest in connection with the "acid theory" for the mechanism of skin vesication of mustard gas proposed by Lynch, Smith and Marshall[2] and contradicted by later work of Peters and Walker.[3]

To make the conditions for this investigation as simple as possible it was proposed to synthesize a series of sulfur-halogen compounds each of which contained but one chlorine atom; this avoided complications such as the reciprocal induced effect of one chlorine atom on another which might occur if more than one chlorine atom is present in the molecule. The series selected was the w-chloroalkyl methyl sulfides, CH_3SCH_2Cl, $CH_3SCH_2CH_2Cl$ and $CH_3SCH_2CH_2CH_2Cl$. In these compounds the sulfur atom is attached on one side to the simplest alkyl radical and the chlorine atom is separated from the sulfur atom by one, two and three carbon atoms, respectively. The synthesis of the first member, unfortunately, was not successful; the reactivity of the second and third members was measured using the procedure which has been previously described.[4]

The following table contains the data obtained from the reaction velocity measurements.

TABLE I

REACTION VELOCITY DATA

Compound	K_{50}	K_{60}	A	Relative reactivity at 50°, *n*-butyl chloride taken as unity
n-C_4H_9Cl	0.0415	0.1189	4920	1.00
$CH_3SCH_2CH_2Cl$	.0629	.1666	4540	1.52
$CH_3SCH_2CH_2CH_2Cl$	.1044	.2373	3830	2.52

The above results illustrate still another case in which the γ-halogen compound is more reactive than the *β*, the ratio being 1.66:1.00 at 50° and 1.42:1.00 at 60°.[5] Although the first member of the series is missing it seems safe to predict that the a-compound would be more reactive than

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[1] Presented before the Detroit meeting of the American Chemical Society, September, 1927.

[2] Lynch, Smith and Marshall, J. *Pharmacol.*, 12, 282 (1919).

[3] Peters and Walker, *Biochem.* J., 17, 260 (1923).

[4] Conant and Kirner, THIS JOURNAL, 46, 232 (1924).

[5] Conant and Kirner, *ibid.*, 46, 232 (1924); 47, 488 (1925); Kirner, *ibid.*, 48, 2745 (1926).

the β- and γ-compounds inasmuch as in all of the various homologous series which have been measured by this method the a-halogen compounds of a **given** series possess, without exception, a very much greater reactivity than any other member. **Also,** chlorodimethyl ether, CH_3OCH_2Cl, the oxygen analog of the missing sulfur compound, was found to possess a very reactive chlorine atom.[6] This is corroborated by the work of Kilpi[7] and Palomaa,[8] who measured the velocity of hydrolysis of various groups, such as Cl, COOR, OCOR, $CONH_2$ and CN when influenced by the presence of an alkyloxy group such as CH_3O, separated from each other by one, two or three methylene groups. In every case they found the order of reactivity to be a > γ > β. Therefore, the evidence points to the existence in the series of ω-halogen alkyl methyl sulfides of a definite, though weak, alternation in reactivity of the chlorine atom through a saturated carbon chain as the chlorine atom is moved further and further from the activating methylthio group.

The relative order of reactivity of the first two members of the series confirms that of Peters and Walker[3] who found that the α,α′-dichlorodimethyl sulfide was hydrolyzed more rapidly than the β,β′-dichlorodiethyl sulfide. The relative reactivity of the β- and y-chloro-alkyl methyl sulfides toward potassium iodide has recently been confirmed, quantitatively, by Bennett and Berry in a study of the β- and y-chloro-alkyl phenyl sulfides; they found that the y-compound reacts about **3.5** times as fast as the β. The order was just reversed, however, when their reactivity was measured by hydrolysis in a 50% aqueous alcoholic solution according to the procedure of Olivier.[10] Although Bennett and Berry state that this method is "likely to be free from the defects of subsidiary reactions," Olivier has shown that the hydrolysis of benzyl chloride under the conditions of the experiment yields benzyl ethyl ether as well as benzyl alcohol, that is, both constituents of the solvent react with the halogen. The results obtained by Olivier on the reactivity of benzyl chloride and various substitution products do not agree with those of Franzen,[11] who carried out his measurements using sodium ethylate and thus worked in an alkaline solution.

The order of reactivity of the ω-chloro-alkyl methyl sulfides toward potassium iodide in absolute acetone solution is undoubtedly α > γ > β; this is not in agreement with the order given by Bennett and Hock[12] for

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[6] Conant, Kirner and Hussey, THIS JOURNAL, 47,489 (1925).

[7] Kilpi, *Z. physik. Chem.*, 80,165 (1912); 86,641 (1914).

[8] Palomaa, *Dissertation*, Helsingfors, 1908; *Chem. Zentr.*, 83, II, 595 (1912); 84, II, 1956 (1913).

[9] Bennett and Berry, J. *Chem. Soc.*, 1927, 1677.

[10] Olivier, *Rec. trav. chim.*, 41, 301, 646 (1922); 42,516 (1923).

[11] Franzen, J. *prakt. Chem.*, 205, 61 (1918); Franzen and Rosenberg, *ibid.*, 209, 333 (1920); see von Braun and Engel, Ann., 436,319 (1924).

[12] (a) Bennett and Hock, J. *Chem. Soc.*, 1927,478; (b) *ibid.*, 127,2676 (1925).

the rate of hydrolysis of the ω,ω'-dichlorodialkyl sulfides which they list as: $\alpha,\alpha' > \beta,\beta' > \gamma,\gamma' < \delta,\delta'$. *But, the order in which the α,α' and β,β' appear was taken from the paper of Peters and Walker, while the position of the β,β' was determined relative to the γ,γ' by comparative hydrolysis in an alcoholic alkaline solution. The δ,δ' compound was not isolated and its reactivity was estimated from the reactivity of the corresponding dihydroxy compound.*

It should be pointed out that the hydrolysis of these dihalogen compounds has been quite well established as a two stage reaction,[13] a fact which may vitiate any conclusions which are drawn, since the reactivity of the two chlorine atoms will be different because the activating group in the first stage is quite different from that in the second. Still more important is the fact that Bennett and Hock measured the hydrolysis of the β,β'- and γ,γ'-dichlorodialkyl sulfides in a nearly $N/5$ alcoholic solution of sodium hydroxide. Although they assume the reaction to be one of simple replacement, it has been shown[14] that treatment of mustard gas with sodium ethylate yields vinyl sulfide as the main product. Even the slow hydrolysis of mustard gas by alkali in 50% alcohol in the cold does not yield thiodiglycol, but a substance which seems to be a polymer of vinyl sulfide. It is evident, therefore, that this reaction is not a simple replacement of the chlorine atom by the hydroxyl group but involves the elimination of hydrogen chloride from the 8-chlorine and the rather reactive a-hydrogen atom. These observations were confirmed by Bales and Nickelson.[15]

The hydrolysis of the α,α'- and γ,γ'-compounds appears to proceed normally since, in the former, the halogens are attached to the same carbon atoms holding the active a-hydrogens and, in the latter, the halogens are removed a sufficient distance from the active a-hydrogens so that there is no tendency for the elimination of hydrogen chloride in either case. Bloch and Höhn[16] were able to substitute the two halogens in the α,α'-compound by methoxy groups using a methyl alcohol solution of potassium hydroxide or ammonium hydroxide; some dihydroxy compound was also formed which then decomposed into formaldehyde, thioformaldehyde and water. Bennett and Hock[12b] prepared the diphenoxy compound from the y,γ'-dihalide and, although they do not report their yield, neither do they mention any of the difficulties which are expressed by Helfrich and Reid in the corresponding reaction on the β,β'-compound.

Therefore, the order of reactivity which is given by Bennett and Hock

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[13] Russell, Report to American Chemical Warfare Section; Wilson, Fuller and Schur, THIS JOURNAL, 44,2762,2867 (1922).

[14] Helfrich and Reid, THIS JOURNAL, 42, 1219; 1224 (1920).

[15] Nickelson, *J. Chem. Soc.*, 121, 2137 (1922).

[16] Bloch **and** Hohn, Ber., **55B,** *55* (1922).

is not derived from a study of the rate at which a given, clearly defined reaction proceeds, but instead is obtained from several reactions which differ in mechanism.

Vesicant Action

A drop of β-chloro-ethylmethyl sulfide from a 4mm. glass rod was applied to the skin on the left forearm and a similar drop of γ-chloropropylmethyl sulfide was applied to the right forearm. The liquid disappeared in the course of a few minutes. In the case of the β-chloroethyl compound a well defined blister, 1 cm. × 0.8 cm. and about 3 mm. high, had developed after about twenty hours and was surrounded by a reddened area about 2 cm. × 1.3 cm. The blister was punctured aseptically and pressed dry, but filled again. A brownish scar was still plainly evident ten months after the substance had been applied. Judging from war reports (for example, The American University Experiment Station Monograph on Dichlorodiethyl Sulfide) concerning the vesicant action of mustard gas, the above substance seems to act as rapidly and in precisely the same manner as does mustard gas. In fact, the description and photographs given by Warthin and Weller[17] concerning the action of mustard gas on a patient's forearm coincide exactly with the observations made by the author in an experiment performed on himself. The γ-chloropropylmethyl sulfide was found to possess no vesicant properties whatsoever.

It is quite apparent that *only when the halogen is in the β-position with respect to the sulfur atom will the resulting compound possess vesicant properties.* A search of the literature has revealed no case where an α-, γ- or δ-halogenalkyl sulfide is reported and confirmed as a vesicant compound. There seems to be no obvious relationship between the reactivity of the chlorine atom (at least in replacement reactions) and vesicant action.

Experimental

A. Preparation of an Aqueous Solution of Potassium Methyl Mercaptide

Methyl mercaptan was prepared according to the directions of Klason (or Claesson)[18] who methylated sodium hydrosulfide with methyl sodium sulfate. The mercaptan was absorbed in a 50% solution of potassium hydroxide and the resulting solution was treated with a saturated solution of lead acetate until a filtered test portion yielded a brilliant yellow precipitate of lead methyl mercaptide uncontaminated with any black lead sulfide; this insured an aqueous solution of potassium methyl mercaptide free from potassium sulfide or hydrosulfide.

B. Preparation of an Anhydrous Ethereal Suspension of Sodium Methyl Mercaptide

An anhydrous ethereal solution of methyl mercaptan was prepared and converted into an anhydrous ethereal suspension of the sodium salt according to Klason.[19] The

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[17] Warthin and Weller, J. Lab. Clin. Med., 3, 454–459 (1917–1918).

[18] Klason, *Ber.*, 20, 3408 (1887).

[19] Klason, *J. prakt. Chem.*, 15, 196 (1877).

absence of water was imperative in the reaction with chloromethyl acetate since it is hydrolyzed readily, particularly in alkaline solution. Higher yields were obtained using the anhydrous suspension of the sodium mercaptide rather than the aqueous alkaline solution in the reactions with the chlorohydrins.

For the preparation of the anhydrous ethereal suspension of sodium methyl mercaptide the aqueous solution of the potassium salt was treated with 1:1 hydrochloric acid and the liberated methyl mercaptan was dried by passing it through a tower containing anhydrous potassium carbonate and then condensed by passing through a coil maintained at −20° and collected in anhydrous ether. The anhydrous ethereal solution thus obtained was placed in a large bottle; metallic sodium, in large pieces, was added and the bottle stoppered and protected from moisture by a calcium chloride tube; it was then placed in an ice-bath and allowed to stand overnight. The sodium did not react with the dissolved mercaptan, only a small amount of grayish sediment being present which was shown to be flakes of metallic sodium. When a little absolute methyl or ethyl alcohol was added to the ethereal solution the reaction started immediately with rapid evolution of hydrogen even at 0° and with the formation of a large amount of a beautiful white flaky precipitate.

The ether used as the solvent had been dried over calcium chloride, then over sodium and finally distilled from phosphorus pentoxide so that it was free from water and alcohol. Apparently a small amount of alcohol is necessary to catalyze the reaction between the sodium and the mercaptan. The mercaptan may be too weak an acid to react with the sodium directly though it reacts with either sodium methylate or ethylate. The following equations represent the probable mechanism of the reaction

$$CH_3SH + Na = \text{No reaction} \quad (1)$$
$$2CH_3CH_2OH + 2Na = 2\,CH_3CH_2ONa + H_2 \quad (2)$$
$$CH_3SH + CH_3CH_2ONa = CH_3SNa + CH_3CH_2OH \quad (3)$$

The alcohol regenerated in Reaction 3 then reacts with more sodium and the cycle repeats until no more mercaptan remains. The non-reactivity of the alcohol-free ethereal solution of mercaptan was not due to the amount of surface exposed by the sodium because sodium wire was also used, which presented a much greater surface than the sticks of sodium originally used. There was no reaction in this case either until a small amount of alcohol was added.

On treating the total ethereal solution with absolute ethyl alcohol (12.5 cc. of alcohol per liter of the ethereal solution), cooling in an ice-bath and allowing the reaction to proceed overnight, it was found that the reaction took place readily and that next morning the bottle was over half full of a white fluffy precipitate of sodium methyl mercaptide. More sodium was added until the reaction was complete; any unreacted sodium was removed and the mercaptide allowed to stand under the ether until ready for use.

C. Preparation of Methylthio Methyl Acetate, $CH_3SCH_2OCOCH_3$

The reactions which were expected to result in the formation of the first member of the series follow.

$$\text{Anhydrous } CH_3SNa + ClCH_2OCOCH_3 = CH_3SCH_2OCOCH_3 + NaCl \quad (1)$$
$$CH_3SCH_2OCOCH_3 + H_2O = CH_3SCH_2OH + CH_3COOH \quad (2)$$
$$CH_3SCH_2OH + SOCl_2 = CH_3SCH_2Cl + HCl + SO_2 \quad (3)$$

Reaction 1 proceeded smoothly and the new compound, methylthio methyl acetate was obtained. Hydrolysis, however, did not yield the expected products.

Chloromethyl acetate was made, using the directions of L. Henry,[20] by chlorination

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[20] Henry, Ber., 6, 740 (1873).

of methyl acetate in the sunlight at 0–5°. A given weight of chloromethyl acetate was added dropwise to about a 10% excess of the ethereal suspension of sodum mercaptide in a flask fitted with a reflux condenser. It was found advisable to use an excess of the mercaptide because the final purification by fractional distillation was greatly simplified. An approximately determined weight of the mercaptide was obtained by shaking the ethereal suspension and pipetting off a definite volume, filtering and weighing the solid. From this weight the volume of suspension to be used in an experiment was determined.

The addition of each drop of chloromethyl acetate caused the ether to boil; the addition was regulated so that the ether slowly refluxed. When the addition was complete the mixture was refluxed three hours and allowed to stand overnight. Next morning the sodium chloride and unchanged mercaptide were filtered off and washed with ether, the filtrate transferred to a flask and the ether distilled off from a water-bath. The residue was placed in a Claissen fractionating flask and fractionated in vacuum. After three complete fractionations a product boiling at 53–55' at 11 mm. was obtained; this fraction was used for analysis. The boiling point at 20 mm. was 60–62°; yield, 38%. The yield could undoubtedly be improved, for the reaction was ——ed out with sodium mercaptide residues which contained about 10% of metallic sodium. The substance was analyzed by weighing it into a thin walled glass bulb which was sealed and heated to redness in a Parr sulfur bomb with 3 g. of sodium peroxide; the sulfur was determined as barium sulfate in the usual manner.

Anal. Subs., 0.1097: $BaSO_4$, 0.2155. Calcd. for $C_4H_8O_2S$: S, 26.7. Found: 27.0.

D. Attempt to Prepare Hydroxydimethyl Sulfide. Hydrolysis of Methylthio Methyl Acetate

The acetate described above was hydrolyzed using a 2.5% solution of hydrogen chloride in absolute methanol. The reaction mixture separated into two layers one of which was insoluble in ether and contained no sulfur and the other was soluble in ether. The latter, after two fractionations, boiled at 70–71° at 48 mm., and contained sulfur but gave a negative Beilstein test. Two analyses gave, respectively, 52.65 and 52.16% S. Calcd. for C_2H_6OS, 41.05. Obviously, some substance other than that desired was produced in the hydrolysis. In view of the instability of the dihydroxydimethyl sulfide prepared by Bloch and Höhn,[16] it is questionable whether the hydroxymethyl methyl sulfide is capable of existence. It probably decomposes readily into methyl mercaptan and formaldehyde.

E. Preparation of β-Hydroxyethyl Methyl Sulfide, $CH_3SCH_2CH_2OH$

The sodium methyl mercaptide was filtered from the ether in which it was suspended, dried on filter paper and its weight determined; 88 g. (1.26 moles) was used. This was placed in a one liter flask fitted with a stirrer and reflux condenser. Three hundred and fifty cc. of dry ether (the same ether from which the mercaptide had been filtered) was added and 101 g. (1.26 moles) of ethylene chlorohydrin was added dropwise. No reaction took place at first, so the flask was warmed in a water-bath until the ether started refluxing and on continued addition of the chlorohydrin enough heat was liberated by the reaction to keep the ether gently boiling. After all of the chlorohydrin was added the mixture was refluxed for three and one-half hours and allowed to stand overnight.

The precipitate of sodium chloride and unreacted mercaptide was filtered off and the ether distilled through a Glinsky column. The residue was transferred to a 300cc. Claissen fractionating flask and twice fractionated in vacuum; 90 g. of a product boiling from 62–70' at 16 mm. was obtained (the main portion boiled at 68–70°), which corresponds to a **78%** yield. The product was a water white liquid of rather unpleasant odor, quite soluble in water and extremely soluble in alcohol and ether. Its boiling point at **30** mm. was **80.5–81°**; $d^{20^\circ}_{20^\circ} = 1.0640$; $n^{30^\circ}_{D} = 1.4867$.

Anal. Subs., **0.0725, 0.0743:** $BaSO_4$, **0.1829, 0.1870.** Calcd, for C_3H_8OS: S, **34.79.** Found: **34.66, 34.58.**

Using an aqueous alkaline solution of potassium methyl mercaptide in the reaction with ethylene chlorohydrin, similar to the method employed by Demuth and Meyer,[21] for the preparation of β-hydroxyethyl ethyl sulfide, the yield was but **33%.**

F. Preparation of γ-Hydroxypropyl Methyl Sulfide, $CH_3SCH_2CH_2CH_2OH$

The procedure used was exactly the same as described above for the lower homolog. One hundred and five grams **(1.5** moles) of dry sodium methyl mercaptide in suspension in **360** cc. of ether and **141.8** g. **(1.5** moles) of trimethylene chlorohydrin were used. Two fractionations yielded **120** g. of a product boiling from 90–97° at **17** tnm., the bulk of the material distilling from **93–94"**; yield, **76%.** The product was a water white liquid of unpleasant odor. It was fairly soluble in water and very soluble in alcohol and ether; boiling point at 30 mm., 105–105.5°; $d^{20^\circ}_{20^\circ} = 1.0314$; $n^{30^\circ}_{D} = 1.4832$.

Anal. Subs., **0.0888:** $BaSO_4$, **0.1973.** Calcd. for $C_4H_{10}OS$: **30.2.** Pound: **30.53.**

Using an aqueous alkaline solution of the potassium salt gave a yield of **54.5%.**

G. Preparation of β-Chloro-ethyl Methyl Sulfide, $CH_3SCH_2CH_2Cl$

This substance was prepared by treatment of the corresponding hydroxy compound with thionyl chloride, using chloroform as the solvent according to the procedure of Steinkopf, Herold and Stöhr.[21b] The entire reaction was carried out in the same flask from which the product was finally distilled. This precaution was taken because of the similarity in structure of this substance to mustard gas and to β-chloro-ethyl ethyl sulfide (which Meyer[22] states is poisonous, but less so than mustard gas).

Fifty grams **(0.54** mole) of β-hydroxyethyl methyl sulfide was dissolved in **100** g. of dry chloroform and placed in a 300-cc. Claissen fractionating flask which was fitted with a thermometer in place for distillation, with a dropping funnel, and with its side arm protected by a calcium chloride tube; **83.3** g. **(0.7** mole) of thionyl chloride dissolved in **200** g. of dry chloroform was placed in the dropping funnel and added dropwise. Each drop produced an evolution of sulfur dioxide and hydrogen chloride and the mixture warmed up and so was cooled at intervals by immersion in ice water. Vigorous shaking was maintained.

After a small amount of thionyl chloride had been added, each additional drop produced a local turbidity which finally resulted in the separation of **a** layer on the surface of the chloroform. About one hour was required for the addition of the thionyl chloride. The mixture was allowed to stand at room temperature for one and one-half hours and then the chloroform was distilled off from a boiling water-bath. During this process the upper oily layer disappeared and the solution became homogeneous. The residue was systematically fractionated in vacuum. After two fractionations a product boiling at 55–56° at **30** mm. was obtained. The yield in a number of experiments varied between **70** and 80%.

The product was a water white liquid with an odor resembling that of mustard gas. The boiling point at **20** mm. was **44'**; $d^{20^\circ}_{20^\circ} = 1.1245$; $n^{30^\circ}_{D} = 1.4902$.

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[21] (a) Demuth and Meyer, *Ann.*, **240,310 (1887).** (b) See also Steinkopf, Herold and Stohr, *Ber.*, **53B,** 1010 **(1920).**

[22] Meyer, *Ber.*, 20, 1729 (1887).

Anal. Subs., 0.1653, 0.1974: $BaSO_4$, 0.3526, 0.4221. Calcd. for C_3H_7SCl: 28.99. Found: 29.30, 29.37.

An unsuccessful attempt was made to prepare the Grignard reagent of this substance, using the ordinary technique and also Baeyer's activated magnesium. This inactivity is analogous to that experienced by Reid and Helfrich[14] in attempting to prepare the Grignard reagent from mustard gas, and to Hamonet's attempts to obtain the magnesium compound of the corresponding oxygen ethers of the type $ROCH_2CH_2Cl$.[23]

H. Preparation of γ-Chloropropyl Methyl Sulfide, $CH_3SCH_2CH_2CH_2Cl$

This substance was made by exactly the same procedure as described above. In this case the addition of the thionyl chloride produced practically no heat and no layers formed during the reaction. After two fractional vacuum distillations a fraction boiling at 62–65' at 21 mm. was obtained. The yields varied between 70 and 75%. The substance was a water white liquid with an odor resembling that of the β compound. The boiling point of the product used for analysis was 71 2" at 29 mm.; $d_{20°}^{20°} = 1.0863$; $n_D^{30°} = 1.4833$.

Anal. Subs., 0.2094: $BaSO_4$, 0.3930. Calcd. for C_4H_9SCl: 25.73. Found: 25.79.

Reaction Velocity Measurements

Procedure

The purification of the reagents used in the titrations, the concentration, and the method of calculation of the reaction velocity constant *K* and the temperature coefficient

TABLE II

REACTION BETWEEN β-CHLORO-ETHYL METHYL SULFIDE AND POTASSIUM IODIDE

At 50°			At 60°		
Time, hours	**Percentage reacted (100z)**	*K*	**Time, hours**	**Percentage reacted (100z)**	*K*
2.0	6.82	0.0654	2.0	14.48	0.1725
6.0	14.18	.0562	3.0	16.82	.1357
8.0	20.99	.0654	4.0	27.96	.1835
15.0	35.36	.0657	6.0	37.09	.1748
20.0	41.83	.0617		Ave. =	.1666
	Ave. =	.0629			

REACTION BETWEEN γ-CHLOROPROPYL METHYL SULFIDE AND POTASSIUM IODIDE

At 50°			At 60°		
Time, hours	**Precentage reacted (100z)**	*K*	**Time, hours**	**Percentage reacted (100z)**	*K*
2.0	11.63	0.1359	2.0	20.68	0.2571
4.0	18.63	.1127	3.0	24.47	.2085
6.0	25.63	.1102	4.0	34.80	.2413
8.0	31.37	.1057	5.0	40.00	.2320
15.0	46.00	.0940	6.0	47.69	.2478
20.0	53.55	.0857		Ave. =	.2373
25.0	60.53	.0869			
	Ave. =	.1044			

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[23] Wurtz, "Dictionnaire de Chimie," 2, 751. Compare Bennett and Hock, *J. Chem. Soc.*, 129, 472 (1927).

A were identical with that previously described.' It was necessary to modify slightly the procedure used in making the titration and to employ the method of extraction which was described in the paper just referred to. When the potassium iodate was added to the mixture being titrated, a yellow color developed which persisted long after the theoretically required amount had been added; this yellow color completely covered the end-point. It was shown to be due to the action of the potassium iodate on the organic sulfur chloride or iodide. Preliminary experiments proved that when the organic sulfur compound was extracted with chloroform before addition of the potassium iodate, sharp end-points were observed and consistent results obtained. Only negligible amounts of iodine were liberated during the reaction proper and on addition of the aqueous acid, so that no correction was necessary:

The author is exceedingly grateful to Professor J. B. Conant who suggested this problem and offered much valuable advice during the course of the work.

Summary

1. The method previously developed for determining the effect of structure of organic halides on their rate of reaction with inorganic halides has been extended to include the influence of the methylthio group. This group causes a definite, though weak, alternation in the reactivity of an w-chlorine atom through at least three carbon atoms in a saturated chain.

2. In an attempt to correlate the structure of w-halogen alkyl sulfides with vesicant action it was found that only when the halogen atom was in the β-position with respect to the sulfur atom did the resulting compound possess vesicant properties. This appears to be true of β,β′-dihalogen alkyl sulfides also. No apparent relationship exists between vesicant action and the chemical reactivity (at least in replacement reactions) of the halogen atom, a fact which is not in agreement with the acid theory of skin vesication.

3. A new vesicant, β-chloro-ethyl methyl sulfide, has been prepared, which judging from rather crude tests seems to produce the same general effects as mustard gas and at approximately the same rate.

4. The following substances have been prepared and their properties described for the first time: methylthio methyl acetate; β-hydroxyethyl methyl sulfide; β-chloro-ethyl methyl sulfide; γ-hydroxypropyl methyl sulfide; y-chloropropyl methyl sulfide.

HOUSTON, TEXAS

[CONTRIBUTION FROM THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH]

THE CRYSTAL STRUCTURE OF UREA AND THE MOLECULAR SYMMETRY OF THIOUREA

BY STERLING B. HENDRICKS

RECEIVED APRIL 27, 1928 PUBLISHED SEPTEMBER 5, 1928

The following study of the crystal structure of urea has been undertaken because it is one of the few simple organic compounds having high crystallographic symmetry. Thiourea is of interest since as a simple derivative of urea it offers an opportunity for comparing the molecular symmetry of the two substances,

Urea

Urea, $CO(NH_2)_2$, crystallizes in the tetragonal scalenohedral division of the tetragonal system[1] with the axial ratio, $a:c = 1:0.8333$. H. Mark and K. Weissenberg[2] have previously made a partial determination of the crystal structure of urea. Their results can be summarized as follows. The dimensions of the unit of structure are $d_{001} = 4.70$ Å., $d_{100} = 5.63$ Å., the space group is 4d–3 with oxygen and carbon at (c)[3] and nitrogen at (e) with $u_N = 0.13$.

Crystals showing development of (111) and (110) were grown from alcohol–water solutions of urea. A Laue photograph made with the incident x-ray beam normal to (110) shows a twofold axis and two planes of symmetry. This observation requires the structure to be isomorphous with one of the point groups 4d, 4e, 4*D* or 4Di. Since point group 4d is in agreement with the previously assigned crystallographic symmetry, the assumption is made that the structure is isomorphous with it.

Laue photographs were made with the incident x-ray beam normal to and making small angles with the normals to (110) and (100). Spectrum photographs were made on which (110) and (001) reflected in the equatorial region of the plate. These faces were initially parallel to the x-ray beam and were oscillated through a 20° angle. In the case of (110) the *c* axis was in the axis of revolution while for (001) the normal to (110) was in the axis. The smallest unit of structure compatible with the data obtained from these photographs (see Tables I–III) has $d_{001} = 4.77$ Å. and $d_{100} = 5.73$ Å. (calculated from the crystallographic axial ratio and the measured value of d_{001}). The density calculated on the basis of such a unit structure containing two $CO(NH_2)_2$ is 1.26 in agreement with the experimentally determined value 1.335.[4]

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[1] P. Groth, "Chemische Kristallographie," Leipzig, 1910, Vol. III, p. 539.

[2] Mark and Weissenberg, *Z. Physik*, **16**, 4 (1923).

[3] R. W. G. Wyckoff, "The Analytical Expression of the Results of the Theory of Space Croups,"' Washington, 1922, p. 74.

[4] G. Mez, Z. *Krist.*, 35, **246** (1901).

TABLE I

TYPICAL SPECTRUM PHOTOGRAPHIC DATA FROM UREA[a]

Plane	Order	Line	d_{hkl}Å./n	Obs. intensity	Calcd $\sqrt{S} = \sqrt{A^2 + B^2}$
110	n	Mo Kβ	4.124	m. s.[b]	
		α_1	4.110	v. s.	2.94
	$2n$	β	4.033	m.	
		α_1	4.031	s.	2.01
	$3n$	β	4.023	m.-m. w.	
		α_1	4.019	m. s.	2.82

[a] Mo K radiation. The following wave lengths were used in the calculation: β, λ = 0.6311 Å.; α_1, λ = 0.7078 Å.

[b] The following abbreviations are used throughout this paper: v. s., very strong; s., strong; m. s., medium strong; m., medium; m. w., medium weak; w., weak; v. w., very weak.

TABLE II

SPECTRUM PHOTOGRAPHIC DATA FROM UREA[a]

Plane	d_{hkl}Å.	Obs intensity	Calcd $\sqrt{S} = \sqrt{A^2}$
110	4.052	v. s.[b]	2.94
200	2.865	s.	1.88
210	2.565	s	1.45
220	2.028	s	2.01
310	1.812	m.	0.95
320	1.589	w	1.28
400	1.433	abs. or v. w.	0.00
410	1.390	abs. or v. w.	0.17
330	1.351	m s.	2.82
420	1.282	m.	1.76
510	1.124	w.	0.82

[a] Oscillation through 30° with the normal to $(1\bar{1}0)$ in the axis of oscillation, (110) was initially parallel to the x-ray beam, Mo K radiation.

[b] It is to be remembered that the times of exposure are not the same for all of the spectra listed.

Reflections were present in the first order from planes (*hkl*) having h, k and *l* odd (Table III). The underlying lattice is therefore the simple tetragonal one necessitating the consideration of only the space groups from 4d–1, to 4d–8. The observed presence of reflection from (001) on spectrum photographs and from (113) and (115) in the first order on Laue photographs cannot be explained by space groups 4d–2, or 4d–4.[5] The presence of reflections from $(03\bar{4})$, $(10\bar{2})$, $(01\bar{5})$ in the first order on Laue photographs eliminates space groups 4d–6, 4d–7 and 4d–8. The observed absence of reflection in the odd orders from (100) (Table II) cannot be accounted for by space groups 4d–1, or 4d–5. In the case of either 4d–1 or 4d–5 if a $CO(NH_2)_2$ group is assumed to be present it would be necessary for two (CO) groups of two different urea molecules to be distributed in

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[5] R. W. G. Wyckoff and S. B Hendricks, *Z. Krist.*, **66**, 86 (1927).

TABLE: III

TYPICAL LAUE PHOTOGRAPHIC DATA PROM UREA[a]

Plane	d_{hkl}Å.	$n\lambda$	Obs. intensity	Calcd[b] $S = A^2 + B^2$
$10\bar{2}$[c]	2 204	0 41	v s	0.67
221	1.865	39	v. s	5 38
122	1 747	38	m. w.	1 37
$\bar{3}\bar{2}0$	1 590	.47	m. w	1 64
$\bar{1}\bar{1}3$	1 482	.45	w	0 41
$13\bar{3}$	1 197	.42	m.-m. s.	2 71
114	1.145	.41	w.-m. w.	1 03
341	1.114	.47	w.	0 96
$\bar{3}0\bar{4}$	1 012	42	m. s.	11 70
$03\bar{4}$	1 012	47	m s	11 70
$\bar{3}\bar{2}4$	0 954	44	w	4 35
$\bar{5}\bar{3}0$	0 982	.39	m. w.	8 58
343	0.930	.45	w.	4 59
$14\bar{4}$	0 906	39	w	10 58
$\bar{4}1\bar{1}$[d]	1 334	.44	s.	3 42
$\bar{4}1\bar{2}$	1 202	46	m.	0 70
412	1 202	.43	m.	0 70
313	1 195	.43	m. s	2 71
114	1 145	41	w.	1 03
510	1 123	40	w.	1 42
$51\bar{1}$	1 093	41	m.	3 74
413	1 047	31	v. v. w.	0 18
$51\bar{2}$	1 017	39	w.-v. w.	1 00
$\bar{3}1\bar{4}$	0 996	41	w.-v. w.	1 26
$01\bar{5}$	0 942	.47	w.-m w.	1 96
$\bar{1}15$	0 929	45	v w.	0 50
$11\bar{5}$	0 929	.47	v w.	0 50
$41\bar{4}$	0.905	.38	w.-m. w.	10 58
325	0 819	.43	v. w.	3 60

[a] Tungsten general radiation, 54,000 V peak.

[b] The structure factor calculations given in this paper are for $u_N = 0.13$; $v_N = 0\ 20$; $v_C = 0\ 32$; $v_O = 0\ 57$. The relative reflecting powers of N, O and C are assumed to be the same.

[c] The incident x-ray beam made an angle of about 8° with the normal to (110).

[d] A second photograph. The incident x-ray beam made an angle of about 2° with the normal to (010)

a linear distance of 4.77 Å., an unlikely distribution. Space group 4d–3 is in agreement with the x-ray data.

If it is assumed that there are two $CO(NH_2)_2$ groups present in the unit of structure, then the C and O atoms of such a group must be at:[3] (c) $0\frac{1}{2}v$; $\frac{1}{2}0\bar{v}$, and the N atoms at *(e)* $u, \frac{1}{2} - u, v$; $\frac{1}{2} - u, \bar{u}, \bar{v}$; $\bar{u}, u + \frac{1}{2}, v$; $u + \frac{1}{2}, u, \bar{v}$. To determine the structure completely it is necessary to evaluate four parameters, three of which are in the c direction.

Without assumptions concerning the relative reflecting powers, the comparisons (see Table II) (420) > (310), and (320) > (410) restrict the value of u_N to 0.10 to 0.14. If one assumes that C, O and N have approximately the same relative reflecting power (within 25%), the comparison (510) > (320) restricts the value of u_N to 0.12 to 0.14; the value of u_N is therefore taken as 0.13 ± 0.01.

If one assumes that the C–O distance is between 1.0—1.7 Å., that the C–N distance is between 1.0–1.5 Å and that C, O and N have approximately the same relative reflecting powers (within 25%), the comparisons, using the value of u_N given above, (002) > (001), $(13\bar{3})$ > $(\bar{1}\bar{1}3)$ and $(\bar{3}0\bar{4})$ > $(\bar{5}\bar{3}0)$ restrict the values of v_N, v_C and v_O to the regions shown in Fig. 1. The intensity differences in these cases are quite large. A further limitation of parameter values can be made by the utilization of planes having less pronounced intensity differences. The restrictions necessitated by the comparisons $(12\bar{2})$ > $(\bar{3}\bar{2}0)$, $(\bar{4}1\bar{1})$ > (412), (510) > $(51\bar{2})$, $(0\bar{1}\bar{5})$ > $(1\bar{1}\bar{5})$ are shown in Fig. 1. The probable parameter values determined in this manner are v_N = 0.20 ± 0.02; v_C = 0.32 ± 0.02; v_O = 0.57 ± 0.03. It must be emphasized that these narrower limits depend upon comparisons between planes the reflections from which do not differ greatly in intensity.

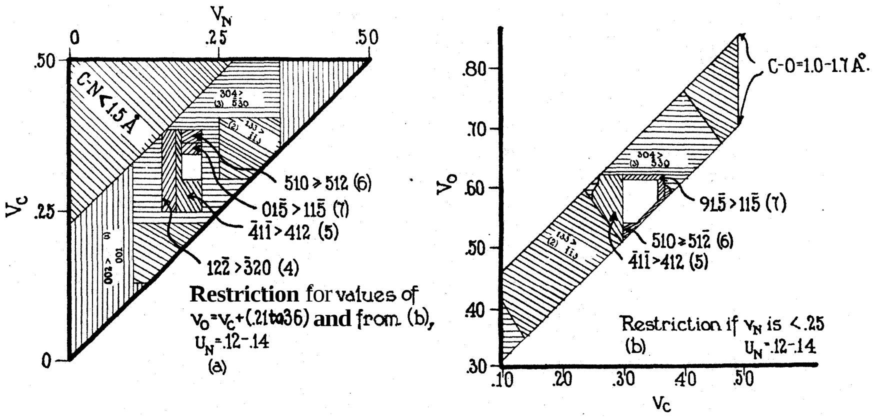

Fig. 1.—Intensity comparisons leading to a restriction of the values of the parameters for urea.

Structure factors, $S = A^2 + B^2$, calculated for reflections from the various planes, are listed in Tables I–III. In these calculations it was assumed that the relative reflecting powers of C, O and N are equal and that the values of the parameters are, u_N = 0.13, v_N = 0.20, v_C = 0.32 and v_O = 0.57. The structure factors calculated for $(14\bar{4})$ and $(10\bar{2})$ change rapidly with small changes in the parameter values. The observed intensities and the calculated structure factors, Tables I–III, are concomitant.

Thiourea

Thiourea, $CS(NH_2)_2$, crystallizes in the rhombic bipyramidal division of the rhombic system with the axial ratio $a:b:c = 0.7163:1:1.1155$.[6] Crystals, tabular parallel to $(100)_{\text{crys.}}$ and $(010)_{\text{crys.}}$, were obtained from alcohol and alcohol–water solutions of thiourea.

Spectrum photographs, with 20° oscillation, were made with the crystallographic axes in the axis of rotation. In these photographs the various pinacoids were initially parallel to the x-ray beam. Partial reproductions (Mo $K\alpha_1$ reflections) of some of these photographs are given in Fig. 4. The smallest unit of structure compatible with these data and with the spectrum and Laue data listed in Tables IV and V has $d_{(001)\text{crys.}} = 8.57$ Å.

TABLE IV

TYPICAL SPECTRUM PHOTOGRAPHIC DATA FROM $(001)_{\text{crys.}}$ OF THIOUREA

Order	Line	d_{hkl}, Å. n	Obs. intensity
n	Mo $K\beta$	8.92	m. s.
	α_1	8.87	v. s.
$2n$	β	8.67	w.
	α_1	8.57	m. s.-m.
$3n$	β	8.57	m. w.
	α_1	8.57	s.
	α_2	8.56	w.
$4n$	β	8.59	w.
	α_1	8.58	m.

TABLE V

LAUE PHOTOGRAPHIC DATA FROM THIOUREA[a]

Plane	d_{hkl}, Å.	n	Obs. intensity	Plane	d_{hkl}, Å.	n	Obs. intensity
$(1\bar{4}2)_{\text{s.g.}}$[b]	1 . 7	0.41	ab.	163	1.032	0.35	m.-m. w.
$1\bar{3}3$	1.468	.43	ab.	$2\bar{6}3$	1.018	.37	ab.
$10\bar{4}$	1.358	.45	ab.	172	1.012	.37	m.-m. w.
$11\bar{4}$	1.338	.47	m. s.	2	0.996	.39	ab.
$1\bar{1}\bar{4}$	1.338	.40	m. s.	$2\bar{7}2$	0.991	.34	ab.
143	1.310	.38	s.	$2\bar{3}5$	0.984	.38	m.-m. w.
$12\bar{4}$	1.281	.47	w.	173	0.935	.31	ab.
$13\bar{4}$	1.200	.43	m.-m. s.	255	0.876	.42	w.
$15\bar{3}$	1.166	.45	ab.	$30\bar{7}$	0.758	.41	w.
$16\bar{2}$	1.148	.45	ab.	114"	1.338	.42	w.
$2\bar{5}3$	1.135	.47	w.	152	1.324	.40	m. s.
$14\bar{4}$	1.108	.38	ab.	143	1.310	.39	m.
170	1.088	.43	ab.	160	1.264	.37	w.
171	1.077	.41	ab.	161	1.233	.36	m. w.
$2\bar{1}5$	1.056	.48	s.	235	0.984	.46	m.

[a] Tungsten general radiation, 54,000 V peak.

[b] The incident x-ray beam made an angle of about 3° with the normal to $(100)_{\text{sp. g.}}$. All of the indices in this table are referred to the space group axes.

[c] A second photograph. The incident x-ray beam was normal to $(100)_{\text{sp. g.}}$.

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[6] Ref. 1, p. 555.

(Table IV), $d_{(010)\text{crys.}} = 7.68$ Å. and $d_{(100)\text{crys}} = 5.50$ Å. The values of $d_{(010)\text{crys.}}$ and $d_{(100)\text{crys.}}$ were calculated from the crystallographic axial ratio and the measured value of $d_{(001)\text{crys.}}$. The density calculated on the basis of such a unit containing $4CS(NH_2)_2$ is 1.371 in agreement with the experimentally determined value 1.406.[6]

The presence of reflections in the first order from $(120)_{\text{crys.}}$ and $(021)_{\text{crys.}}$ requires the lattice to be the simple orthorhombic one. The observed presence of reflections in the first order from $(120)_{\text{crys.}}$, $(021)_{\text{crys.}}$, $(101)_{\text{crys.}}$ and $(110)_{\text{crys.}}$ can be accounted for only by space groups $2Di-1$, $2Di-5$, $2Di-13$, and $2Di-16$. The characteristic absences of reflections required by the general positions of these space groups are:[7] $2Di-1$, none; $2Di-5$, $(h0l)$ in odd orders when l is odd; $2Di-13$, $(hk0)$ in odd orders when $(h + k)$ is odd; $2Di-16$, $(h0l)$ in odd orders when $(h + 1)$ is odd; $(hk0)$ in odd orders when k is odd. Reflections were absent on the spectrum photographs from the following planes having one index zero which were in position to reflect (crystallographic axes): (012), (014), (016), (034), (102), (203), (104), (205), (106), (201), (401), (302), (410), (210), (220), (001), (003), (010), (030), (100), (300), (160), (025), (023), (520), (220). The only one of the above space groups explaining these absences of reflections is $2Di-16$. This space group, in the general case, does not account for absence of reflections from (410), (210), (160), (025), (023), (220). The relationships between the crystallographic indices and the space group indices are: $h_{\text{sp. g.}} = l_{\text{crys.}}$; $k_{\text{sp. g.}} = k_{\text{crys.}}$; $l_{\text{sp. g.}} = h_{\text{crys.}}$.

Inspection of the Laue data listed in Table V shows that first order reflections are present from only two planes having $(h + k + 1)$ odd, namely, $(160)_{\text{sp. g.}}$ and $(12\bar{4})_{\text{sp. g.}}$. The listed planes from which reflections were not obtained represent all planes having interplanar spacings between 0.935 Å and 1.547 Å which were in position to reflect in the first order between $\lambda = 0.24$–0.48 Å. All of these planes have $(h + k + l)$ odd with $h_{\text{sp. g.}}$ either equal to one or two. Inspections of the spectrum data (Fig. 4) shows that first order reflections are present from a number of planes having $(h + k + 1)$ odd, in particular (space group axes) (160), (320), (120), (021) and (041). With the exception of $(220)_{\text{crys.}}$ all of the previously listed planes, the absence of reflections from which are not accounted for by the general space group criteria, have $(h + k + 1)$ odd.

In order to have a $CS(NH_2)_2$ group in the unit of structure the C and S atoms of such a molecule must be at $2Di - 16$,[8] (c) $0uv$; $\frac{1}{2}, \frac{1}{2} - u, \bar{v}$; $0, u + \frac{1}{2}, \frac{1}{2} - v$; $\frac{1}{2}, \bar{u}, v + \frac{1}{2}$, with the nitrogen atoms in the general positions (d) $x\,y\,z$; $x + \frac{1}{2}, \frac{1}{2} - y, \bar{z}$; $\bar{x}, y + \frac{1}{2}, \frac{1}{2} - z$; $\frac{1}{2} - x, \bar{y}, z + \frac{1}{2}$; $\frac{1}{2} - x, \frac{1}{2} - y, \bar{z}$; $\bar{x}yz$; $x + \frac{1}{2}, \bar{y}, z + \frac{1}{2}$; $x, y + \frac{1}{2}, \frac{1}{2} - z$, or in two crystallographi-

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[7] R. W. G. Wyckoff, *Z. Krist.*, **61**, 425 (1925).

[8] Ref. 3, p. 64.

cally non-equivalent sets at (c). The observation that the 6th order reflection from $(100)_{\text{sp. g.}}$ is stronger than the 4th order can be explained only if the nitrogen atoms are at (d).

Examination of the special types of reflections required by the above arrangement shows that in the case of (c) if the value of u is $\frac{1}{4}$ or $\frac{3}{4}$ then reflections will be absent in the odd orders from planes having (h + k + l) odd. It must be remembered that the sulfur atom is much heavier than the carbon, nitrogen or hydrogen atom and thus at a particular wave length probably has a relative increasingly greater effective scattering power for x-rays, with decreasing interplanar spacings. Thus if the sulfur atom is at (c) with the value of u_S equal, or approximately equal, to $\frac{1}{4}$ or $\frac{3}{4}$, then reflections from planes having (h + k + l) odd would be due to the carbon and nitrogen atoms alone. One would thus expect the relative intensity of the reflections from such planes to decrease rapidly with decreasing interplanar spacings. Such an explanation would be in accord with the experimental observation.

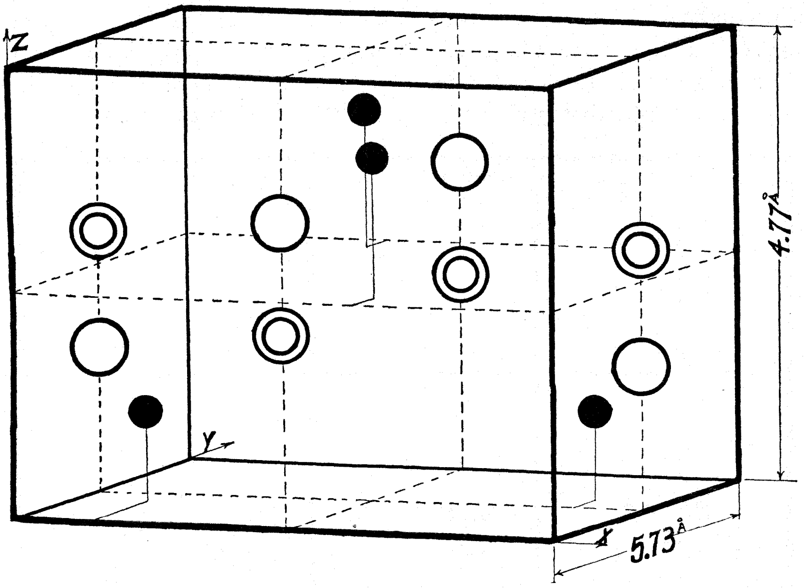

Fig. 2.—A representation of the unit of structure containing two $CO(NH_2)_2$. The nitrogen atoms are represented by the small black circles, the oxygen atoms by the ringed circles and the carbon atoms by the large circles.

The intensity observations, $(600)_{\text{sp. g.}} > (400)_{\text{sp. g.}}$, and $(800)_{\text{sp. g.}} \geqslant (400)_{\text{sp. g.}}$, can be explained only if x_N = 0.10—0.16. The intensity distribution for these planes shows that x_N is probably equal to 0.14 ± 0.02. The observed low intensity of reflection of (040), $(060) >> (040)$ cannot be explained if y, = 0.22—0.28, under the assumption that $u_S = \frac{1}{4}$ or

In fact the data could best be explained by a value of y_N not differing greatly from 0.15 or 0.35. The presence of seven parameters prevents a more complete analysis of the structure at the present time.

Discussion

A representation of the unit of structure containing two $CO(NH_2)_2$ is shown as Fig. 2. Within the probable limits of the parameter values the interatomic distances within a particular molecule are: C–O, 1.05 to 1.42 Å; $C–NH_2$, 1.07 to 1.30 Å. Even though the limits are broad these distances are much less than the C–C distance in the diamond. They are in agreement with the values found for $C–N(CH_2–NH_3)$ and $C–C(CH_2–CH_2)$ distances in the mono-alkyl ammonium halide series which are being studied in this Laboratory.[9] The value as a rule is between 1.20 to 1.30 Å. with no particular distinction between carbon and nitrogen.

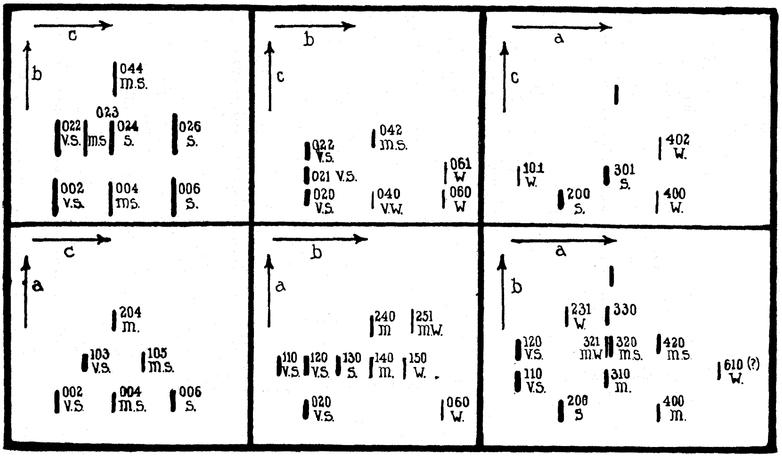

Fig. 3.—A partial reproduction of spectrum photographic data (Mo Kα_1 lines only) from thiourea. 20° oscillation. Crystallographic indices.

The $CO(NH_2)_2$ molecule has a twofold axis and two planes of symmetry (point group 2e). The angle between the axis of a (CO) group and a line connecting (NH_2) with the carbon atom of a $CO(NH_2)_2$ group is 52–73.5". The resulting configuration of a $CO(NH_2)_2$ molecule is shown as Figure 4a.

The results of crystal structure investigations of inorganic compounds have led many authors to a concept of space filling with spherical or approximately spherical atoms in crystals of inorganic compounds. The expression of ionic radii on such a basis has been of great assistance in investigations of the structures of complex inorganic substances. An examination of the very limited results obtained with molecular compounds,

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[9] S. B. Hendricks, Z. *Krist.* (in press).

the crystal structure of which have been completely determined, indicates that the only structural similarity is the approximate constancy of certain interatomic distances. The closest distances between atoms of separate molecules are usually much greater than the interatomic distances within the molecules, and greater than the values calculated from the inorganic "ionic radii." Such a result is of course not an unexpected one.

In the case of urea the closest possible distance of approach between two atoms not of the same molecule is ($O-NH_2$) about 3.0 Å., with a probable value of approximately **3.15** Å. In the previously determined structure of carbon dioxide[10] the C–O distance within a CO_2 molecule is about 1.05 Å., while the closest distance of approach O–O is about **3.23** Å. In the structure of hexamethylenetetramine[11] the closest approach between two atoms not of the same molecule is (C–C) about **3.72** Å. with a corresponding distance (C–N) of about **1.33** Å. within the molecule. In the determined structure of benzene hexahydrobromide and chloride[12] the closest distances of approach between halogen atoms are Br–Br about 3.40 Å. and 3.748. with the smaller distance probably that within the $C_6H_6Br_6$ molecule.

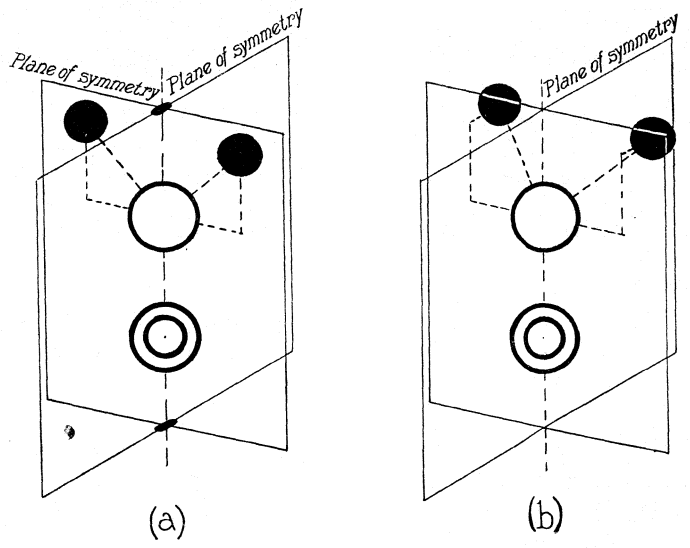

Fig. 4.—Possible configurations of the (a) urea and ((a) and (b)) of the thiourea molecule. The nitrogen atoms are represented by the small black circles, the oxygen atoms by the ringed circles and the carbon atoms by the large circles.

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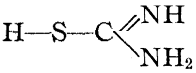
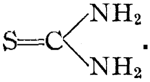
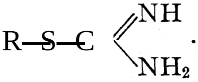
[10] **W. H. Keesom and J. De Smedt,** *Verslag. Akad. Wetenschappen. Amsterdam,* **33,** *888* **(1924). The results of the above authors were checked by L. Thomassen and S. B. Hendricks (unpublished work), $a_0 = 5.60$, $u_0 = 0.11$.**

[11] **R. G. Dickinson and A. L. Raymond,** THIS JOURNAL, **45, 22 (1923).**

[12] **R. G. Dickinson and C. Bilicke,** *ibid.,* **50, 764 (1928).**

The presence of the hydrogen atoms undetermined in positions vitiates the above analysis except in the discussion of carbon dioxide. Only in the case of the hexahydrohalides of benzene are the distances of closest approach near the values suggested by the inorganic "atomic radii."

The analysis of the structure of thiourea is not complete enough to allow close comparison with that of urea. The geometrical relationships between the molecules cannot be similar for the two compounds. The minimum molecular symmetry of thiourea is that of the point group 2c, which has a plane of symmetry. It is possible, as is shown in Fig. 4a, that all of the atoms of a thiourea molecule might be coplanar.

It has been suggested that thiourea has the formula  $H-S-C{\Large\langle}^{NH}_{NH_2}$ rather than  $S=C{\Large\langle}^{NH_2}_{NH_2}$. The existence of salts of the general formula  $R-S-C{\Large\langle}^{NH}_{NH_2}$ ·HI, the behavior of thiourea on oxidation in acid solutions and other chemical properties are said to be evidence in favor of the first formula. The observed crystallographic equivalence of the nitrogen atoms shows that in the solid state the symmetrical formula is correct.

Summary

The crystal structure of urea $CO(NH_2)_2$ has been determined by the use of Laue and spectrum photographs. The unit of structure containing two $CO(NH_2)_2$ has d_{100} = 5.73 Å. and d_{001} = 4.77 Å. The space group is $4d-3$ (V_d^3) with O and C at (c) $0\frac{1}{2}v$, $\frac{1}{2}0\bar{v}$; and N at (e) $u, \frac{1}{2}-u, v$; $\frac{1}{2}-u$, 4, $\bar{v}$; $\bar{u}, u+\frac{1}{2}, v$; $u+\frac{1}{2}, u, \bar{v}$. The probable parameter values are $u_N = 0.13 \pm 0.01$, $v_N = 0.20 \pm 0.02$, $v_C = 0.32 \pm 0.02$ and $v_O = 0.57 \pm 0.03$.

Laue and spectrum photographs were made from crystals of thiourea. The unit of structure containing four $CS(NH_2)_2$ has a_0 = 5.50 Å., b_0 = 7.68 Å. and c_0 = 8.57 Å. The space group is 2Di—16 (V_h^{16}) with S and C at (c) $0uv$; $\frac{1}{2}, \frac{1}{2}-u, \bar{v}$; $0, u+\frac{1}{2}, \frac{1}{2}-v$; $\frac{1}{2}$, a, $v+\frac{1}{2}$ and with N in the general positions. The molecular symmetry is that of the point group $2c$ (C_S) which has a plane of symmetry.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF BUFFALO]

NITRO-AMINOGUANIDINE

BY ROSS PHILLIPS AND JOHN F. WILLIAMS

RECEIVED MAY 11, 1928 PUBLISHED SEPTEMBER 5, 1928

Nitroguanidine, $HN{=}C(NH_2)NHNO_2$, was first prepared by Jousselin[1] by dissolving guanidine nitrate in concentrated sulfuric acid, when the compound separated upon dilution with water. More recently several articles[2] have appeared concerning this compound. It is used principally as an explosive. Thiele[2a] prepared nitrosoguanidine as well as aminoguanidine, $HN{=}C(NH_2)NHNH_2$, by reduction of nitroguanidine. Hofmann and Stollé[3] and also Pellizzari and co-workers[4] prepared diaminoguanidine hydrochloride, $HN{=}C(NHNH_2)_2{\cdot}HCl$, by the action of cyanogen chloride on hydrazine in ethereal or aqueous solutions. Pellizzari and Gaiter[5] also prepared triaminoguanidine by treating guanidine or its mono- or diamino derivative with the calculated amount of hydrazine. This work was verified and a good yield of triaminoguanidine obtained by heating an alcoholic solution of guanidine nitrate and hydrazine at 100° for five hours.

Apparently nitro-aminoguanidine, $HN{=}C(NHNO_2)NHNH_2$, has never been prepared, as no reference to it was found in the literature. In 1920, while working on guanidine compounds, it was found that an interesting substance formed when nitroguanidine was heated with a solution of hydrazine. This substance is the subject of the present investigation.

Preparation of Nitro-aminoguanidine

The nitroguanidine used in this experiment was prepared by dissolving guanidine nitrate in concd. sulfuric acid, and pouring this solution into ice water. The crystals obtained were twice recrystallized from water.[2c,e]

Hydrazine sulfate, 32.53 g., was placed in a 2000-cc. Erlenmeyer flask with 200 cc. of distilled water and 500 cc. of *N* ammonia water. When the hydrazine sulfate had dissolved, 26 g. of nitroguanidine was added. The flask was then heated to 50–60°, during which time the nitroguanidine went into solution, nitrous oxide gas began to evolve and the reaction liquor turned to an orange-red color. In about one hour at the above temperature, gas ceased to form and the liquor was rapidly evaporated to about one-third its volume. On cooling, a white crystalline powder separated which was filtered off, washed with cold water and dried in the air; yield, 13.1 g. This was purified by dissolving in boiling water containing decolorizing carbon, and filtering. Upon chill-

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[1] (a) Jousselin, *Compt. rend.*, 88, 1087 (1879); (b) Pellizzari, *Gazz. chim. ital.*, *21*, II, 405 (1891).

[2] (a) Thiele, *Ann.*, 270, 1 (1892); (b) Boehringer and Sohne, *J. Chem. Soc.*, (Abs.), 90,637 (1906), D. R. P. 167,637; (c) Ewan and Young, *J. Soc. Chem. Ind.*, 40, 109 (1921), (d) Davis, THIS JOURNAL, 44, 868 (1922); (e) *ibid.*, 47, 1063 (1925); (f) Davis and Abrams, *Proc. Am. Acad. Arts Sci.*, *61*, 437 (1926).

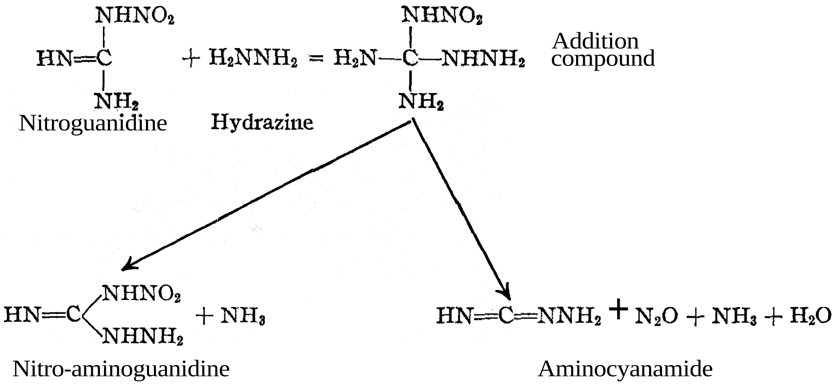
[3] Hofmann and Stollé, *Ber.*, 37, 4524 (1904).

[4] Pellizzari and Cantoni, *Gazz. chim. ital.*, *35*, I, 291 (1905).

[5] Pellizzari and Gaiter, *ibid.*, 44, 72 (1914); Gaiter, ibid., 45, I, 450 (1915).

ing the filtrate a pure crystalline powder formed. Changes in the above procedure were tried but no better yield was obtained.

Repeated yields of approximately 50% were obtained, which would seem to indicate the following reaction.



No indication of aminocyanamide (which is perhaps decomposed in the reaction liquor) was obtained. Nitro-aminoguanidine and ammonia were formed in the quantities indicated above and nitrous oxide came off freely.

Analysis of Nitro-aminoguanidine

The analysis of nitro-aminoguanidine presented **a** difficulty not easily met. The standard processes for the determination of nitrogen, such as the modified Kjeldahl, nitrometer and alkaline fusion methods, failed to yield the nitrogen expected. The following procedure proved successful.

One five-hundredth mole, 0.2383 g., was dissolved in 2 cc. of 1:1 sodium hydroxide solution and washed into a nitrometer with 3 cc. of water. Two grams of cupric sulfate dissolved in 4 cc. hot water was next introduced. Gas immediately formed and slowly subsided. The nitrometer bulb was now cautiously and later vigorously heated with steam for two hours. On cooling the gas measured 70.2 cc. at 0°. There was then carefully introduced 10 cc. of concd. sulfuric acid, and after gently mixing there still remained an insoluble copper precipitate. The nitrometer bulb was again heated with steam for one hour and cooled. The gas now measured 96.7 cc. at 22° and at 741 mm. and was then analyzed. The liquid remaining in the nitrometer measured 18 cc. and was reserved for a separate analysis. By passing aliquot portions of the gas into Hempel gas pipets containing, respectively, 1:1 sodium hydroxide, cuprous chloride and alkaline pyrogallol solutions, a shrinkage with the first indicated that 9% of the gas was carbon dioxide, while no shrinkage in the remaining solutions showed the absence of carbon monoxide and oxygen. A small portion mixed with air failed to give a brown coloration showing the absence of nitric oxide. The gas consisted of a mixture of nitrogen and nitrous oxide, the latter as shown by the splinter-glow test, and its solubility in alcohol indicated approximately one volume of nitrous oxide to three volumes of nitrogen. This residual mixture of 88.0 cc. of gas was calculated as nitrogen by substitution in the Dumas formula

$$V_0 = \frac{V(B - W)}{760} \times \frac{273}{273\ t}$$

$$88.0\text{ cc.} \times \frac{732}{760} \times \frac{273}{295} \times 0.00125 = 0.09787 \text{ grams of nitrogen}$$

This represented about 70% of the calculated quantity of nitrogen.

The liquid remaining in the nitrometer was analyzed by the Gunning modification of the Kjeldahl method[6] and 0.0421 g. of nitrogen obtained in the form of ammonia: nitrogen as gas, 0.09787 g.; nitrogen as NH_3, 0.04210 g.; nitrogen found, 0.13997 g.; calcd., 0.14008.

Properties of Nitro-aminoguanidine

Nitro-aminoguanidine is a white, crystalline powder belonging to the monoclinic system; soluble in water to the extent of 0.34% at 20° and 3.0% at 70°; insoluble in most organic solvents. It dissolves readily in caustic alkali solutions with the formation of a yellow color, does not evolve ammonia when this solution is boiled but loses its identity after standing for several hours in the caustic alkaline solution. It melts accompanied by explosion at about 190°. It reduces solutions of permanganate and dichromate, Nessler's reagent and ammoniacal silver nitrate in the cold. With the latter reagent gas is evolved and metallic silver is precipitated, along with an explosive silver compound.

Similarly, it reduces Fehling's solution with the formation of an explosive copper compound. With nickel solutions interesting and characteristic reactions occur. If to a solution of nitro-aminoguanidine containing caustic alkali a trace or more of a nickel salt is added, an intense deep blue color develops and lasts for fifteen to twenty minutes. This test can be made to detect as little as 0.0002 mg. of nickel. Cobalt and a number of other metals failed to give this test. In the absence of caustic alkali, however, and in the presence of ammonia, nitro-aminoguanidine will yield, with solutions of nickel, a fawn colored nickel precipitate which will be described later. Like nitroguanidine it may be ground in a mortar without detonation, but differs from the former when heated near a flame on an iron spatula. Each separate particle of nitro-aminoguanidine explodes as it becomes ignited by the flame, leaving a yellow, insoluble residue. It condenses with aldehydes and ketones, as will be described.

Tests for Nitro-aminoguanidine

Although the above-described nickel test is characteristic, other tests for the compound may be mentioned. Davis and others[2]" give qualitative tests for nitroguanidine. The first is based upon the purple color which develops when a few drops of sodium hydroxide solution is added to a solution of nitroguanidine containing a little ferrous sulfate. The second test depends upon the reduction of copper or silver acetates by the re-

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[6] "Methods of Analysis," A. O. A. C., 1925, p. 9.

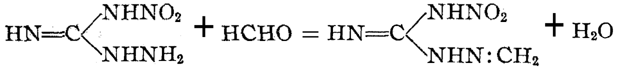
duced nitroguanidine, that is, the aminoguanidine formed when nitroguanidine is treated with zinc dust in acetic acid solution.

We found that nitro-aminoguanidine gives both these tests. In fact, in the second test, it reacts more energetically than does nitroguanidine. A simple qualitative test for nitro-aminoguanidine was found to be as follows. When 2 mg. or more is dissolved in warm, concd. sulfuric acid, gas is evolved and a light green solution develops and lasts. When a few drops of a 5% ferrous sulfate solution is added, the color changes to a cherry red. Nitroguanidine, nitro-urea and hydrazine do not give this test.

Reactions of Nitro-aminoguanidine

A. Reactions with Aldehydes and Ketones

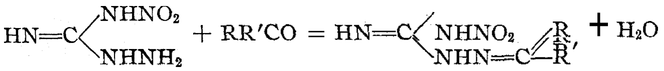
When aldehydes or ketones were added to a saturated solution of nitro-aminoguanidine, crystalline precipitates formed. For example, the formaldehyde reaction took place as follows. To about 10 cc. of a warm saturated solution of nitro-aminoguanidine there was added 4 to 5 drops of 37% formaldehyde solution. Upon standing and cooling, long needles of the condensation product formed, the reaction taking place, perhaps, in the following manner



$$HN{=}C\begin{matrix}\diagup NHNO_2\\ \diagdown NHNH_2\end{matrix} + HCHO = HN{=}C\begin{matrix}\diagup NHNO_2\\ \diagdown NHN{:}CH_2\end{matrix} + H_2O$$

Similar hydrazones were obtained with acetaldehyde, citral, benzaldehyde and vanillin. The aromatic aldehyde hydrazones were nearly insoluble in water while the aliphatic hydrazones were somewhat soluble in water.

Ketones yielded in a similar manner their corresponding products and white, needle-like crystals were obtained with acetone, methylethyl ketone, diethyl ketone and pyruvic acid, $CH_3COCOOH$. The general reaction with ketones is expected to take place as follows



$$HN{=}C\begin{matrix}\diagup NHNO_2\\ \diagdown NHNH_2\end{matrix} + RR'CO = HN{=}C\begin{matrix}\diagup NHNO_2\\ \diagdown NHN{=}C\begin{matrix}\diagup R\\ \diagdown R'\end{matrix}\end{matrix} + H_2O$$

These condensation products with aldehydes and ketones were observed, when dried, to detonate when ignited. This was not the case when similar compounds of diaminoguanidine (the benzaldehyde compound was prepared and examined) were ignited. This property of detonation was considered evidence that the nitro group is retained in the former case. Also, the property of nitro-aminoguanidine of forming condensation products with aldehydes and ketones was considered evidence of the presence of a hydrazine group. Indication of the reduction of the nitro group in the benzaldehyde hydrazone was obtained. This compound was suspended in water slightly acidified with hydrochloric acid and zinc dust was added. After standing for two hours at room temperature, the solution was filtered and on evaporation the filtrate gave abundant crystals of a hydrochloride which did not detonate. Nitro-aminoguanidine did not yield insoluble, crystalline hydrazones with glucose, fructose, galactose or arabinose,

B. Reactions with Metals

The composition of the explosive compounds of silver and copper with nitro-aminoguanidine has not been determined. They differ from the nickel compound in that they are formed during the decomposition of nitro-aminoguanidine, while the nickel compound is in the nature of an addition product.

Preparation of Nickel Nitro-aminoguanidine

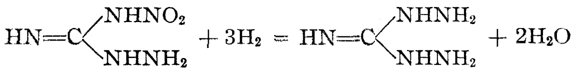
Five cc. of nickel sulfate solution, containing 0.093 g. of metallic nickel, was placed in a 250cc. beaker and diluted with 100 cc. of hot water. Five cc. of N ammonia water was added, followed immediately by a solution of 0.5 g. of nitro-aminoguanidine dissolved in 50 cc. of hot water. The precipitate formed was boiled gently for fifteen to twenty minutes, filtered through a weighed crucible, washed with hot water and dried at 110°. The weight became constant in three hours, giving 0.4955 grams of the compound. The filtrate was evaporated and a delicate test made for the presence of nickel but none was found. Since the solution of nickel sulfate used contained a known amount of nickel (electrolytically determined) and all of it was shown to have reacted, the precipitate contained 18.75% Ni; calcd. for $NiO[HN{=}C(NHNO_2)NHNH_2]_2$, 18.76%. The filtrate, after the removal of the nickel compound, was found to have 0.225 g. of ammonium sulfate together with the excess of nitro-aminoguanidine.

The precipitate is insoluble in hot or cold water and organic solvents. It dissolves in caustic alkali solutions with the formation of an intense deep blue color. It is decomposed by sulfuric acid with the formation of a toxic gas. It explodes with a flash when placed in a flame but may be heated in a test-tube to 220° without detonation. It explodes mildly when struck with a hammer.

It would seem that nitro-aminoguanidine may serve as a reagent for nickel determination, having the advantage over dimethylglyoxime of being water soluble.

Reduction of Nitro-aminoguanidine

If the new compound has the structure assigned, then it should yield diaminoguanidine on reduction, as follows



$$HN{=}C\begin{cases}NHNO_2\\NHNH_2\end{cases} + 3H_2 = HN{=}C\begin{cases}NHNH_2\\NHNH_2\end{cases} + 2H_2O$$

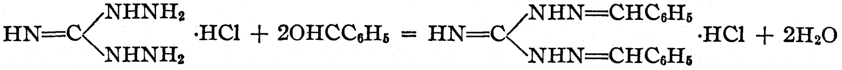
This was actually found to be the case.

The experiment was made in the following manner: 1.19 g. of nitro-aminoguanidine was mixed with 7 g. of zinc dust and cracked ice in a 200cc. cylinder. There was then slowly introduced with stirring 50 cc. of 10% acetic acid solution. The temperature was kept below 10° by repeated additions of ice. After stirring for one hour, the solution was allowed to reach room temperature and then filtered. The zinc was removed from the filtrate by hydrogen sulfide, and after the removal of the zinc sulfide the solution was evaporated on the steam-bath with the aid of a current of air. When the excess of acetic acid was evaporated, the residue was dissolved in a little water and the calculated amount of hydrochloric acid, 20 cc. of $N/2$, added. After again evaporating to dryness, a slight excess of hydrochloric acid was added to insure complete removal of acetic acid. The dried residue was next extracted with hot alcohol, filtered and upon cooling in the ice box crystals were obtained; weight 0.75 g., 60% yield. They were again recrystallized from alcohol, dried and examined; melted with decomposition at 176°. Hofmann reported 174°; Pellizzari, 185°.

Anal. Calcd. for HCl: 29.0. Found: 28.90.

The nitrate was prepared from the hydrochloride by double decomposition with silver nitrate (in excess of nitric acid) and recrystallized from alcohol. The slightly impure crystals melted from 140–144°. Pellizzari reported 143°. These salts of diaminoguanidine agreed with those reported by Hofmann and Pellizzari by forming yellow radiating needles with picric acid, reduced ammoniacal silver nitrate in the cold and also solutions of gold, platinic and cupric salts, and with benzaldehyde they formed crystalline condensation products in the cold.

The benzaldehyde compound with diaminoguanidine, dibenzylidenediaminoguanidine, was prepared as follows. To a solution of diaminoguanidine hydrochloride there was added an excess of benzaldehyde and, after stirring, a white precipitate formed. The reaction took place in the following manner



$$HN{=}C\begin{cases}NHNH_2\\NHNH_2\end{cases}\cdot HCl + 2OHCC_6H_5 = HN{=}C\begin{cases}NHN{=}CHC_6H_5\\NHN{=}CHC_6H_5\end{cases}\cdot HCl + 2H_2O$$

The excess benzaldehyde was removed with ether, the crystals were washed with water, dissolved in sodium carbonate solution and extracted with ether. After the ether was evaporated the residue was recrystallized from alcohol and yellow crystals of dibenzylidenediaminoguanidine were obtained, m. p. 178° (corr.); reported by Hofmann 176°; by Pellizzari, 180°. The base was insoluble in water but soluble in alcohol. The hydrochloride of dibenzylidenediaminoguanidine was prepared from the base and when recrystallized from alcohol yielded fine, cotton-like, nearly white crystals, m. p. 230°; reported by Hofmann, 232°; by Pellizzari, 230°. This sums up the evidence showing the reduction of nitro-aminoguanidine to diaminoguanidine.

It is likely that the new compound, nitro-aminoguanidine, in addition to being useful in analytical chemistry with reference to nickel, aldehydes and ketones, may also find use in the chemistry of explosives.

The assistance of Professor E. Raymond Riegel is gratefully acknowledged.

Summary

1. The preparation of nitro-aminoguanidine is described as well as its analysis, properties and reactions.

2. Its structure is indicated by its method of preparation, its power to form hydrazones, its yielding the characteristic purple color with alkaline ferrous sulfate, its reduction to diaminoguanidine and, finally, its analysis for nitrogen.

3. Crystalline compounds with aldehydes and ketones were prepared.

4. The compound nickel nitro-aminoguanidine is described, which may lead to a new qualitative and quantitative test for nickel.

5. A special procedure for nitrogen determination is given.

BUFFALO, NEW YORK

[CONTRIBUTION FROM THE INSECTICIDE DIVISION, BUREAU OF CHEMISTRY AND SOILS]

THE PREPARATION OF SOME PYRROLIDINE DERIVATIVES[1,2]

BY F. B. LAFORGE

RECEIVED MAY 18, 1928 PUBLISHED SEPTEMBER 5, 1928

It is rather surprising that among the many synthetic and natural organic compounds which have been tested as contact insecticides, so few have been found to possess outstanding toxic action.

In the present state of our knowledge it would seem that of the natural products, the pyrethrins, rotenon (from derris) and nicotine are in a class by themselves. Whatever insecticidal action may be possessed by any other compound, either natural or synthetic, is in every case of a distinctly lower order, and it is not possible to arrange a list of compounds of progressively higher toxicity up to that of the order of the three mentioned. However, further study may yield results which will invalidate this generalization.

Owing to the work of Staudinger and Ruzicka[3] the chemical nature of the pyrethrins is well understood. They are both complicated esters containing a number of unsaturated bonds and asymmetric carbon atoms. As far as is known; even the slightest change in the complicated chemical structure of either lowers its specific action to a marked degree and generally destroys it altogether.

From what is known of tubotoxin, it seems probable that the same will hold true for that compound.

The investigations reported in this paper were undertaken to determine, if possible, whether the toxicity of nicotine is specific for the whole molecule or whether this effect is owing to some special grouping of its component parts.

From the formula for nicotine, which is β-pyridyl-α-N-methylpyrrolidine, it might be reasonable to assume that either the pyridine or the pyrrolidine group were responsible for its insecticidal property. Accordingly, a number of new substituted pyrrolidines were prepared and tested, besides a number of known ones, but none were found to possess toxicity approaching that of nicotine.

Substitution of the methyl or phenyl group in the a-position of the pyrrolidine molecule leads to comparatively inert compounds which do not show increased toxicity if they are in addition methylated on the

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[1] A study of the insecticidal action of these compounds is being made in cooperation with Dr. C. H. Richardson, Deciduous Fruit Insect Investigations, Bureau of Entomology.

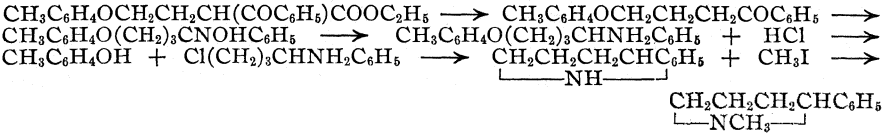
[2] Presented at the Insecticide Symposium, St. Louis meeting of the American Chemical Society, April, 1928.

[3] Staudinger and Ruzicka, *Helv. Chim. Ada*, 7, 177–259, 377458 (1924).

nitrogen. For instance, a-methyl, α,α-dimethyl[4] and a-phenylpyrrolidine, and their N-methyl derivatives were only slightly toxic.

The preparation of a-phenyl-N-methylpyrrolidine presented unusual difficulties. The action of methylamine on 1-phenyl-1,4-dibromobutane, $C_6H_5CHBr(CH_2)_2CH_2Br$, resulted in an unsaturated compound instead of the expected phenylmethylpyrrolidine. Although it was possible to prepare a-phenylpyrroline, attempts to reduce it were unsuccessful, nor was it possible to close the side chain of 1-phenyl-1-N-methylaminobutane by the method of Löffler.[5]

The compound was finally prepared from *β-p*-cresoxy-ethylbenzoylacetic ester by the following steps.



$$\begin{aligned}&CH_3C_6H_4OCH_2CH_2CH(COC_6H_5)COOC_2H_5 \longrightarrow CH_3C_6H_4OCH_2CH_2CH_2COC_6H_5 \longrightarrow\\ &CH_3C_6H_4O(CH_2)_3CNOHC_6H_5 \longrightarrow CH_3C_6H_4O(CH_2)_3CHNH_2C_6H_5 + HCl \longrightarrow\\ &CH_3C_6H_4OH + Cl(CH_2)_3CHNH_2C_6H_5 \longrightarrow \underbrace{CH_2CH_2CH_2CHC_6H_5}_{NH} + CH_3I \longrightarrow\\ &\underbrace{CH_2CH_2CH_2CHC_6H_5}_{NCH_3}\end{aligned}$$

α-Methylpyrrolidine.—This derivative has been prepared and studied by Penner and Tafel,[6] but it may be more conveniently obtained by the general method of Gabriel.[7]

β-p-Cresoxy-ethylacetoacetic Ester.—Fifty grams of acetoacetic ester (twice the theoretical quantity) was added to a solution of 4.5 g. of sodium in 75 cc. of alcohol, followed by 41 g. of *β-p*-cresoxy-ethyl bromide.[8] The solution was allowed to stand several hours and then was boiled for five hours under reflux. The alcohol was evaporated, the residue suspended in water and the insoluble oil extracted with ether. The ether solution, which was dried with calcium chloride, yielded about 70 g. of oil on evaporation.

The oil was distilled in a vacuum of 16 mm. The fraction boiling up to 130° con-

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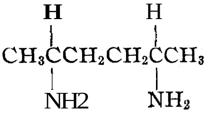
[4] The reduction of acetonylacetonedioxime prepared by the method of Paal (*Ber.*, 18, 59 (1885))under the same conditions as those used by Tafel in the case of the corresponding hydrazone (*Ber.*, 22, 1860 (1889)), results in a mixture of dimethylpyrrolidine and 2,5-diaminopentane. The last compound shows no tendency to form the ring structure and can only be transformed into dimethylpyrrolidine by dry distillation of the hydrochloride. Since two dimethylpyrrolidines should exist according to theory, it would appear that the one represented by the space formula  $CH_3\underset{NH_2}{\overset{H}{C}}CH_2CH_2\underset{NH_2}{\overset{H}{C}}CH_3$ might easily lose ammonia to form dimethylpyrrolidine, whereas if the position of one amino group were reversed, this reaction might not take place except under drastic conditions and would then result in an isomeric compound. A whole series of isomeric substituted pyrrolidines is possible with increase in the number of methyl groups, up to six optical pairs of tetramethylpyrrolidines, analogous to the hexitols in the sugar group.

[5] Löffler and Flügel, *Ber.*, 42, 3431 (1909).

[6] Fenner and Tafel, *Ber.*, 31, 909 (1898).

[7] Gabriel, *Ber.*, 24, 3234 (1891).

[8] Weddige, *J. prakt. Chem.*, 24,242 (1881).

sisted mostly of acetoacetic ester. About 10 g. of a fraction boiling at 130-196° was obtained. The fraction boiling at 196–206° consisted of *β-p*-cresoxy-ethylacetoacetic ester. It was refractionated and yielded 25 g. of a product boiling at 202-204" (uncorr.).

Anal. Subs, 0.1874: CO_2, 0 4634; H_2O, 0.1212. Calcd. for $C_{15}H_{20}O_4$: C, 68.77; H, 7.43. Pound: 67.43, 7.19.

γ-*p*-Cresoxypropylmethyl Ketone, $CH_3C_6H_4O(CH_2)_3COCH_3$.—Twelve grams of *β-p*-cresoxy-ethylacetoacetic ester was heated on the steam-bath with 2 g. of sodium hydroxide in 75 cc. of alcohol. Sodium bicarbonate separated out during the heating. The solution was diluted with water, acidified with acetic acid and the alcohol evaporated off. The separated oil was taken up in ether and the ether residue was distilled at 16 mm., yielding 6 g. of a fraction boiling at 163–180°. Several similar fractions were combined and the fraction boiling at 175–175° was collected. This material crystallized on standing and was freed from adhering oil by pressing between filter paper. It was easily soluble in all organic solvents and was analyzed without further purification.

Anal. Subs., 0.1560: CO_2, 0.4314; H_2O, 0.1163. Calcd. for $C_{12}H_{16}O_2$: C, 75.00; H, 8.33. Found: C, 75.42; H, 8.28.

The seniicarbazone of the ketone prepared in the usual manner crystallized from alcohol in needles melting at 158°.

γ-*p*-Cresoxybutyric Acid.—The combined alkaline solutions from the saponification of 100 g. of *β-p*-cresoxy-ethylacetoacetic ester yielded 10 g. of γ-*p*-cresoxybutyric acid on acidification. It was recrystallized from 40% alcohol and melted at 84–85°.

Anal. Subs., 0.1630: CO_2, 0.4087; H_2O, 0.1035. Calcd. for $C_{11}H_{14}O_3$: C, 68.04; H, 7.21. Found: C, 68.37; H, 7.05.

γ-*p*-Cresoxypropylmethyl Ketoxime.—The oxime was obtained in good yield by warming 8 g. of the ketone dissolved in 75 cc. of an alcoholic solution of hydroxylamine prepared from 3 g. of the hydrochloride. After evaporation of the solvent, the residue crystallized to a solid cake. It was dissolved in ether, the solution was washed with water and dried with potassium carbonate and the solvent removed. The oxime may be recrystallized from petroleum ether or dilute alcohol and when pure melts at 54°.

Anal. Subs., 0.1647: CO_2, 0.4214; H_2O, 0.1214. Calcd. for $C_{12}H_{17}NO_2$: C, 69.57; H, 8.21. Found: C, 69.78; H, 8.18.

1-*p*-Cresoxy-4-amino-*n*-pentane, $CH_3C_6H_4O(CH_2)_3CHNH_2CH_3$.—Twenty-three grams of the oxime was dissolved in 300 cc. of 95% alcohol and reduced with 1000 g. of 2 5% sodium amalgam added in four portions of 250 g. each, followed by 25 cc. of glacial acetic acid over a period of four hours. The separated sodium acetate was filtered off and the solution diluted with 800 cc. of water and placed in a freezing mixture. About 14 g. of unchanged oxime was recovered by this treatment and was reduced again with sodium amalgam. The combined filtrates were concentrated to 150 cc. and extracted with ether. The ethereal solution yielded a small quantity of oxime. The aqueous solution was treated with sodium hydroxide, the separated oil taken up in ether and the ethereal solution dried with solid potassium hydroxide. About 10 g. of pure amine was obtained, boiling at 280–283° (uncorr.) at 760 mm.

Anal. Subs., 0.1570: CO_2, 0.4265; H_2O, 0.1355. Calcd. for $C_{12}H_{19}NO$: C, 74.61; H, 9.84. Found: C, 74.09; H, 9.59.

The amine combines with carbon dioxide from the air, forming a solid crystalline carbonate. The hydrochloride is also crystalline but somewhat hygroscopic.

α-Methylpyrrolidine.—Twenty grams of the hydrochloride was sealed in a glass tube with 70 cc. of aqueous hydrochloric acid, saturated at 0° and heated for fifteen hours at 100°. The contents of the tube presented two layers, the lighter one being *p*-cresol which was removed by extraction with ether from the aqueous solution of the hydrochloride of 1-chloro-4-aminopentane. On evaporation the compound was left as a thick sirup.

The product was dissolved in a small quantity of water and the solution made strongly alkaline. On the addition of solid potassium hydroxide, the methylpyrrolidine separated as an oily layer, which was separated and further dehydrated with potassium hydroxide. The product distilled between 94 and 97°, which agrees fairly well with the figure given by Fenner and Tafel.[6] The yield was 8 g.

Anal. Subs., 0.1300: CO_2, 0.3340; H_2O, 0.1555. Calcd. for $C_5H_{11}N$: C, 70.58; H, 12.94. Found: C, 70.07; H, 13.29.

1-Phenyl-1-bromobutane and **1-Phenyl-1-methylaminobutane.**—Twenty grams of phenylpropylcarbinol prepared by the method of Klages[9] was saturated with hydrobromic acid gas at 0°. In a few minutes the liquid became turbid and after standing overnight had separated into two layers The oily layer was taken up in ether, and the excess hydrobromic acid was removed by washing with water. The ethereal solution was dried with calcium chloride and yielded 32 g. of residue. It was not analyzed. The bromo compound was dissolved in 50 cc. of methyl alcohol and poured into 160 cc. of a 25% methyl alcoholic solution of methylamine. After standing overnight, the solution was evaporated, leaving a mixture of oil and crystalline methylamine hydrobromide. It was dissolved in dilute hydrochloric acid and the solution was extracted with ether. The aqueous solution was made alkaline, and the separated oil was extracted with ether and dried with potassium carbonate. On evaporation it yielded 20 g. of oily residue, which boiled at 117–118° at 33 mm. (220' at 765 mm.).

Anal. Subs., 0.1378: CO_2, 0.4097; H_2O, 0.1258. Calcd. for $C_{11}H_{17}N$: C, 80.98; H, 10.43. Found: C, 81.22; H, 10.14.

The amine is insoluble in water, and it is probably owing to this property that efforts to close the side chain to the pyrrolidine ring by brominating on the nitrogen and eliminating the hydrobromic acid in accordance with the method of Loffler were unsuccessful.

A second attempt was made to prepare a-phenyl-N-methylpyrrolidine through the following steps

$$C_6H_5CHOHCH_2CH{=}CH_2 + 2HBr \longrightarrow C_6H_5CHBr(CH_2)_2CH_2Br + NH_2CH_3 \longrightarrow C_6H_5\underline{CH(CH_2)_2CH_2N}CH_3$$

It resulted, however, in an isomeric, open-chain unsaturated compound.

1-Phenyl-1,4-dibromobutane.—Twenty grams of allylphenylcarbinol[10] was saturated in direct sunlight in a quartz flask with hydrobromic acid gas. In two hours the reaction was complete and no more gas was absorbed. The product was taken up in ether, washed with ice water and the solution dried with calcium chloride. The residue weighed 36.5 g., which is close to the theoretical yield. The product could not be distilled. Thirty-two grams of the crude product was added in small portions to 200 cc. of a 25% methyl alcoholic solution of methylamine.

After standing overnight, the solvent and excess amine were removed by evaporation and the residue was dissolved in dilute hydrochloric acid and extracted with ether. The aqueous solution yielded an oily product, which was taken up in ether, and the solution was dried with solid potassium hydroxide. The ether residue consisted of 17 g. of oil, which when twice distilled at 770 mm. yielded 10 g. of product, boiling at 209–216°.

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[9] Klages, *Ber.*, 37, 2312 (1904).

[10] Klemenko, J. *Russ. Phys.-Chem. Soc.*, 43,212 (1911).

The analysis agrees for $C_{11}H_{15}N$, but its reactions indicate that it is unsaturated, and its properties do not agree with those of α-phenyl-N-methylpyrrolidine, which was finally prepared by another procedure.

Anal. Subs., 0.1202: CO_2, 0.3595; H_2O, 0.0980. Calcd. for $C_{11}H_{15}N$: C, 81.99; H, 9.31. Found: C, 81.56; H, 9.05.

The compound should be represented by one of the three formulas $C_6H_5CH{=}CH\text{-}CH_2CH_2NHCH_3$, $C_6H_5CHNCH_3CH_2CH{=}CH_2$ or $C_6H_5CH{=}CHCH(NHCH_3)CH_3$.

Benzoyltrimethylene.—This compound was prepared from benzoylacetic ester[11] and ethylene bromide according to the method of Perkin[12] slightly modified. The method consists in heating the ester in alcoholic solution under pressure with half the theoretical quantities of ethylene bromide and sodium ethylate. The only change made was to repeat this treatment with one-half the original quantities of bromide and sodium ethylate, which resulted in a better yield. Benzoyltrimethylene bromide was prepared according to the Perkin directions.[12]

α-Phenyl-N-methylpyrroline.—Seventeen grams of benzoyltrimethylene bromide was added to about 75 cc. of 25% methyl alcoholic methylamine. After evaporation of the solvent, the oily residue was extracted with dilute hydrochloric acid. The insoluble portion was extracted with ether and the solution dried and evaporated, yielding about 8 g. of product, boiling at 136–139° at 34 mm. and at 239–246° at 760 mm. It contained no nitrogen. The analysis and boiling point indicate that it was regenerated benzoyltrimethylene.

Anal. Subs., 0.1735: CO_2, 0.5201; H_2O, 0.1105. Calcd. for $C_{10}H_{10}O$: C, 82.19; H, 6.85. Found: C, 81.84; H, 7.09.

Perkin[12] refers to the action of silver nitrate and sodium ethylate on benzoyltrimethylene bromide and states that the resulting compound is probably 3-benzoyl-*n*-propyl alcohol. He did not analyze his product, but we have found that any base will regenerate the benzoyltrimethylene from the bromide. The acid solution referred to above was treated with sodium hydroxide, the separated oil was taken up in ether and the solution was dried with potassium carbonate and evaporated. The residue boiled at 134–139° at 34 mm. The analysis agreed for phenylmethylpyrroline.

Anal. Subs., 0.1427: CO_2, 0.4327; H_2O, 0.1021. Calcd. for $C_{11}H_{13}N$: C, 83.01; H, 8.17. Found: C, 82.69; H, 7.96.

The compound could not be made to absorb hydrogen in the presence of a platinum catalyst nor were any other attempts to reduce it successful.

β-*p*-Cresoxyethylbenzoylacetic Ester, $CH_3C_6H_4OCH_2CH_2CH(COC_6H_5)COOC_2H_5$.—One hundred and seven grams of benzoylacetic ester and 60 g. of *p*-cresoxy-ethylene bromide (one-half of the equivalent quantity) were dissolved in an absolute alcoholic solution of sodium ethylate prepared from 150 cc. of absolute alcohol and 6.4 g. of sodium. After boiling for six hours under reflux, the solvent was removed, water added and the reaction products were dissolved in ether. The ethereal solution was washed with water and dried with calcium chloride, yielding 145 g. of oily product on evaporation. It was subjected to fractional distillation in vacuum. The fraction boiling below 260° (8 mm.) was discarded. About 40 g. of product distilling at 240–250" consisted of impure *p*-cresoxyethylenebenzoylacetic ester. There was some decomposition during distillation and the compound could not be prepared absolutely pure. It was again distilled for analysis.

Anal. Subs., 0.1575: CO_2, 0.4353; H_2O, 0.0823. Calcd. for $C_{20}H_{22}O_4$: C, 73.62; H, 6.75. Found: C, 74.73; H, 5.80.

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[11] Claisen, Ann., 291, 70 (1896).

[12] Perkin, J. *Chem. Soc.*, 47,836 (1885).

γ-*p*-Cresoxypropylphenyl Ketone, $CH_3C_6H_4O(CH_2)_3OCC_6H_5$.—The ketone cleavage of the ester was carried out by heating with slightly more than the calculated quantity of alcoholic potassium hydroxide for four hours on the steam-bath. The product remaining after evaporation of the solvent was an oil, which was dissolved in ether, and the solution was dried and evaporated. The product was fractionated at 8 mm. The major portion boiled at 250–260° with slight decomposition. The distillate crystallized at once and, after removal of adhering oil by pressing between filter paper, it was recrystallized from about 5 parts of 95% alcohol. It crystallizes in large prisms which melt at 63°. The yield was from 40 to 50% of the weight of the ester employed.

In subsequent operations the ester was not distilled, the fractions boiling below ZOO° at 32 mm. being removed and the crude ester saponified. The ketone may also be obtained from the crude ester by saponification and distilling off the products boiling under 200" and allowing the undistilled material to crystallize. Analysis of the pure ketone gave the following results.

Anal. Subs., 0.2021: CO_2, 0.5965; H_2O, 0.1269. Calcd. for $C_{17}H_{18}O_2$: C, 80.31; H, 7.08. Pound: C, 80.49; H, 6.97.

γ-*p*-Cresoxypropylphenyl Ketoxime.—Five grams of ketone was dissolved in an alcoholic solution of hydroxylamine prepared from 1.5 g. of hydroxylamine hydrochloride and 0.5 *g.* of sodium. After the solution was heated for one hour on the steam-bath, the solvent was removed, leaving a sirupy product which crystallized to a solid cake. It crystallized from petroleum ether in long prisms, melting at 75°. The yield was quantitative.

Anal. Subs., 0.1617: CO_2, 0.4462; H_2O, 0.1012. Calcd. for $C_{17}H_{19}NO_2$: C, 75.47; H, 7.06. Found: C, 75.27; H, 6.88.

1-*p*-Cresoxy-4-amino-4-phenylbutane Hydrochloride, $CH_3C_6H_4O(CH_2)_3CH(NH_2\text{-}HCl)C_6H_5$.—Twenty-five grams of oxime was dissolved in 500 cc. of 95% alcohol and reduced with 1800 g. of 2.5% sodium amalgam which was added in portions of about 250 g. each, followed by the addition of 25 cc. of glacial acetic acid over a period of three hours. The temperature was kept below 40" during the reaction.

The sodium acetate was filtered off and washed with alcohol, and the alcoholic solutions were concentrated on the steam-bath to 150 cc. An oily substance, probably the acetate of the amine, separated out and was extracted with ether.

On being shaken with 75 cc. of 15% hydrochloric acid, the ether solution became filled with a mass of white crystals of the hydrochloride of the base. The aqueous solution was made alkaline with sodium hydroxide and extracted with ether. The ether was evaporated, leaving an oil which also crystallized when treated with dilute hydrochloric acid. The combined yield was 20 g. of the hydrochloride. It was crystallized from hot water, from which it separated in long needles. The nitrate is also difficultly soluble in water and crystallizes in plates.

Anal. Subs., 0 1616: CO_2, 0.4145; H_2O, 0.1100. Subs., 0.1215: AgCl, 0.0595. Calcd. for $C_{17}H_{22}NOCl$: C, 70.22, H, 7.57; Cl, 11.87. Found: C, 69.95; H, 7.56; Cl, 11.68.

1-Phenyl-1-amino-4-chlorobutane Hydrochloride.—Twenty-two grams of p-cresoxy-aminophenylbutane hydrochloride was heated in a sealed tube with 150 cc. of aqueous hydrochloric acid saturated at 0" for twenty hours. The separated cresol was removed with ether and the aqueous solution concentrated on the steam-bath. The compound crystallized on evaporation. A part was recrystallized for analysis from about 5 parts of hot water. It melted with decomposition at 200–205°. The yield was 13 g.

Anal. Subs., 0.1340: AgCl, 0.1749. Calcd. for $C_{10}H_{15}NCl_2$: Cl, 31.65. Found: 31.06.

α-Phenylpyrrolidine.—Twelve grams of phenylaminochlorobutane hydrochloride was dissolved in water and a strong solution of potassium hydroxide added. The oil which separated reacted suddenly with evolution of heat to form a-phenylpyrrolidine. The product was extracted with ether and the solution dried with solid potassium hydroxide. The ether residue boiled at 236–238° (uncorr.) at 757 mm. The yield was 8 g.

Anal. Subs., 0.1400: CO$_2$, 0.4155; H, 0.1154. Calcd. for $C_{10}H_{13}N$: C, 81.63; H, 8.84. Found: C, 80.94; H, 9.15.

α-Phenyl-N-methylpyrrolidine.—Four grams of α-phenylpyrrolidine was dissolved in 25 cc. of methyl alcohol containing 4 g. of methyl iodide. After twelve hours the solvent was evaporated and the residue treated with strong potassium hydroxide solution. Most of the oil was soluble in ether but a part remained undissolved. The ethereal solution was dried with solid potassium hydroxide and the ether evaporated, leaving 2.6 g. of base, which distilled at 760 mm. at 225–227° (uncorr.). The yield of pure product was 2.2 g.

Anal. Subs., 0.1460: CO$_2$, 0.4374, H_2O, 0.1161. Subs., 0.1560: N, 11.2 cc. at 29° and 762 mm. Calcd. for $C_{11}H_{15}N$: C, 81.99; H, 9.31; N, 8.69. Found: C, 81.71; H, 8.83; N, 8.23.

Summary

A number of pyrrolidine derivatives have been prepared with reference to their chemical relation to nicotine and tested as contact insecticides.

Methods are described for the preparation of a-methyl- and α-phenylpyrrolidine and a-phenylpyrroline and their N-methyl derivatives. The various intermediary compounds and the results of several unsuccessful attempts to prepare substituted pyrrolidines are described in the experimental part.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE INSECTICIDE DIVISION, BUREAU OF CHEMISTRY AND SOILS]

THE PREPARATION AND PROPERTIES OF SOME NEW DERIVATIVES OF PYRIDINE[1,2]

BY F. B. LAFORGE

RECEIVED MAY 18, 1928 PUBLISHED SEPTEMBER 5, 1928

In a previous article it was pointed out that whereas nicotine, which is β-pyridyl-α-N-methylpyrrolidine, stands out as one of the few known organic compounds possessing insecticidal properties of a very high order, none of the several other substituted pyrrolidines which have been tested approach it in toxicity.

It is natural to inquire whether or not the pyrrolidine group is essential to the specific toxic effect of nicotine on insects and whether or not some

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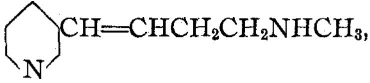
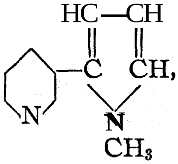
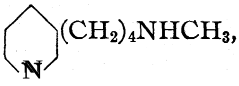
[1] A study of the insecticidal action of these compounds is being made in cooperation with Dr. C. H. Richardson, Deciduous Fruit Insect Investigations, Bureau of Entomology.

[2] Presented at the Insecticide Symposium, St. Louis meeting of the American Chemical Society, April, 1928.

other groups attached to the pyridine radical would result in compounds of the same order of toxicity.

Accordingly, a number of new synthetic pyridine derivatives were prepared and tested on insects. All these derivatives were of a very low order of toxicity. On the other hand, three known compounds derived from nicotine itself, metanicotine,  nicotyrine,  and dihydrometanicotine,  were of high toxicity, the first compound being almost equal to nicotine itself in this respect. The other two, although less toxic than metanicotine, still exhibited this property to a degree which far exceeded that of any purely synthetic pyridine derivative which we have prepared and tested. These synthetic compounds are all open chain pyridylamino derivatives which were obtained by reduction of the oximes or hydrazones of pyridyl ketones.

Since considerable quantities of these ketones were required for the investigations, it was necessary to develop satisfactory methods for their preparation. A number of pyridyl ketones have been described by Engler,[3] who prepared them by distillation of pyridinecarboxylic acid calcium salts with the calcium salts of the fatty acids, and by Pinner[4] by the condensation of pyridinecarboxylic acid esters with the esters of fatty acids in the presence of sodium ethylate and cleavage of the resulting pyridoylacetic esters. The method of Engler gives low yields of very impure products. Pinner does not state his yields, but numerous attempts to prepare pyridyl ketones by the method described by him were unsuccessful. Even when every precaution was taken in carrying out the reaction, the yields were at the best exceedingly small and usually nothing but nicotinic acid could be recovered from the reaction product.

The method by which methyl and propyl pyridyl ketones were finally prepared leaves something to be desired, but it was adequate for the preparation of several hundred grams of these compounds.

Nicotinic acid hydrochloride or the free acid prepared from the cheaper nitrate was the starting material, It was esterified and the ester transformed into the acid amide which was converted into the cyanide. These operations are described by R. Camps, but as the directions given by that author are somewhat inadequate, some slight changes in the methods were introduced.

According to Blaise,[5] aromatic cyanides react with the Grignard reagent,

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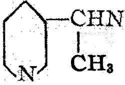
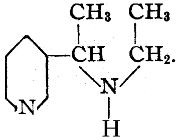
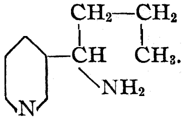
[3] Engler, Ber., 22, 597 (1889), 24, 2541 (1891).

[4] **Pinnw,** *Ber.*, **34,4234** (1901).

[5] **Blaise,** *Compt.* **rend., 333,** 1217 (1900).

producing fairly good yields of the aromatic alkyl ketones. This method was used for the preparation of pyridyl ketones.

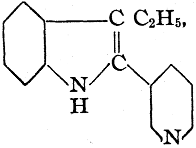
β-Pyridylethylamine,  was prepared by reduction of the β-pyridyl methyl ketoxime and from this the corresponding N-ethyl derivative was obtained. The resulting compound differs from nicotine in that it has an open four carbon chain instead of the closed pyrrolidine ring, and it is not methylated on the nitrogen atom. It may be represented by the formula .

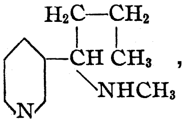
β-Pyridylpropyl ketone was prepared from β-pyridine cyanide and *n*-propyl iodide by the Grignard reaction. As the oxime of the ketone could not be obtained in crystalline form, the hydrazone was prepared and reduced to the β-pyridylbutyl amine represented by the formula .

The hydrazone of this ketone as described by Engler was prepared from the crude ketone, and was made for the purpose of isolating the ketone itself in pure condition.

It was found that a crystalline hydrazone could be obtained easily from the crude ketone prepared by the Grignard reaction, but it differed in its chemical and physical properties from the one described by Engler. Its melting point (130°) differed from that recorded by Engler (182°), and it could not be changed even by repeated recrystallization.

Engler prepared the pure ketone from his hydrazone by decomposition with concentrated hydrochloric acid.

When the same treatment was applied to the hydrazone prepared by us, it resulted in a quantitative yield of a crystalline base, which is in all probability 1-pyridyl-2-ethylindol , analogous to the methylindol from acetone hydrazone.

The amine resulting from the reduction of the hydrazone was methylated on the nitrogen to β-pyridylbutyl-N-methylamine, , which differs from nicotine in that an open chain of the same number of carbon atoms is substituted for the N-methylpyrrolidine ring.

Ethyl Nicotinate.—The following method, which is a slight modification of the one described by R. Camps,[6] was found most convenient for the preparation of ethyl nicotinate. Eighty grams of nicotinic acid hydrochloride or 70 g. of the free acid was dissolved in a mixture of 150 g. of absolute alcohol and 150 g. of concentrated sulfuric acid, and the solution was heated for about four hours in a flask on the steam-bath. The

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[6] R. Camps, *Arch. Pharm.*, 240,366 (1902).

solution was cooled and divided roughly into three portions, which were poured onto cracked ice. Ammonia was then added in a quantity sufficient to render the solution strongly alkaline. Generally some ester separated as an oily layer but most of it remained dissolved. The solution was extracted four times with ether, the last two or three ether extracts being used to extract the other portions.

The ethereal solutions were washed with water and dried with potassium carbonate, after which the solvent was removed. The yield of pure ester boiling between 222 and 224° was always from 71 to 75 g. If pure material is used to start with, it is not necessary to distil the ester if it is to be used for the preparation of the amide.

Nicotinic Acid **Amide.**—Since the directions for the preparation of this derivative are rather inadequate, it seems desirable to add a few details to those given by Camps.

One hundred grams of nicotinic ester was covered with about 1.5 volumes of concentrated aqueous ammonia saturated at 0°. The flask was kept loosely closed for about eighteen hours, after which time the lower layer generally dissolved on shaking. The solution was again saturated with ammonia gas and allowed to stand for several hours. The process was again repeated, after which, as a rule, crystals of the amide began to appear in the solution. At this stage the contents of the flask was evaporated to dryness in a dish on the steam-bath. The crystalline cake was ground and further dried at 120°. The yield was nearly quantitative.

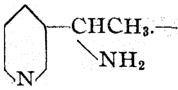
β-Pyridine Cyanide.—In the preparation of the cyanide from the amide, a few details should be added to those given by Camps.[6]

Eighteen grams of powdered amide and 25 g. of phosphorus pentoxide were placed in a distilling flask of about 150 cc. capacity and mixed by shaking. The mixture was subjected to distillation in a vacuum of about 30 mm. The heating must be done by means of an oil-bath, the temperature of which is rapidly raised to about 300°. The oil-bath was then removed and the heating continued with a free flame as long as a distillate was obtained. The cyanide crystallized on cooling to a snow-white solid which was redistilled at ordinary pressure. All but a trace boiled at 201° at 760 mm. The yield was consistently from 19.5 to 20.5 g. This cyanide was used for the preparation of pyridyl ketones.

β-Pyridylmethyl Ketone.—Twenty grams of β-pyridyl cyanide dissolved in about 100 ce. of dry ether was slowly added with vigorous stirring to the solution of Grignard reagent prepared from 40 g. of methyl iodide and 7 g. of magnesium in about 150 ce. of ether. A voluminous yellow precipitate of the addition compound was produced. At this stage most of the ether is distilled off and replaced by an equal quantity of dry benzene. After boiling for about an hour, the contents of the flask was decomposed by the addition of water followed by about 100 g. of 40% sulfuric acid. The red aqueous solution was made alkaline with sodium hydroxide and subjected to steam distillation until about 2 liters of distillate was collected. The distillate was acidified with hydrochloric acid and concentrated to 60 ce. on the steam-bath. The solution was treated with sodium hydroxide and the separated oil extracted with ether. The dried ethereal solution yielded about 14 g. of oily residue, which was distilled at ordinary pressure. The yield of pure product varied from 11 to 12 g. The boiling point, 217–220°, agreed with that found by Engler.

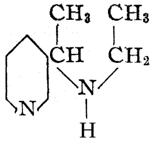
β-Pyridylmethyl Ketoxime.—Fifteen grams of the ketone was dissolved in 75 cc. of a solution of hydroxylamine prepared from 9 g. of the hydrochloride. After standing for about twelve hours the solution was heated on the steam-bath for a short time and then evaporated to a sirup.

The residue crystallized on cooling to a solid cake, which was washed with benzene and then recrystallized from the same solvent. The yield of pure product was 15 g. It melted at 113°. Engler gives 112° as the melting point of the compound.

β-Pyridylethylamine, 
—Five grams of the oxime was dissolved in 75 cc. of 95% alcohol and 40 g of zinc dust and 40 g of glacial acetic acid were added alternately in small portions over a period of several hours. After about twenty-four hours the undissolved zinc and zinc acetate were filtered off and washed with alcohol. The alcoholic solution was evaporated to a small volume and after the addition of water the evaporation was repeated several times to remove as much as possible of the acetic acid. Strong potassium hydroxide solution was added to the concentrated solution and the separated oil extracted with ether. The dried ethereal solution yielded on evaporation about 4.5 g. of residue, practically all of which distilled between 219 and 221° at 765 mm.

Anal. Subs., 0.2370, 0.1632 CO_2, 0.5951, 0 4087: H_2O, 0.1738, 0.1165. Subs., 0 1350: N, 27.4 cc. at 23° and 772 mm. Calcd. for $C_7H_{10}N_2$: C, 68.84; H, 8.19; N, 22.95. Found: C, 68.48, 68.29; H, 8.14, 7.93, N, 23.13.

The picrate formed in aqueous solution melted at 186–187°.

β-Pyridylethyl-N-ethylamine, 
—Four grams of the primary amine, was added to 5 g. of ethyl iodide in 10 cc. of absolute alcohol and the solution was allowed to stand for forty-eight hours at room temperature.

The alcohol was expelled on the steam-bath, the residue was dissolved in 25 cc. of water and made strongly alkaline with potassium hydroxide. The separated oil was only partly soluble in ether. The ether residue was dissolved in about 15 cc. of 10% hydrochloric acid, and the solution was cooled and treated with a solution of 4 g. of sodium nitrite in 10 cc. of water.

The nitroso compound separated as an oil on addition of sodium hydroxide solution. It was extracted with ether and the ether residue was heated for one-half hour on the steam-bath with 7 ec. of concentrated hydrochloric acid. The secondary amine was separated by the addition of concentrated potassium hydroxide solution and extraction with ether. The dried ethereal solution gave 3 g. of crude product on evaporation. It was twice distilled at 773 mm. and yielded 2 g. of product boiling between 223 and 226". In another experiment 16 g. of the primary amine gave 8 *g.* of the ethyl derivative.

Anal. Subs., 0.2114: N, 35.0 cc. at 19° and 767 mm. Calcd. for $C_9H_{14}N$: N, 18.67. Found: 19.11.

β-Pyridylpropyl Ketone.—Twenty grams of β-pyridine cyanide in 100 cc. of dry ether was slowly added to the Grignard reagent prepared from 7.7 g. of magnesium and 55 g. of n-propyl iodide. The reaction product was boiled for two hours and then cooled with ice and decomposed with water and finally with saturated ammonium chloride solution. Nearly all of the yellow precipitate formed in the reaction dissolved. The ethereal solution was separated and dried, yielding about 28 g. of crude product. The fraction which distilled between *235* and 260° contained the ketone.

It was redistilled and the fraction of 240–248° was analyzed for nitrogen, but the figures obtained on several preparations ranged from 10.9 to 11.3% instead of the theoretical 9.4% for $C_9H_{11}NO$. Closer figures could not be obtained on analysis of the steam distilled product. Therefore the crude product was converted into the phenyl hydrazone.

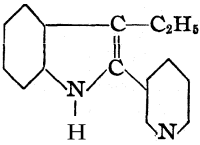
β-Pyridylpropyl Ketone Phenylhydrazone.—This derivative has been described by Engler, who prepared it from the impure ketone which he obtained by distillation of the mixture of nicotinic and propionic acid calcium salts. The author employed the hydrazone for the purpose of isolating the pure ketone, which is stated to be easily obtainable by cleavage of the hydrazone with hydrochloric acid.

Thirty grams of the crude ketone fraction boiling between 235 and 260° was heated for two hours on the steam-bath with 25 g. of phenylhydrazine. Crystallization took place on cooling. The crude product was extracted with 50% alcohol and then recrystallized by dissolving in the necessary quantity of hot 95% alcohol and adding an equal volume of hot water. The recrystallized substance melted at 129–130°. The yield was 24 g. For analysis it was twice recrystallized from acetic ester without altering its melting point. Engler gives 182° as the melting point of the hydrazone.

Anal. Subs., 0.1248: CO_2, 0.3450; H_2O, 0.0835. Calcd. for $C_{15}H_{17}N_3$: C, 75 31; H, 7.11. Found: C, 75.40; H, 7.43.

Semicarbazone of β-Pyridylpropyl Ketone.—The semicarbazone was obtained by heating the crude ketone in alcoholic solution with the calculated quantity of semicarbazide. The resulting product recrystallized from water melted at 169–170°.

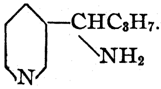
Anal. Subs., 0.1845: N, 44.2 cc. at 21° and 768 mm. Calcd. for $C_{10}H_{14}N_4O$: N, 27.19. Found: 27.43.

1-β-Pyridyl-2-ethylindol,  —When the hydrazone is brought into contact with strong hydrochloric acid, it instantly changes to a bright yellow, crystalline product difficultly soluble in water.

The resulting compound was dissolved in hot water, and on addition of alkali the free base was obtained as a pure white, crystalline solid melting sharply at 158'.

Anal. Subs., 0.1821: CO_2, 0.5383; H_2O, 0.1000. Subs., 0.2058: N, 22.9 cc. at 24° and 764 mm. Found: C, 80.80; H, 6.10; N, 12.48.

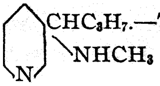
These figures agree for a compound of the formula $C_{15}H_{14}N_2$, differing from that of the hydrazone, $C_{15}H_{17}N_3$, by —NH_3. It seems altogether probable that the substance is an indol derivative of the formula given above, for which the theory requires C, 81.08; H. 6.30; N, 12.61.

1-β-Pyridylbutylamine,  —Twenty-three grams of the hydrazone was dissolved in 300 cc. of 95% alcohol and 200 g. of zinc dust and 200 g. of glacial acetic acid were added alternately in small quantities over a period of several hours. After standing for about eighteen hours, the solution was filtered and the undissolved material was washed with alcohol. The filtrate was concentrated on the steam-bath to a small volume and the evaporation was repeated to remove most of the acid. The solution was finally concentrated to a sirup, which was dissolved in 150 cc. of water, cooled and treated with saturated sodium hydroxide solution until the precipitate of zinc hydroxide which at first formed had almost completely dissolved.

At the same time the amine, together with the aniline formed in the process, separated as an oily layer, which was extracted with ether. The dried ethereal solution yielded 16 g. of the mixture.

The aniline was separated by suspending the oil in 60 cc. of water and adding dilute hydrochloric acid until the aqueous solution was acid to litmus paper. The undissolved aniline was extracted with ether and the pyridyl amine was recovered from the acid solution by addition of sodium hydroxide and extraction with ether. The yield of crude product was 13 g., 9.4 g. of which boiled between 247 and 251°.

Anal, Subs., 0.1678: CO_2, 0.4438; H_2O, 0.1372. Subs., 0.1532: N, 24.0 cc., at 23° and 778 mm. Calcd. for $C_9H_{14}N_2$: C, 72.00; H, 9.33; N, 18.67. Found: C, 72.13; H, 9.09; N, 18.15.

1-β-Pyridylbutyl-N-methylamine,  $C_5H_4N\cdot CH(C_3H_7)NHCH_3$.—Thirteen grams of the primary amine was dissolved in 40 cc. of water, the solution was cooled with ice and 12 g. of dimethyl sulfate was added in small portions with constant shaking. After several hours a solution of potassium hydroxide was added and the reaction product was extracted with ether. The dried ethereal solution was evaporated and the resulting oil, which weighed 11 g., was distilled. The yield of the product boiling between 240 and 250° was 6.5 g. It was redistilled at 760 mm. and the fraction boiling between 244 and 247" was taken for analysis.

Anal. Subs., 0.1422: CO_2, 0.3810; H, 0.1213. Subs., 0.1735: N, 26.4 cc. at 26° and 765 mm. Calcd. for $C_{10}H_{16}N_2$: C, 73.17; H, 9.75; N, 17.07. Found: C, 73.08; H, 9.48; N, 16.91.

Metanicotine.—This derivative was prepared according to the method of Pinner.[7] It boiled between 275 and 278" at 760 mm. As a check on its purity, its optical activity was determined: 1.1368 g. of substance in 10.275 g. of water rotated in a 1dm. tube −0.062°, indicating that the quantity of nicotine in the preparation could not be greater than 3%.

Dihydrometanicotine.—Löffler[8] has prepared this compound by reduction of metanicotine with hydriodic acid. It may be obtained more easily by direct reduction with hydrogen in the presence of reduced platinum oxide catalyst by the method of Adams.[9]

Fourteen grams of metanicotine in 100 cc. of alcohol and 14.4 cc. of concentrated hydrochloric acid absorbed the required quantity of hydrogen in about one hour. The alcohol was evaporated and the base set free with potassium hydroxide and extracted with ether. The ether residue weighed 14 g., 12 g. of which distilled within 1.5" of the boiling point (258–259°) recorded by Löffler.

Summary

A new method is described for the preparation of pyridyl alkyl ketones by the use of the Grignard reaction. Methyl- and propylpyridylamines were obtained by reduction of the corresponding oximes or hydrazones. Although these compounds are chemically very similar to nicotine, they were, nevertheless, of low toxicity to insects, as were also their N-alkyl substitution products.

Metanicotine, nicotyrin and dihydrometanicotine were of a high order of toxicity, the first mentioned being only slightly below that of nicotine.

WASHINGTON, D. C.

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[7] Pinner, *Ber.*, 27, 2865 (1894).

[8] Löffler, *Ber.*, 42, 3431 (1909).

[9] Adams, THIS JOURNAL, 45, 1072 (1923).

[CONTRIBUTION FROM THE INSECTICIDE DIVISION, BUREAU OF CHEMISTRY AND SOILS]

THE PREPARATION OF ALPHA-, BETA- AND GAMMA-BENZYLPYRIDINES[1,2]

BY F. B. LAFORGE

RECEIVED MAY 18, 1928 PUBLISHED SEPTEMBER 5, 1928

In a recent paper by Tattersfield and Gimingham[3] the announcement was made that benzylpyridines possess unusual insecticidal properties. The material used by these authors was a mixture of the *a*- and γ-benzylpyridines prepared by the method of Tschitschibabin.[4]

Since this method is extremely simple, and gives satisfactory yields, it would probably be capable of development into a commercial process should it be established that the benzylpyridines were of value as insecticides.

In order to provide material for insecticidal studies considerable quantities of this benzylpyridine mixture have been prepared. α-Benzylpyridine was separated by the picrate method, but a more convenient process than that described by Tschitschibabin was found for obtaining the γ-derivative. This consisted in the oxidation of the benzylpyridine mixture to the corresponding ketones, the separation of the y-ketone by recrystallization of the picrate and reduction of the ketone back to the benzyl compound.

β-Benzylpyridine was prepared from β-pyridylphenyl ketone by reducing its oxime to the corresponding amine, from which the carbinol was obtained and reduced with hydriodic acid. By these methods, which are described below in detail, the three benzylpyridines were prepared in pure condition.

a- and y-Benzylpyridine

The method of Tschitschibabin has been simplified by omitting the first treatment with sodium hydroxide and ether extraction, the hot reaction mixture being poured directly into water, which dissoves the hydrochlorides of the bases, leaving the tarry materials. The nearly colorless, aqueous solution is poured off and treated with sodium hydroxide solution. The bases are collected in ether and after evaporation of the solvent are distilled. The fraction boiling at 270–310° consists almost entirely of benzylpyridines. The portion boiling at 310–370° is probably a very indefinite mixture containing dibenzylpyridines.

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[1] A study of the insecticidal action of these compounds is being made in cooperation with Dr. C. H. Richardson, Deciduous Fruit Insect Investigations, Bureau of Entomology.

[2] Presented at the Insecticide Symposium, St. Louis meeting of the American Chemical Society, April, 1928.

[3] Tattersfield and Gimingham, *Annals of Applied Biology*, *14*, 217 (1927).

[4] Tschitschibabin, *J. Russ. Phys.-Chem. Soc.*, 33, 249 (1901); 47, 1297 (1915); *Chem. Zentr.*, [2] 72, 127 (1901); [2] 87, 146 (1916).

The proportions employed were usually 72 g. of pyridine, 98 g. of benzyl chloride and 1 g. of copper-bronze powder. The yield of the benzylpyridine fraction is about 60 *g.* About 15 g. of the higher fraction and from 15 to 20 g. of pyridine are recovered. Analysis of the first fraction gave the following results.

Anal. Subs., 0.0989: CO_2, 0.3074; H_2O, 0.0576. Calcd. for $C_{12}H_{11}N$: C, 85.21; H, 6.51. Found: C, 84.77; H, 6.47.

The a-derivative may be prepared from the mixture of benzylpyridines in a pure state by fractional crystallization of the picrates.

The picrate mixture obtained from alcoholic solution consists of prisms and needles which do not differ much in solubility in any solvent. A rough separation may be made by quickly treating the mixture with a quantity of boiling water insufficient for complete solution. The undissolved portion consists mostly of the prisms of the a-compound. It is dissolved in warm acetone, from which large prisms of the a-compound crystallize on cooling. The solvent is poured off before the needles of the β-compound begin to be deposited. These prisms are finally recrystallized from alcohol and melt sharply at 139–140° (uncorr.).

The free base obtained from the picrate boiled at 275–276° (corr.), which boiling point is in agreement with the figures reported by Tschitschibabin.

The picrate of y-benzylpyridine could not be separated from the mixture in a pure state by crystallization from benzene, as reported by that author. The pure base was, however, obtained by an indirect method.

The original mixture of the two benzylpyridines was oxidized to the ketones with potassium permanganate.[5] From the mixture of the two ketones the picrate of the y-form is very easily separated from the picrate of the a-compound by crystallization from alcohol. It melts as reported by Tschitschibabin at 160°.

The free ketone was obtained from the picrate in the form of a white, crystalline solid. It was dissolved in ether and after removal of the solvent boiled at 315° (corr.). After recrystallization from petroleum ether it melted at 72°.

Reduction of the γ-Benzyl Ketone by the Method of Clemmensen.[6]—Eleven grams of the pure ketone was dissolved in about 200 cc. of 10% hydrochloric acid and heated with 50 g. of amalgamated zinc for ten hours on the steam-bath. The colorless solution was decanted and neutralized with sodium hydroxide solution. The precipitate which formed consisted of the zinc double salt of γ-benzylpyridine, together with some zinc hydroxide. It was filtered off and extracted repeatedly with 70% acetone, which dissolved the zinc double salt. The acetone was evaporated on the steam-bath, leaving the crystalline zinc compound, which is nearly insoluble in water. It is easily obtained

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[5] Tschitschibabin, J. *Russ. Phys.-Chem. Soc.*, **33**, 300 (1901); *Chem. Zentr.*, *73*, 206 (1902).

[6] Clemmensen, Ber., 46, 1837 (1913); 47, 61 (1918).

pure by recrystallization from benzene. The yield of the pure compound was 11 g. It melts sharply at 161° (uncorr.).

Anal. Subs., 0.1403, 0.1790: CO_2, 0.3162, 0.3999; H_2O, 0.0652, 0.0812. Calcd. for $C_{24}H_{22}N_2{\cdot}ZnCl_2$: C, 61.01; H, 4.66. Found: C, 61.46, 60.94; H, 5.15, 5.04.

The zinc double salt was boiled for ten minutes with a 50% potassium carbonate solution, and the resulting colorless oil was extracted with ether. The ether residue boiled at 287° (corr.) at 760 mm., which is the figure given by Tschitschibabin for γ-benzylpyridine. The yield was 6.5 g.

β-Benzoylpyridine.—β-Benzoylpyridine has been prepared by Bernthsen and Mettegang[7] and Jeiteles[8] from β-benzoylpyridinecarboxylic acid obtained by the condensation of quinolinic acid anhydride and benzene in the presence of aluminum chloride. It may be more conveniently prepared from β-pyridine cyanide and bromobenzene by the Grignard method.

Twenty grams of β-pyridine cyanide[9] in about 200 cc. of dry ether was slowly added with constant stirring to the Grignard reagent prepared from 38 g. of bromobenzene and 5.8 g. of magnesium in about 400 cc. of ether. A yellow precipitate separated which was decomposed by the slow addition of water. Saturated ammonium chloride solution was then added and the flask shaken until practically all of the solid had dissolved. The ethereal solution was dried and the solvent evaporated, leaving a red oil.

The quantity varied somewhat, but was usually about 35 grams. It contains the ketone, together with considerable quantities of impurities. If treated with fairly strong hydrochloric acid solution, it completely resinifies, but it may be separated into a basic and non-basic portion by suspending it in 150 to 200 cc. of water and carefully adding 10% hydrochloric acid with constant stirring until no more of the oil dissolves. It is best to pour off the solution after about 50 cc. of acid has been employed and to treat the undissolved oil with more dilute acid. The non-basic oil usually amounts to about 9 g. The acid solution yields about 25 g. of oil on addition of sodium hydroxide. This oil is still impure, but the major portion distils between 270 and 320°. The distillate, which weighed about 17 g., was dissolved in 300 cc. of hot alcohol and a hot alcoholic solution of picric acid was added, The picrate of the ketone crystallized even from the hot solution in balls of needles, which melt at 161° (uncorr.). The melting point was not changed by recrystallization. The yield was 24 g. The picrate was decomposed by suspending in 250 cc. of hot water and adding 30 cc. of concentrated ammonia. The ketone separated as a light yellow oil, which was taken up in ether and the ethereal solution washed with water and dried. The ether residue boiled between 318 and 319" (corr.).

Anal. Subs., 0.2108: CO_2, 0.6114; H_2O, 0.0993. Calcd. for $C_{12}H_9NO$: C, 78.70; H, 4.92. Found: C, 79.11; H, 5.24.

The oxime was prepared by dissolving 8 g. of the ketone in 60 cc. of an alcoholic solution of hydroxylamine prepared from 6 g. of the hydrochloride and 2 g. of sodium and filtering from the sodium chloride. After heating for several hours on the steam-bath the solution was concentrated to one-half of its volume and 2 volumes of water was added. The oxime crystallized in good yield and melted between 140 and 155". It was recrystallized from benzene and melted at 161°.[8]

Anal. Subs., 0.1510: CO_2, 0.4066; H_2O, 0.0738. Calcd. for $C_{12}H_{10}N_2O$: C, 72.81; H, 5.05. Found: C, 73.44; H, 5.40.

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[7] Bernthsen and Mettegang, *Ber.*, 20, 1209 (1887).

[8] Jeiteles, *Monatsh.*, 17, 515 (1896).

[9] R. Camps, *Arch. Pharm.*, 240,366 (1902).

β-Pyridylphenylmethylamine.—Sixteen and one-half grams of pure oxime were dissolved in 200 cc. of 95% alcohol, the solution was treated with 150 g. of zinc dust and 150 g. of glacial acetic acid was added alternately in small quantities over a period of about two hours. After the solution had stood overnight, the residue of zinc acetate and unaltered zinc was filtered off and washed with alcohol. The alcoholic solution was concentrated on the steam-bath with addition of water from time to time to expel the alcohol and most of the excess acid. The concentrated solution was treated with an excess of strong sodium hydroxide solution, and the separated oil was extracted with ether. The ether residue was distilled and yielded 14 g. of pure product, boiling at 329–331° (corr.), at 760 mm.

Anal. Subs., 0.1934: CO_2, 0.5565; H_2O, 0.1168. Calcd. for $C_{12}H_{12}N_2$: C, 78.26; H, 6.52. Found: C, 78.54; H, 6.71.

β-Pyridylphenylcarbinol.—The amine was transformed into the corresponding alcohol by dissolving it in about the calculated quantity of dilute hydrochloric acid and adding an aqueous solution of sodium nitrite, which caused a vigorous evolution of nitrogen. After standing for a few hours the solution was made alkaline with sodium hydroxide solution and the separated oil extracted with ether. The ether residue was a thick sirup which could not be made to crystallize. The yield was 9 g. from 11 g. of amine.

β-Benzylpyridine.—β-Benzylpyridine has been prepared by Tschitschibabin[10] by direct reduction of the corresponding ketones, but the fact is not mentioned in the reference books, and this compound was prepared by the method described before the original article was noted.

The crude sirupy carbinol was reduced by heating in a sealed tube for three and one-half hours with 30 g. of fuming hydriodic acid. The contents of the tube presented two layers. The heavy, black liquid, consisting of the periodide of benzylpyridine, insoluble in water, was separated, washed with water and decomposed by warming with concentrated sodium hydroxide solution. The separated dark oil was taken up in ether and the solution was shaken with sodium bisulfite to remove dissolved iodine. The ether residue was light brown and yielded on distillation 4.5 g. of the pure compound, boiling at 287–288° (corr.) at 760 mm. After standing for several days it crystallized to a solid cake. The analysis agrees for benzylpyridine. The picrate recrystallized from alcohol melts at 119° (uncorr.).

Anal. Subs., 0.1818: CO_2, 0.5661; H_2O, 0.1091. Calcd. for $C_{12}H_{11}N$: C, 85.21; H, 6.51. Found: C, 84.93; H, 6.67.

Summary

The method of Tschitschibabin for the preparation of α- and γ-benzylpyridine has been modified and a more convenient process found for the separation of the γ-derivative.

A new method is described for the preparation of β-benzylpyridine.

WASHINGTON, D. C.

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[10] Tschitschibabin, *Ber.*, *36*, 2711 (1903).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA]

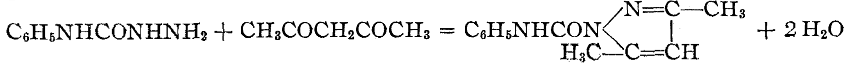
DIKETONES. I. THE REACTION BETWEEN 4-PHENYLSEMICARBAZIDE AND ACETYLACETONE

ALVIN S. WHEELER AND R. D. NORTON[1]

RECEIVED MAY 28, 1928 PUBLISHED SEPTEMBER 5, 1928

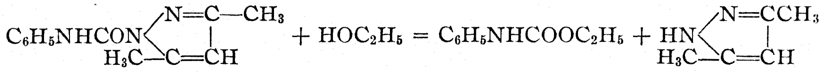
Two earlier attempts[2] were made in this Laboratory to solve the problem presented in the reaction between 4-phenylsemicarbazide and acetylacetone. Posner[3] worked out the reaction between semicarbazide and acetylacetone, obtaining 3,5-dimethylpyrazole-1-carbonamide. In our reaction two compounds are produced: one with a low melting point and very soluble in organic solvents; the other of high melting point and insoluble in organic solvents. The amount of either can be greatly increased by small changes in conditions. The low melting compound seemed to be a pyrazole on account of its pleasant odor but it could not be purified. At 60–70° it melted to an opaque liquid and above 200° to a clear liquid. Nitrogen determinations were too high. In the present study a purification method was found and a correct nitrogen analysis obtained by increasing the length of the combustion tube 100%. The reaction is carried out in alcoholic solution with very little water present. Purification was effected by extraction with petroleum ether, since both hot alcohol and hot water decompose the product. The investigation of the high melting compound (m. p. 255–257°) is reserved for future study.

The low melting compound (m. p. 69°) was proved to be a new substance, 1-phenylcarbamyl-3,5-dimethylpyrazole, according to the following equation



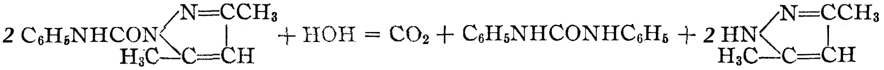
$$C_6H_5NHCONHNH_2 + CH_3COCH_2COCH_3 = C_6H_5NHCON\begin{array}{l}N{=}C{-}CH_3\\ \quad\quad |\\ H_3C{-}C{=}CH\end{array} + 2\,H_2O$$

We were able to split off the long side chain, C_6H_5NHCO, with boiling alcohol, obtaining phenylurethan and 3,5-dimethylpyrazole



$$C_6H_5NHCON\begin{array}{l}N{=}C{-}CH_3\\ \quad\quad |\\ H_3C{-}C{=}CH\end{array} + HOC_2H_5 = C_6H_5NHCOOC_2H_5 + HN\begin{array}{l}N{=}CCH_3\\ \quad\quad |\\ H_3C{-}C{=}CH\end{array}$$

Boiling water reacts with two molecules, giving carbanilide, carbon dioxide and dimethylpyrazole



$$2\,C_6H_5NHCON\begin{array}{l}N{=}CCH_3\\ \quad\quad |\\ H_3C{-}C{=}CH\end{array} + HOH = CO_2 + C_6H_5NHCONHC_6H_5 + 2\,HN\begin{array}{l}N{=}CCH_3\\ \quad\quad |\\ H_3C{-}C{=}CH\end{array}$$

Bromine reacts with the phenylcarbamyl derivative in methyl alcoholic solution, substituting the hydrogen atom in Position 4. Boiling water

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[1] Mr. R. D. Norton, Research Assistant, Rockefeller Fund

[2] O. A. Pickett, *Thesis*, **1916**; E. O. Moehlmann, Master's *Thesis*, **1923**.

[3] Posner, *Ber.*, **34**, 3980 (1901).

splits this product, giving 3,5-dimethyl-4-bromopyrazole, described by Morgan and Ackerman.[4]

Experimental Part

1-Phenylcarbamyl-3,5-dimethylpyrazole, $C_{12}H_{13}ON_3$.—Nine and five-tenths g. of 4-phenylsemicarbazide hydrochloride was dissolved in the least possible amount of water and mixed with 45 cc. of alcohol. Another solution was made of 4 6 cc. of acetylacetone, 30 cc. of alcohol and 5 g. of sodium acetate dissolved in the least possible amount of water. The second solution was slowly added with stirring to the first. A white precipitate of microscopic crystals formed at once as a rule. After standing for thirty minutes this was filtered off. Water was added to the filtrate and a second precipitate was filtered and added to the original product. The yield was about 9 g. On heating it melted to an opaque liquid at 60–70° and to a clear liquid above 200°. Petroleum ether extracted only the low melting compound. Upon its evaporation with an air jet long, white needles separated. These melted to a clear liquid at 69°. The product possesses the pleasant odor of dimethylpyrazole. As much as 8.5 g. of the pure product has been obtained with the above quantities. The amount of water used greatly affects the yield. The product is insoluble in water but soluble in the usual organic solvents

Anal. Calcd. for $C_{12}H_{13}ON_3$: N, 19.53. Found: 19.49, 19.86.

In order to get good analyses it was necessary to use a combustion tube 155 mm. in length.

Proof of Structure

Reaction with Boiling Alcohol.—One g. of the product was dissolved in *25* cc. of absolute alcohol and boiled under a reflux for an hour. The alcohol was evaporated off on the steam-bath and a viscous liquid remained which crystallized on cooling. This solid was treated with hot water, an oily substance remaining insoluble. This was filtered off and it crystallized on standing. The filtrate was concentrated over steam to a very small volume. On cooling flake-like crystals separated. They melted at 106–107° and had a very pleasant odor. This compound was 3,5-dimethylpyrazole, described by Rosengarten.[5] Its picrate and double silver salt were prepared in order to more fully identify it. The picrate formed fine, yellow needles melting at 166–167°. The double silver nitrate salt was formed by treating the compound with silver nitrate in water solution. The voluminous precipitate was recrystallized from hot water, forming long, white needles melting at 162°. Rosengarten gives 152°.

Anal. Calcd. for $(C_5H_8N_2)_2 \cdot AgNO_3$: Ag, 29.79. Found: 29.36, 29.45.

The oily substance which crystallized on cooling was recrystallized from petroleum ether. The ether was warmed slightly and decanted from an oily substance which settled out on the bottom of the beaker. If the solution is heated too much and agitated, the impurity also goes into solution. Long, white needles were obtained on cooling the ether, melting at 51–52', which is the melting point of phenylurethan. The latter was more fully identified by boiling with aniline, forming carbanilide, melting at 238°.

Reaction with Boiling Water.—The phenylcarbamyl derivative was boiled with water under a reflux for an hour. The condenser was connected with a tube containing lime water. Carbon dioxide was evolved, as evidenced by the formation of calcium carbonate. A second product condensed in considerable quantity in the condenser. This proved to be carbanilide, melting at 238°.

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[4] Morgan and Ackerman, J. *Chem. Soc.*, **123,** 1316 **(1923).**

[5] Rosengarten, *Ann.,* 279, 237 (1894).

Anal. Calcd. for $C_{13}H_{12}ON_2$: N, 13.20. Found: 13.15.

The carbanilide was converted into acetanilide (m. p. 116°) by heating with acetic anhydride.

The aqueous solution in the flask was concentrated to small volume and dimethylpyrazole crystallized out.

Reaction with Ammoniacal Silver Nitrate.—The phenylcarbamyl derivative was boiled with an ammoniacal alcoholic silver nitrate solution under a reflux for an hour. A grayish powder separated. This was analyzed for silver.

Anal. Calcd. for $C_5H_7N_2Ag$: Ag, 53.19. Found: 52.94.

In this product an atom of silver has replaced the side chain attached to nitrogen. The silver was removed with hydrochloric acid and dimethylpyrazole obtained.

1-Phenylcarbamyl-3,5-dimethyl-4-bromopyrazole, $C_{12}H_{12}ON_3Br$.—One g. of the phenylcarbamyl derivative was dissolved in 25 cc. of absolute methyl alcohol and 0.75 g. of bromine, dissolved in a little methyl alcohol, was added dropwise with stirring. White, plate-like crystals formed. These were filtered off and washed with methyl alcohol They melted at 100-101°.

Anal. Calcd. for $C_{12}H_{12}ON_3Br$: Br, 27.21. Found: 26.83.

The bromo derivative was hydrolyzed with boiling water. The product containing the bromine melted at 123° and proved to be 3,5-dimethyl-4-bromopyrazole, described by Morgan and Ackerman,[4] who gave 118° as the melting point. However, we brominated dimethylpyrazole according to their directions and obtained the melting point 123°.

Summary

1. 1-Phenylcarbamyl-3,5-dimethylpyrazole is formed by the action of 4-phenylsemicarbazide on acetylacetone, together with a substance of high melting point.
2. It yields with boiling alcohol phenylurethan and 3,5-dimethylpyrazole.
3. It yields with boiling water carbanilide, carbon dioxide and 3,5-dimethylpyrazole.
4. With bromine in alcoholic solution it gives a monobromo derivative with bromine in position 4.

CHAPEL HILL, NORTH CAROLINA

[CONTRIBUTION FROM GEORGE WASHINGTON UNIVERSITY]

THE CONDENSATION OF RHODANIC ACIDS WITH 5-NITRO-ISATIN. RHODANAL-$\Delta^{5,3'}$-5'-NITRO-OXINDOLES[1]

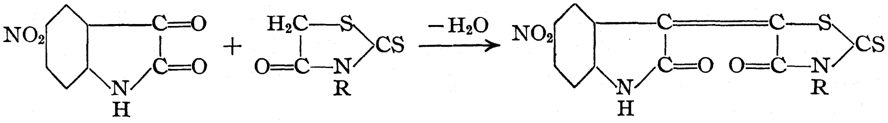
BY HOWARD A. JONES[2] AND RAYMOND M. HANN[3]

RECEIVED MAY 28, 1928 PUBLISHED SEPTEMBER 5, 1928

The susceptibility to reaction of various heterocyclic rings containing as an integral portion of their structure the CO-CH_2-S linkage has resulted in considerable study of these compounds. Among the more interesting of such heterocycles may be mentioned the rhodanic acids, the anhydrides of substituted dithiocarbamoglycolic acids. The methylene hydrogen of these 2-thio-4-thiazolidones reacts readily in the presence of a condensing agent with ketonic and quinoid oxygen. Advantage has been taken of this fact to prepare derivatives with aldehydes,[4] alloxan,[5] isatin[6] and phenanthraquinone.[7]

Hill and Henze[8] have condensed isatin and isatin-a-chloride with hydantoin and substituted hydantoins to obtain the corresponding oxindoles and pseudo indoxyls. Gränacher and Mahal[9] have demonstrated conclusively that isatin and rhodanic acid condense with elimination of the ketonic oxygen in the 3-position with formation of rhodanal oxindole. The generality of the reaction has been further examined in this Laboratory by the preparation of a series of substituted rhodanal-$\Delta^{5,3'}$-oxindoles.[10]

In continuing a study of the effect of constitutional variation upon absorption of light, we have had occasion to prepare certain rhodanal-$\Delta^{5,3'}$-5'-nitro-oxindoles, and the present paper reports the preparation and properties of these new derivatives. The condensation of rhodanic acids with 5-nitroisatin proceeds normally in an acetic acid medium in the presence of sodium acetate, the indigoid derivatives being separated by addition of water. The reaction is as follows



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[1] Presented at the Tulsa meeting of the American Chemical Society, April 5–9, 1926.

[2] Assistant Chemist, Bureau of Chemistry and Soils, U. S. Department of Agriculture, Washington, D. C.

[3] Fellow, Mellon Institute of Industrial Research, Pittsburgh, Pennsylvania.

[4] Andreasch and Zipser, Monatsh., 26, 1191 (1905).

[5] Butscher, *ibid.*, 32, 9 (1911).

[6] Gendelman, *ibid.*, 43, 537 (1922).

[7] Hann, *Thesis*, George Washington University, June, 1926.

[8] Hill and Henze, THIS JOURNAL, 46, 2806 (1924).

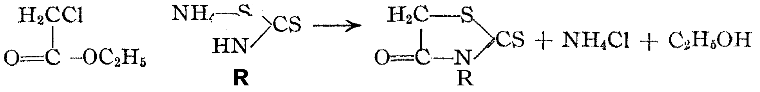
[9] Gränacher and Mahal, *Helv. Chim. Acta*, 6, 467 (1923).

[10] Hann, THIS JOURNAL, 47, 1189 (1925).

Experimental

Preparation of rhodanic acids. The rhodanic acids used in this investigation were prepared by the Miolati–von Braun synthesis. The general steps in this synthesis are (1) the preparation of the substituted ammonium dithiocarbamate from the primary amines and (2) the interaction of these intermediate products with esters of a-halogen fatty acids, resulting in loss of alcohol and ammonium halide and subsequent ring closure to yield rhodanic acids. The reactions are

$$RNH_2 + CS_2\ 4\ NH_4OH = HNRCSSNH_4 + H_2O \qquad (1)$$


(2)

The synthesis for phenyl, o- and *p*-anisyl, *ψ*-cumyl and *β*-naphthyl homologs was carried out along the general procedures of Andreasch and Zipser,[11] Antulich,[12] Kaluza[13] and Wagner[14] with the substitution of bromo-acetic ester in place of the corresponding chloro compound. The yield was increased by this procedure, due to a more complete reaction in ring closure.

Preparation of 5-Nitro-isatin.—The substituted isatin was prepared by nitration of isatin according to the directions of Calvery, Noller and Adams.[15] The yield was excellent and the substance was used without further purification.

Preparation of **Aryl Rhodanal-$\Delta^{5,3'}$-5′-nitro-oxindoles.**—Two grams of 5-nitro-isatin was dissolved in 25 cc. of glacial acetic acid and to this solution a molecular quantity of rhodanic acid and 5 g. of fused sodium acetate were added. The solution was then refluxed under a condenser for about three hours, unless bumping due to separation of reaction product became too violent to allow such treatment. In the latter case, the solution was cooled, the solid filtered off and the filtrate again refluxed until the time of total heating was three hours. After cooling, the solution was treated with water to precipitate the condensation product and dissolve any separated sodium acetate. The combined solid products of reaction were recrystallized or reprecipitated from glacial acetic acid.

The rhodanal-$\Delta^{5,3'}$-5′-nitro-oxindoles are red, crystalline derivatives, somewhat soluble in acetic acid and insoluble in water. They dissolve in sulfuric acid with the production of brilliant red colors. The melting points of the derivatives were obtained by Mr. J. F. Clevenger[16] in the micro melting point apparatus recently designed and described by him.

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[11] Andreasch and Zipser, *Monatsh.*, 24, 499 (1903).

[12] Antulich, *ibid.*, 31, 891 (1910).

[13] Kaluza, *ibid.*, 30, 701 (1909).

[14] Wagner, *ibid.*, 27, 1233 (1906).

[15] Calvery, Noller and Adams, THIS JOURNAL, 47, 3059 (1925).

[16] Clevengrr, *Ind. Eng.* Chem., 16,854 (1924).

TABLE I

TABLE OF ARYL RHODANAL-$\Delta^{5,3'}$-5'-NITRO-OXINDOLES ANALYSIS (SALICYL-SULFONIC ACID METHOD)

Aryl group	M. p., °C.	Weight	0.1 *N* acid, cc.	N found, %	N calcd., %
Phenyl	260-267	0.1731	13.6	11.01	10.97
o-Anisyl	247	.1289	9.1	9.89	10.17
p-Anisyl	370	.1277	9.2	10.09	10.17
ψ-Cumyl	245	.1293	9.0	9.75	9.88
β-Naphthyl	330	.1053	7.3	9.71	9.70

Summary

Phenyl, o- and *p*-anisyl, *ψ*-cumyl and *β*-naphthyl rhodanic acids have been condensed with 5-nitro-isatin to form the corresponding aryl rhodanal-$\Delta^{5,3'}$-5'-nitro-oxindoles.

MELLON INSTITUTE OF INDUSTRIAL RESEARCH,
PITTSBURGH, PENNSYLVANIA

[CONTRIBUTION NO. 27 FROM THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, RESEARCH LABORATORY OF ORGANIC CHEMISTRY]

CHLOROFORM SOLUBLE METAL PYRIDINE CYANATES

BY TENNEY L. DAVIS AND ALBERT V. LOGAN

RECEIVED JUNE 5, 1928 PUBLISHED SEPTEMBER 5, 1928

Many compounds of pyridine with inorganic salts have been prepared and described.[1] The first mention that any of these substances is soluble in chloroform appears to be in the paper of Spacu,[2] in which the author described a delicate qualitative test in which cupric pyridine thiocyanate was precipitated from a water solution of cupric thiocyanate by the addition of pyridine. Chloroform dissolved the substance more readily than water and yielded an emerald green solution which served for the detection of one part of copper in 300,000–800,000, one of pyridine in 2000 and one of thiocyanate in 50,000. Spacu, on the basis of copper and nitrogen determinations, assigned to his substance the composition, $Cu(NCS)_2 \cdot 2C_5H_5N$. E. A. Werner[3] later developed a similar test for cyanate. The

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[1] Pyridine compounds with the cadmium halides, zinc iodide and cyanide and nickel bromide, Varet, *Compt. rend.*, 115, 464 (1892), 124, 1155 (1897); with the permanganates of silver, copper, cadmium, zinc and nickel, Klobb, *Compt. rend.*, 118, 1271 (1894); with the sulfates and halides of iron, cobalt, nickel, cadmium, lead, copper, and manganese, Reitzenstein, Ann., 282, 267 (1894); Z. *anorg. Chem.*, 18, 253 (1898); with copper sulfate, nitrate and acetate, Tombeck, *Ann. chim. phys.*, 21, 433 (1900), 22, 113 (1901); with cupric and cuprous thiocyanate, Litterscheid, *Arch. Pharm.*, 239, 336 (1901), 240, 74 (1902); with the thiocyanates of silver, lead, copper, manganese, nickel, cadmium, zinc, mercury, cobalt and iron, Grossmann, *Ber*, 37, 559 (1904); with copper nitrate, Pfeiffer and Pimmer, Z. *anorg. Chem.*, 48, 98 (1905); and with the halides of cobalt and chromium, Werner, Feenstra and Osann, *Ber.*, 39, 1538 (1906), etc.

[2] Spacu, *Bull. soc. Stiinte Cluj.*, 1, 284 (1922).

[3] Werner, *J. Chem. Soc.*, 123, 2577 (1925).

azure blue chloroform solution on evaporation yielded a bluish-lilac colored substance to which, on the basis of a copper determination, he assigned the composition, $Cu(NCO)_2 \cdot 2C_5H_5N$.

Since cupric pyridine sulfate, nitrate, chloride, etc., are insoluble in chloroform, it seems probable that the solubility of the cyanate and thiocyanate in that solvent is due to the organic nature of their acid constituents. We have found that the cupric, cobaltous and nickelous salts of the aliphatic nitramines and the cupric derivatives of biuret and various related substances combine with pyridine to form complex salts which are soluble in chloroform. Before studying these substances further, it has seemed best to gain a fuller knowledge of the metal pyridine cyanates.

We have found that copper, nickel, cobalt, cadmium, zinc and silver all form pyridine cyanates which are soluble in chloroform, and have established the composition of the complex salts by analysis for the metal and for pyridine. Cupric, nickelous, cobaltous and cadmium cyanates each form two pyridine compounds, one with more and one with less pyridine, one stable only in an atmosphere saturated with pyridine and one fairly stable in open vessels in the laboratory. Zinc dipyridine cyanate and silver monopyridine cyanate deliquesce in an atmosphere saturated with pyridine, evidently forming compounds with more of that material. These metal pyridine cyanates are insoluble in petroleum ether and carbon tetrachloride, insoluble or slightly soluble in ether, benzene and toluene, and varying from very slightly to very readily soluble in methyl and ethyl alcohol and acetone.

Cobaltous hexapyridine cyanate forms rose-colored crystals which lose pyridine rapidly in the open to leave a bright blue mass of the dipyridine compound. In chloroform solution the hexapyridine compound apparently dissociates to form the dipyridine compound and free pyridine, for the solution possesses an intense blue color. On strong cooling the solution becomes violet or lilac or pink-colored according to the degree of cold, and the same color changes are produced at room temperature by the addition of pyridine—which evidently retards the dissociation. When the pink or almost colorless solution is heated to boiling, it takes on an intense blue color even if a large excess of pyridine is present. By the careful addition of pyridine to a chloroform solution of cobaltous hexapyridine cyanate we have obtained a liquid which shows a striking change of color between the temperature of tap water, room temperature and the temperature of the body. Similar color changes occur in water solution and to a less striking degree in various organic solvents. Solutions in methyl or ethyl alcohol, acetone or xylene are purple, lavender, light blue or pale dirty brown, respectively, at low temperatures or when an excess of pyridine is present.[4]

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[4] Schonn, *Z.* anal. *Chem.*, **9,** 209 (1870), used sodium thiocyanate as a qualitative test for cobalt. If the amount of cobalt is very small, the blue color appears only on warming.

Cobaltous hexapyridine cyanate and cupric hexapyridine cyanate[5] raise the boiling point of chloroform more than would be expected if they were completely dissociated in the solution into pyridine and the metal dipyridine cyanate. The solutions do not appear to contain ions, for they have no action on a piece of metallic zinc.

Preparation of the Compounds.—One-tenth of a mole of potassium cyanate and an equivalent amount of the metal salt were dissolved separately in water and the solutions were mixed. Pyridine was added until no further change occurred and then a little more so that a slight excess was present. The precipitated metal pyridine cyanate was extracted with 100–200 cc. of chloroform. The solution was filtered through paper previously wet with chloroform and allowed to evaporate spontaneously. The deposited crystals were freed from superficial pyridine by means of filter paper and were kept in a desiccator which contained pyridine and sticks of caustic potash in separate vessels. This procedure yielded the pyridine saturated compounds. The compounds containing less pyridine were obtained by leaving the saturated compounds uncovered in watch glasses for periods varying from two days to a week. After the samples had assumed the appearance of homogeneity they were bottled for analysis.

Determination of **Pyridine.**—For the determination of pyridine the samples were decomposed by boiling with caustic soda and the pyridine was distilled off and titrated. Since the pyridine was accompanied by ammonia from the hydrolysis of the cyanic acid, it was necessary to use a procedure which would take account of ammonia, and that of A. C. Houghton[6] for the determination of pyridine in ammonia liquors was finally adopted. The accuracy of the method was tested by blank determinations on weighed samples of purified pyridine, b.p. 114–115°. The pyridine was dissolved in 100 cc. of water, a few drops of ammonia added, the whole neutralized with sulfuric acid and then made alkaline with 5 cc. of normal sodium hydroxide solution and steam distilled from a 1000-cc. round-bottomed flask. The vapors passed through a 500-cc. Erlenmeyer flask containing sodium hypobromite solution (from 2.5 cc. of bromine and 100 cc. of 10% sodium hydroxide solution) which destroyed the ammonia, thence through a Kjeldahl bulb into the condenser and finally into a known amount of $N/10$ sulfuric acid solution. Best results were secured by collecting 100–125 cc. of distillate during thirty to forty minutes. Methyl red, Congo red, cochineal, methyl red-methylene blue mixture and methyl orange were all tried as indicators; none gave a very sharp end-point but methyl orange proved to be the best. After the method had been worked out, blank determinations were made as follows.

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[5] The only ones which we have tried.

[6] Houghton, J. Ind. Eng. *Chem.*, 1, 698 (1909).

TABLE I

BLANK DETERMINATIONS

Pyridine taken, g.	Pyridine found By titration of aliquot					Average	Error, %
0.4493	0.4475	0.4450	0.4440			0.4455	−0.85
.5206	.5240	.5180	.5280	0.5230		.5232	+.50
.5546	.5610	.5640	.5540	.5450	0.5550	.5577	+.22
.4960	.4974	.4960	.5050	.4920	.4950	.4971	+.09
.6047	.6045	.6035	.6050	.5960		.6023	−.39
.5567	.5458	.5475	.5410			.5475	−2.10
.6073	.6200	.6210				.6205	+2.17
.4855	.4890	.4870	.4900	.4840	.4790	.4858	+.06
						Average error, %	0.798

The results show that the method is accurate to about 1%. The metal pyridine cyanates were analyzed by treating a sample of about 1 g. with water and 5 cc. of normal sodium hydroxide solution, and proceeding as described above.

Description of the Compounds.—Cupric hexapyridine cyanate[7] crystallizes from chloroform in azure blue prisms which retain their color and form as long as they remain in an atmosphere of pyridine. Exposed to the air for a short time the crystals change to a pale blue or bluish-lilac colored powder of cupric dipyridine cyanate, described by Werner.[3] After exposure to the air for several months, or after heating at 100° for a few hours, the latter substance changes to a pale green powder of cupric cyanate.

Nickelous hexapyridine cyanate[8] crystallizes from chloroform in blue prisms of a lighter color than those of the cupric compound. It loses pyridine to form a pale blue powder of nickelous tetrapyridine cyanate and finally an apple green powder of nickelous cyanate.

When pyridine is added to the bright blue solution which results from the interaction of potassium cyanate and cobaltous chloride, a blue precipitate forms at once and changes to one of a pink color when an excess of pyridine is added. This dissolves in chloroform and the solution, which contains free pyridine, deposits rose-colored hexagonal prisms of cobaltous hexapyridine cyanate. That substance in the open loses pyridine rapidly to yield bright blue cobaltous dipyridine cyanate, which on long exposure or heating yields lilac-colored cobaltous cyanate, which in a moist atmosphere changes in part to carbonate and oxide.

Cadmium hexapyridine cyanate[9] is considerably less soluble in chloro-

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[7] Pfeiffer and Pimmer (Ref. 1) found cupric pyridine nitrates which contained two, three, four and six molecules of pyridine.

[8] Grossmann (Ref. 1) obtained a nickelous tetrapyridine thiocyanate and Varet (*ibid.*) nickelous di- and tetrapyridine bromides.

[9] Grossmann (Ref. 1) and Varet (*ibid.*) have obtained hexa- and dipyridine compounds of cadmium thiocyanate and of the halides, as well as some compounds containing one and four molecules of pyridine.

form than the corresponding copper and nickel compounds. It crystallizes in small white crystals which lose pyridine to farm a white powder of cadmium cyanate.

Zinc dipyridine cyanate[10] was more difficult to prepare than the other compounds, for it was not easily extracted by chloroform from water solution and an excess of pyridine interfered with its crystallization. It crystallizes from chloroform in granular white crystals which do not lose

TABLE II

RESULTS OF ANALYSES[a]

Compound	Pyridine, % Calcd.	Pound	Metal, % Calcd.	Found
$Cu(NCO)_2\cdot 1C_5H_5N$	34.89	. . . .	28.05	. . . . .
$Cu(NCO)_2\cdot 2C_5H_5N$	51.70	52.33, 52.05 51.00	20.85	21.7, 21.8, 21.8, 21.5
$Cu(NCO)_2\cdot 3C_5H_5N$	61.60	. .	16.53	. . . . .
$Cu(NCO)_2\cdot 5C_5H_5N$	72.80	. .	11.72	. . . . .
$Cu(NCO)_2\cdot 6C_5H_5N$	76 26	76.82, 75.93	10.23	10.78, 10.42, 10.74, 10.65
$Cu(NCO)_2\cdot 7C_5H_5N$	78.94	. . .	9.07	. . . .
$Ni(NCO)_2\cdot 3C_5H_5N$	62.42	. .	15.45	. . . . .
$Ni(NCO)_2\cdot 4C_5H_5N$	68.89	67.60, 68.33	12.79	13.04, 12.74, 32.70
$Ni(NCO)_2\cdot 5C_5H_5N$	73.46	. . . .	10.95	. . . . .
$Ni(NCO)_2\cdot 6C_5H_5N$	76.86	76.50, 77.36	9.51	9.38, 9.57, 9.47
$Ni(NCO)_2\cdot 7C_5H_5N$	79.49	. . .	8.44	. . .
$Co(NCO)_2\cdot 1C_5H_5N$	35.59	. . .	26.56	. . . . .
$Co(NCO)_2\cdot 2C_5H_5N$	52.49	51.88, 52.09	19.59	19.68, 19.59
$Co(NCO)_2\cdot 3C_5H_5N$	62.37	. .	15.52	. . . . .
$Co(NCO)_2\cdot 5C_5H_5N$	73.42	. . . .	10.96	. . . . .
$Co(NCO)_2\cdot 6C_5H_5N$	76.82	76.43, 76.96	9.56	9.16, 9.25, 9.58, 9.64
$Co(NCO)_2\cdot 7C_5H_5N$	79.46	. . .	8.47	. . . . .
$Cd(NCO)_2\cdot 1C_5H_5N$	28.68	. . . . .	40.81	. . . . .
$Cd(NCO)_2\cdot 2C_5H_5N$	44.58	43.54, 43.27	31.72	32.13, 31.75
$Cd(NCO)_2\cdot 3C_5H_5N$	54.68	. . . . .	25.93	. . . . .
$Cd(NCO)_2\cdot 5C_5H_5N$	66.83	. . . .	19.00	. . . . .
$Cd(NCO)_2\cdot 6C_5H_5N$	70.70	70.38, 70 78	16.77	16.60, 16.90, 16.77, 16.57
$Cd(NCO)_2\cdot 7C_5H_5N$	73.79	. . . . .	15.00	. . . . .
$Zn(NCO)_2\cdot 1C_5H_5N$	34.60	. . .	28.06	. . . . .
$Zn(NCO)_2\cdot 2C_5H_5N$	51.40	51.64, 52.18	20.80	21.08. 21.14, 20.93,[b] 20.66[b]
$Zn(NCO)_2\cdot 3C_5H_5N$	61.34	. . . . .	16.53	. . . .
$AgNCO\cdot 1C_5H_5N$	34.53	35.36, 34.80	47.12	46.75, 46.70
$AgNCO\cdot 2C_5H_5N$	51.33	. . . . .	35.31	. . . . .

[a] In order that it may be evident that the analyses really fix with certainty the amount of pyridine in the complexes, the calculated values for the substances containing one more and one less molecule of pyridine than the found substances are included in the table. The figures reported for pyridine are in each case the average results from the titration of four or five aliquots.

[b] Analyzed after exposure for a week to the open air.

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[10] Grossmann (Ref. 1) and Varet (*ibid.*) obtained zinc thiocyanates, cyanides and halides with two, three and four molecules of pyridine.

their form on exposure to the air and which retain their pyridine rather strongly, for analysis showed no appreciable loss of pyridine after a week's exposure. In an atmosphere saturated with pyridine it deliquesces to form a sirupy liquid, a phenomenon which suggests that a compound containing more than two molecules of pyridine is formed.

Silver monopyridine cyanate[11] crystallizes from chloroform in very thin, silky, white needles which deliquesce in an atmosphere of pyridine and are but little affected by light. On exposure to the air it loses pyridine to form silver cyanate which is markedly more sensitive to the action of light.

Effect on Boiling Point of Chloroform.—An attempt was made to determine the extent to which cobaltous hexapyridine cyanate dissociates in chloroform solution by observation of its effect in raising the boiling point of that solvent. Preliminary experiments showed that pyridine alone in chloroform solution, even as much as 9 g. in 80 g. of solvent, behaved as a non-volatile solute and had the normal effect in raising the boiling point. The results of a typical experiment, in which 64.2 g. of chloroform was used, are tabulated below.

TABLE III

RESULTS OF EXPERIMENT

$Co(NCO)_2 \cdot 6C_5H_5N$, g.	Observed ΔT, °C.	Expected ΔT if no dissociation	Apparent number of molecules
0.1740	0.11	0.016	6.87
.2255	.14	.021	6.67
.2085	.11	.019	5.79
.6080	.36	.056	6.43

When pyridine was added to the solution which remained at the end of the experiment, it acted normally in its effect in raising the boiling point still farther.

Sixty-eight one-hundredths g. of cupric hexapyridine cyanate raised the boiling point of 76.6 g. of chloroform 0.34°, or 6.54 times as much as the amount (0.052°) which would be expected if no dissociation had occurred. The abnormal results deserve further study.

Summary

Cupric hexapyridine and dipyridine cyanate, nickelous hexapyridine and tetrapyridine cyanate, cobaltous hexapyridine and dipyridine cyanate, cadmium hexapyridine and dipyridine cyanate, zinc dipyridine cyanate and silver monopyridine cyanate have been prepared and characterized by analysis for pyridine and for the metal.

Cobaltous hexapyridine cyanate and cupric hexapyridine cyanate raise the boiling point of chloroform about six and one-half times as much as would be expected if they were undissociated molecules.

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[11] Grossmann (Ref. 1) prepared silver monopyridine thiocyanate.

Cobaltous hexapyridine cyanate yields a blue solution in chloroform which turns lilac-colored or pink if the temperature is lowered or if pyridine is added. By adjusting the amount of excess pyridine in such a solution, a liquid may be secured which changes color with very moderate changes of temperature.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF ILLINOIS]

STUDY OF THE POSSIBLE ISOMERISM OF CERTAIN ANALOGS OF RESOLVABLE DIPHENYL COMPOUNDS[1]

BY J. F. HYDE AND ROGER ADAMS

RECEIVED JUNE 18, 1928 PUBLISHED SEPTEMBER 5, 1928

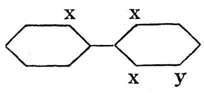
A configuration in which the two aromatic nuclei are coaxial and not in the same plane apparently accounts for all of the known facts concerning the optical activity in certain diphenyl compounds. It is generally accepted that the asymmetry arises from the influence which the groups located in the ortho position to the connecting bond have in preventing free rotation of the two nuclei. The exact nature of the interference to free rotation remains still to be determined.

Mills[2] considers it to be entirely mechanical in nature. The groups are unable to get by each other due to their size and proximity in space. Meisenheimer[3] has offered additional evidence to favor mechanical interference and has pointed out that spacings of the groups from the nucleus as well as between the two rings must be considered.

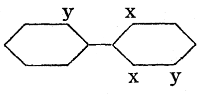
Turner and Le Fèvre[4] consider the problem from the point of view of residual affinity on each ring and the influence of the electrical nature of the ortho substituted groups.

It seems reasonably certain that the isomerism is not due to the specific effect of any particular group on the nuclei.[5]

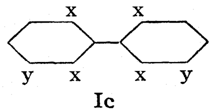
Diphenyl derivatives of the general types Ia, Ib, Ic, in which the ortho



Ia



Ib



Ic

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[1] This communication is a portion of a thesis submitted by J. F. Hyde in partial fulfilment of the requirements for the Degree of Doctor of Philosophy in Chemistry at the University of Illinois.

[2] Mills, *Chemistry Industry*, 45,883,905 (1926).

[3] Meisenheimer and Höring, *Ber.*, 60, 1425 (1927).

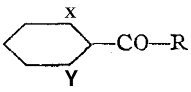
[4] Turner and Le Fèvre, *Chemistry Industry*, 45,831 (1926).

[5] Christie and Kenner, *J. Chem. Soc.*, 121, 614 (1922); *ibid.*, 123, 779 (1923); Christie, James and Kenner, *ibid.*, 123, 1948 (1923); Christie, Holderness and Kenner, *ibid.*, 129, 671 (1926); Bell and Kenyon, *Chemistry Industry*, 45, 864 (1926); Turner and Le Fèvre, *ibid.*, 46, 218 (1927).

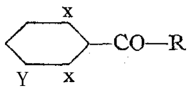
substituting groups may be the same and in which the individual rings are asymmetric should be capable of resolution. The free rotation is prevented in these cases by groups in the ortho positions which are identical, The asymmetry is introduced by the same or different groups in another part of the molecule. If the restricted rotation is due simply to mechanical interference, these substances should be resolvable. If, on the other hand, the influence is entirely electrical, the two rings might assume a coplanar position resulting in a compound that is non-resolvable. While the resolution of such a compound might not make the cause of steric hindrance clearer, it would certainly establish the present mechanical theory more firmly.

This investigation had as one of its objects the preparation and resolution of an individual compound falling in one of the types mentioned. Although this part of the work is not completed, the publication of Mascarelli[6] setting forth in detail the views just given, though without any experimental evidence, has made it advisable to publish the completed results on closely related compounds.

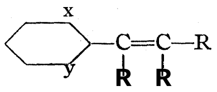
If the prevention of free rotation is entirely a matter of the space occupied by interfering groups and does not require a direct association of two aromatic rings, then it should be possible to resolve still other types of compounds which could become asymmetric due to steric hindrance. Such types are represented by the general formulas IIa, IIb, IIIa, IIIb, where R stands for groups of the proper size.



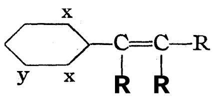
IIa



IIb



IIIa



IIIb

In such compounds as IIa, IIb, IIIa and IIIb, any effect due to the direct joining of two rings to each other is eliminated. The carbon–carbon double bond and possibly the carbon–oxygen double bond adjacent to the ring should have more or less of a directive influence on the valencies of that carbon as is the case with a rigid ring structure. The molecules would undoubtedly be less rigid, but if the free rotation around the bond joining the unsaturated linkage to the substituted ring is prevented, any position of the olefin or carbonyl group and the unsubstituted ring in space should give an asymmetric molecule. The possibility of this occurring in the case of the carbonyl compounds as in types IIa and IIb seems much less probable than in the olefins IIIa and IIIb. If the carbonyl group itself will not interfere with free rotation, it is possible that the R groups in the molecules, if large enough, might cause interference.

Although the syntheses of representatives of types I, II and III are

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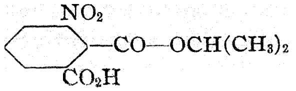
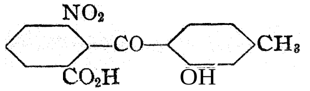
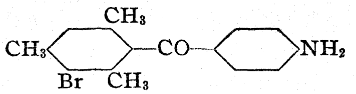
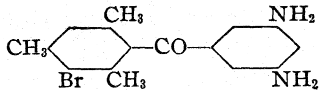
[6] Mascarelli, *Atti. accad. Lincei,* [6] **6,** 60 **(1927).**

under way, in this paper merely compounds falling into group II will be described and discussed. The following four compounds were prepared


IV


V


VI


VII

The one numbered IV was made directly by the action of isopropyl alcohol on 3-nitrophthalic anhydride, the one numbered V by the condensation of nitrophthalic anhydride with m-cresol, and those numbered VI and VII by the condensation of nitro- and dinitro-benzoyl chloride with bromomesitylene followed by subsequent reduction. The resolution of IV and V was attempted with brucine and of VI and VII with camphorsulfonic acid.

In carrying out the fractional crystallization of the salts there was no definite separation, nor did the relative size of the fractions give any indication of salts of different solubilities. In order to prove the possibility of the existence of optical isomerism, it was considered essential to isolate a sample of the material which should show at least momentary rotatory power and be entirely free from optically active reagent. In no case were optically active compounds obtained by decomposition of the salts.

It was shown that the carbonyl group in such ketones as VI was very unreactive, as indicated by failure of all attempts to reduce it or to cause it to react with the Grignard reagent. The carbonyl group is, therefore, protected from influences outside of the molecule and it must be that the volume of the carbonyl group is not sufficient to interfere (on rotation) with the ortho groups of the substituted ring. Moreover, the o-hydroxy substituted phenyl group apparently has no effect.

Certain anomalies appeared in the rotation of the salts. The brucine salt of 2-(2-hydroxy-4-methylbenzoyl)-3-nitrobenzoic acid, V, has an α_D $+18.3°$, while under the same conditions brucine has an α_D $-119°$. Kuhn and Albrecht[7] noticed a similar phenomenon in the case of the quinine salt of 4,4′-dinitrodiphenic acid, which had an α_D $+110°$, whereas in the same solvent quinine had an α_D $-117°$. No active acids, however, were isolated. They also observed that the quinine salts of *m*-nitrobenzoic acid and of phthalic acid have, under the same conditions, a rotation similar to that of quinine. A possible explanation for such abnormal rotations in the salts would be the assumption that a complete transformation to one form of two possible diastereoisomers had occurred

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[7] Kuhn and Albrecht, *Ann.*, 455, 272 (1926).

upon the addition of the optically active reagent. Haworth[8] in reviewing the work of Kuhn on diphenyl compounds, has accepted this observation of abnormal rotation as conclusive evidence of the existence of labile optical isomers in diphenyl compounds with only one ortho substituting group in each ring. He suggests that this behavior serves to distinguish these compounds from those diphenyl derivatives with three ortho substituting groups of proper size and character which make possible the isolation of the two diastereoisomeric salts and the two enantiomorphic diphenyl compounds. These conclusions of Haworth cannot be considered of more than passing interest as they are based on far too few facts. He has made no mention of the extensive work of Hilditch,[9] who has studied a large variety of salts of various alkaloids and has observed just such anomalous effects as have appeared in this investigation and in the investigation of Kuhn and Albrecht. Hilditch has shown that if there are conjugated systems in proximity to the optically active part of the molecule, the rotatory power is markedly influenced. He has also observed that the nature of the groups, particularly in the ortho position to the one combined to the active reagent, may induce anomalous rotations. These latter types are quite similar in character to the diphenyl compounds studied by Kuhn and to the substances described in this research, though the anomalies could hardly be attributed to the same cause as that assigned by Haworth to 4,4′-dinitrodiphenic acid and its salt.

The camphorsulfonic acid salts of amino and diamino-benzoylbromomesitylene led to negative results as far as optically active amines were concerned. The salts, however, showed a curious behavior. In certain solvents the substances changed in rotation upon standing. At first this was assumed to be a gradual change of one salt to the diastereoisomer. However, it is significant that this was observed only in chloroform. The camphorsulfonate of aminobenzoylbromomesitylene had an α_D +13.8° at first and an α_D +7.6° after several hours' standing. Upon evaporation of the solution after determining the second rotation, the solid salt was obtained. If this was redissolved in chloroform, however, the original rotation was again observed, and only after standing did it diminish. Apparently other salts of camphorsulfonic acid show this same phenomenon. The aniline salt was studied and showed an even greater variation in rotation on standing in chloroform solution. It appears to be due to a change in the character of the molecule either by tautomerism or by combination with a solvent.[10] Whatever the change may be, it does not appear to be a permanent one and is not characteristic of the base used.

The synthesis of compounds of the type I has been attempted by diazo-

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[8] Haworth, "Annual Reports," Gurney and Jackson, London, 24, 101 (1928).

[9] Hilditch, J. *Chem. Soc.,* 93, 1388 (1908); 95, 335, 1570 (1909); 99, 224 (1911).

[10] Pope and Read, *ibid.*, 105, 800 (1914).

tizing methyl anthranilate and other analogous amines and coupling with bromomesitylene in order to produce diphenyl derivatives. Amino bromomesitylene has also been diazotized, and attempts to couple it with various benzene derivatives in order to produce the proper diphenyl compound have all resulted as yet in failure. Now, however, it seems possible to get a diphenyl compound of the type desired through dimesityl.

Experimental Part

Benzoylbromomesitylene.—A mixture of 0.33 mole of bromomesitylene and 0.3 mole of benzoyl chloride was dropped very slowly into a reaction flask containing 0.47 mole of aluminum chloride and 260 g. of carbon disulfide. This took about an hour and the stirring was continued for about two hours longer. Finally, part of the carbon disulfide was distilled off, using a water-bath. The reaction mixture was then decomposed by pouring into ice water containing some hydrochloric acid. The product distilled as a light yellow, viscous oil at 173–175° at 1 to 2 mm., which was practically colorless on redistillation, The yield was 91 g. (92%). This viscous liquid on stirring and allowing to stand for several hours solidified to a white, granular, crystalline mass with a melting point of 48–49°. No attempt was made to recrystallize the compound.

Anal. (Parr Bomb). Subs., 0.2101: 7.05 cc. of 0.1005 N $AgNO_3$. Calcd. for $C_{16}H_{15}OBr$: 26.40. Found: 26.76.

An attempt was made to condense benzoylbromomesitylene with ethyl bromoacetate in the presence of zinc. After several trials it was found that no reaction had taken place and merely the original product was obtained. Phenylmagnesium bromide also would not react with this compound.

An attempt to oxidize the benzoylbromomesitylene to the benzoylbromodimethylbenzoic acid resulted in the formation of a neutral, viscous liquid. The reaction was accompanied by the evolution of carbon dioxide.

A Clemmensen reduction to the corresponding hydrocarbon gave negative results.

***p*-Nitrobenzoylbromomesitylene.**—This was prepared in exactly the same way as that described for benzoylbromomesitylene except that the bromomesitylene had to be heated in order to make the acid chloride dissolve in it and it was necessary to continue the heating during the reaction (about four hours) to prevent crystallization. Upon decomposing, some chloroform was added so that the solvent was a mixture of carbon disulfide and chloroform. The resulting ketone, after removing the carbon disulfide and chloroform, was crystallized by dissolving in acetone, filtering and adding twice the volume of ethyl alcohol to the hot solution. After recrystallizing once more from the same combination of solvents, the product consisted of light yellow plates, melting at 154–155°. The yield was 29.5 g. (85%).

Anal. (Parr Bomb). Subs., 0.2269: 6.44 cc. of 0.1005 *N* $AgNO_3$. Calcd. for $C_{16}H_{14}O_3NBr$: 22.98. Found: 22.86.

3,5-Dinitrobenzoylbromomesitylene.—This was prepared in an analogous way to the mononitro. Very poor results were obtained unless the reaction mixture was warmed somewhat and stirred for at least four or five hours. The product was not distilled but merely crystallized from acetone. It formed light yellow plates melting at 160–161.5°. The yield was 9.5 g. (24%).

Anal. Subs., 0.2366: 11.74 cc. of 0.0502 N $AgNO_3$. Calcd. for $C_{16}H_{13}O_5N_2Br$: 20.35. Found: 20.09.

***p*-Aminobenzoylbromomesitylene.**—A suspension of 21 g. of nitrobenzoylbromomesitylene in 50 cc. of alcohol was reduced with 0.1 g. of platinum-oxide platinum black[11] and hydrogen. When the theoretical amount of hydrogen was absorbed, the catalyst was filtered and the solvent evaporated. The product was purified by dissolving in carbon disulfide and by adding gradually an equal amount of benzene. It crystallized in fine, white needles; melting point, 138°.

Anal. Subs., 0.1735: 10.66 cc. of 0.0502 *N* $AgNO_3$. Calcd. for $C_{16}H_{16}ONBr$: 25.15. Found: 24.67.

p-Aminobenzoylbromomesitylene Hydrochloride.—This was prepared by dissolving the free base in ethyl acetate and treating with hydrogen chloride. The hydrochloride crystallized out rather slowly in white, needle-like crystals and was recrystallized from the same solvent.

Anal. Subs., 0.1291: 3.66 cc. of 0.1005 N $AgNO_3$. Calcd. for $C_{16}H_{17}ONBrCl$: 10.01. Found: 10.12.

If, instead of using ethyl alcohol as a solvent, ethyl acetate was used, and 0.05 g. of catalyst for 14.4 g. of nitro compound, the reduction did not go readily to completion and a light red azo compound was found contaminating the amine. The former was removed by ethyl alcohol, in which it was insoluble. It melted at 203–205°.

Anal. Subs., 0.1295: 8.06 cc. of 0.0502 *N* $AgNO_3$. Calcd. for $C_{16}H_{14}ONBr$: 25.31. Found: 25.02.

3,5-Diaminobenzoylbromomesitylene.—This was reduced in a manner similar to the mono-amino compound and formed yellowish-brown crystals from alcohol, melting at 168–169°, which turned dark brown upon standing for a short time.

Anal. Subs., 0.1301: 7.92 cc. of 0.0502 *N* $AgNO_3$. Calcd. for $C_{16}H_{17}ON_2Br$: 24.02. Found: 24.44.

p-Aminobenzoylbromomesitylene d-Camphorsulfonate.—The d-camphorsulfonic acid used melted from 190–191" and gave α_D $+21.08°$ in water. The salt was readily produced by dissolving 5 g. of the amino ketone in 30 cc. of ethyl acetate and adding this hot solution to a solution of 3.48 g. of d-camphorsulfonic acid in 30 cc. of ethyl acetate. After standing for half an hour, 7 g. of the possible 8.5 g. of salt crystallized in white, flat plates, melting at 175–200° with decomposition. The rotations were determined in a Schmidt-Haensch saccharimeter, using a 2-decimeter tube. The weighed sample was in each case dissolved in 20 cc. of the desired solvent at 20°. This salt gave a value α_D $+13.7°$ (15 minutes) in chloroform, which, on standing for several hours, gradually became smaller and smaller until a constant value of +7.1° (38 to 40 hours) resulted. The fraction from the mother liquors gave essentially the same initial rotation and only a slightly higher final rotation. A rather large sample of this salt was fractionally crystallized. After three times the rotation was determined. The specific rotations on three fractions were, respectively, +12.7°, +12.8° and +11.4°, using acetone as a solvent. Two of these fractions in chloroform gave rotations of approximately +14° which, on standing, dropped to approximately +7°. Upon removing the chloroform from a solution which had given the low rotation, a product was obtained which, on redissolving in chloroform, gave a rotation of over 14°, which again gradually fell off upon standing.

Anal. Subs., 0.1938: 7.01 cc. of 0.0502. *N* $AgNO_3$. Calcd. for $C_{16}H_{16}ONBr$-$C_{10}H_{16}SO_4$: 14.54. Found: 14.53.

3,5-Diaminobenzoylbromomesitylene d-Camphorsulfonate.—This was prepared from equimolecular quantities of the acid and the amine in acetone solution. The

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[11] Adams, Shriner and Voorhees, "Organic Syntheses," John Wiley and Sons, Inc., New York, **8**, 92–99 (1928).

precipitated salt was in the form of fine, white needles, melting at 216–218°. It was fractionated five times and the rotations of the individual fractions were taken in methyl alcohol, using a 2-decimeter tube and making the solution up to 20 cc. at 20°. The rotation was +21.2° for the first fraction, +20.2° for the second, +16.4" for the third, +15.0" for the fourth and +18.2° for the fifth. Upon standing these solutions became colored and fluorescent and further readings were impossible. It was noticed, however, that the readings gradually fell off irregularly, somewhat as in the case of the monoamino compound. In this case decomposition of some sort obviously was taking place.

Anal. Subs., 0.1943: **4.75** cc. of 0.0502 N $AgNO_3$. Calcd. for $C_{16}H_{17}ON_2Br_2\cdot 2C_{10}H_{16}SO_4$: 10.03. Found: 9.82.

The carefully fractionated salts of the mono- and diaminobenzoylbromomesitylenes were decomposed with ammonia by adding concentrated ammonia water to a methyl alcoholic solution of the salt. Further dilution with water precipitated the free organic base. The free bases obtained from these salts with acid melted exactly as they had before forming the salt and showed no detectable rotation.

Brucine Salt of **2-Carboisopropoxy-3-nitrobenzoic** Acid.—The free acid prepared by the method of Nicolet and Sacks[12] was converted to the brucine salt by mixing its ethyl acetate solution with a similar solution of brucine. The brucine used melted at 174–176°, and had an α_D −119.0". The salt formed bright yellow needles melting indefinitely from 90–95° with decomposition. After five careful fractional crystallizations from acetone, the rotations of the fractions were taken in chloroform. A 2-decimeter tube was used and the solutions were made up to 20 cc. at 20°. The α_D of the five fractions were, respectively, −19.0°, −19.4°, −19.9°, −18.8" and −21.3". No changes in rotations were observed on standing. Upon treating the chloroform solution of the crystallized salt with dry ammonia and then dissolving the precipitated ammonium salt in water and acidifying, the isopropylnitrophthalic acid was recovered and showed no signs of rotation.

Anal. Subs., 0.2217: CO_2, 0.5056; H_2O, 0.1264. Calcd. for $C_{34}H_{37}N_3O_{10}$: H, 5.71; C, 63.06. Found: H, 6.37; C, 62.20.

Brucine 2(2-Hydroxy-4-methylbenzoyl)3-nitrobenzoic Acid.—The acid was obtained by the method of Eder and Widmer[13] and the salt was formed in hot ethyl acetate. It forms yellow, needle-like crystals melting from 160–165° with decomposition. Upon fractionating four times from benzene, the rotations of the various fractions were determined. The α_D values were +18.3 for the salt initially, +18.39 for the first fraction and +16.3 for the fourth fraction. A 2-decimeter tube was used as in other cases. The samples were made up to 20 cc. at 20°, using acetone as a solvent. No rotation was observed in the free acid obtained by the precipitation of the ammonium salt and then acidification of the water solution.

Anal. Subs., 0.1169: CO_2, 0.2842; H_2O, 0.0546. Calcd. for $C_{38}H_{37}N_3O_{10}$: C, 65.60; H, 5.32. Found: C, 66.30; H, 5.26.

Aniline-*d*-camphorsulfonate.—The salt was prepared in the usual way and in chloroform gave the following rotations, using a 2-decimeter tube: 0.2079 *g.* subs. in 20 cc. of chloroform at 20° gave α_D +33.3° (ten minutes), +26.8° (five hours), +16.6° (seven hours), +6.6° (forty-eight hours).

Summary

1. *p*-Aminobenzoylbromomesitylene, 3,5-diaminobenzoylbromomesitylene, 2-carbo-isopropoxy-3-nitrobenzoic acid and 2-(2-hydroxy-4-methyl-

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[12] Nicolet and Sacks, This Journal, **47**, 2348 (1925).

[13] Eder and Widmer, *Helv. Chim. Acta*, 6,421 (1923).

benzoyl)-3-nitrobenzoic acid were prepared and attempts made to resolve them into optical components without success. A discussion of the relation of the compounds to optically active diphenyl compounds is included.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BARNARD COLLEGE]

ADDITION REACTIONS OF UNSATURATED ALPHA-KETONIC ACIDS. II

BY MARIE REIMER AND MARION HOWARD

RECEIVED JUNE 21, 1928 PUBLISHED SEPTEMBER 6, 1928

It has been previously shown[1] that the action of sunlight on the methyl ester of benzalpyruvic acid brings about addition of two molecules at the ethylenic linkage, cyclobutane derivatives being formed. The fact that p-methoxybenzalpyruvic acid and its methyl ester did not form such addition products, being entirely unaffected by sunlight, led to a comparative study of the addition reactions of the two ketonic acids and their esters with bromine[2] in which it was found that the ease with which both compounds combined with bromine was the same.

This study of unsaturated a-ketonic acids has now been continued with benzalpyruvic acid in which a substituting methoxyl group is in the *ortho* instead of the *para* position to the side chain. It has been found that the o-methoxybenzalpyruvic acid and its methyl ester also combine readily with bromine but that in almost all other respects the properties of the compound have been changed to a marked degree by this shift in the position of the methoxyl group. The color is deepened, that of o-methoxybenzalpyruvic acid being a brilliant orange, that of the *p*-methoxy acid a bright yellow.[3] The solubilities of the o-methoxy acid, its sodium salt and its methyl ester in the appropriate solvents are greater than those of the corresponding *p*-methoxy compounds; the acid and its esters do not combine with solvent of crystallization, a conspicuous characteristic of benzalpyruvic acid and its p-methoxy derivatives; the dibromo addition products are less stable than those of the other unsaturated a-ketonic acids studied, hydrogen bromide being lost with great ease. The most striking difference between the two methoxy derivatives is that *o*-methoxybenzalpyruvic acid and its methyl ester are sensitive to light; the aqueous solution of the acid is hydrolyzed rapidly in the sunlight; the acid, exposed in the dry condition, slowly loses its brilliant color; the methyl ester exposed to bright sunlight liquefies within a few minutes due to admixture with a light product.

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[1] Reimer, THIS JOURNAL, 46, 783 **(1924).**

[2] Reimer, *ibid.,* **48, 2454 (1926).**

[3] Hodgson and Handley, *J. Chem. Soc.,* **1928, p. 162.**

Benzalpyruvic acid and its *p*- and a-methoxy derivatives react with concentrated sulfuric acid to give brilliantly colored solutions as is ordinarily the case with α,β-unsaturated ketones. That the ketone group in these ketonic acids is essential for this color reaction is proved by the fact that loss of this group by oxidation with hydrogen peroxide to give derivatives of cinnamic acid is accompanied by loss in the ability to form these brilliantly colored compounds. Most striking is the unexpected effect of the bromine atom in the methoxy compounds, the *ortho* and *para* compounds in this case giving similar results. If bromine is in the side chain, a distinct series of color changes, yellow to red-violet, takes place on addition of concentrated sulfuric acid; if there is also bromine in the ring another quite different series of color changes to blue or green ensues. The difference is so marked that it is possible by this reaction to determine, with very small quantities of material, whether bromine is present in the side chain, also in the ring or absent, as well as to detect the presence of the ketone group. This behavior is described more fully in the experimental part.

Experimental Part

Preparation of o–Methoxybenzalpyruvic Acid

Seventeen and six-tenths grams (**0.2** mole) of pyruvic acid was added to **160** cc. of 10% sodium hydroxide solution (**0.4** mole), the solution cooled to 0°, **27.2** g. (**0.2** mole) of o-methoxybenzaldehyde added and the mixture shaken vigorously. At the end of an hour the emulsion which was at first formed had entirely disappeared and the brownish colored solution was clear. There was no separation of a sodium salt as in the preparation of benzal- and *p*-methoxybenzalpyruvic acids. When this reaction mixture was allowed to stand overnight, a procedure necessary with *p*-methoxybenzalpyruvic acid to insure good yields, the o-methoxy compound was found to have been almost completely hydrolyzed to o-methoxybenzaldehyde and pyruvic acid. Addition of chilled concentrated hydrochloric acid to the cooled, strongly alkaline solution immediately after one hour of shaking precipitated the bright yellow sodium salt of o-methoxybenzalpyruvic acid in about **80%** yield. The hydrochloric acid was added with vigorous stirring until the first traces of an orange-colored substance appeared. The yellow, granular sodium salt was filtered, freed from mother liquor by suction, dissolved in cold water and the solution acidified. The *o*-methoxybenzalpyruvic acid precipitated as a granular solid of a brilliant orange color. A less pure product was obtained in small quantity from the mother liquor.

The acid separates from boiling water in long, fine needles; from benzene in compact needles of a brilliant red-orange. As boiling with water or exposure of the aqueous solution to the light brings about hydrolysis of the acid, crystallization from benzene is to be recommended. The acid is readily soluble in the usual organic solvents. It melts at **131°**.

Anal. Subs., **0.2035:** CO_2, **0.4804;** H_2O, **0.0904.** Calcd. for $C_{11}H_{10}O_4$: **C, 64.07;** H, 4.85. Found: C, 64.37; H, 4.97.

On exposure of the dry, finely powdered acid to bright sunlight, the brilliant color soon fades noticeably. The colorless, light product protects most of the acid from the light so that this reaction proceeds with extreme slowness.

The Methyl Ester of the acid was obtained in pure condition with great difficulty owing to its extreme solubility in almost all solvents and to its unusual ease of hydrolysis. The ester was repeatedly prepared by the reaction of methyl alcohol and hydrogen chloride, by the use of dimethyl sulfate and of diazomethane from carefully purified acid. In all cases it separated as a heavy oil from which, after long standing, a few crystals separated. The oily product, very soluble in the usual solvents, was purified by dissolving it in a large volume of ligroin, cooling the solution slowly, finally in a freezing mixture. The ester separated in long, bright yellow needles melting at 48°.

Anal. Subs., 0.1167: CO_2, 0.2782; H_2O, 0.0581. Calcd. for $C_{12}H_{12}O_4$: C, 65.43; H, 5.57. Found: C, 65.01; H, 5.49.

After standing for several weeks in the dark, but exposed to the moisture of the air, a sample was found to have been largely hydrolyzed to the bright, orange-colored acid. When the ester was exposed to the bright sunlight it liquefied within a few minutes due to admixture with light products. There was no hydrolysis. The two crystalline products of this light reaction will be reported on in a later paper.

The Ethyl Ester prepared by the action of ethyl alcohol saturated with hydrogen chloride is a bright yellow oil boiling at 223° (15 mm.).

Anal. Subs., 0.1630: CO_2, 0.3971; H_2O, 0.0926. Calcd. for $C_{13}H_{14}O_4$: C, 66.64; H, 6.03. Found: C, 66.44; H, 6.35.

Reactions with Bromine

o-Methoxybenzalpyruvic Acid Dibromide, $o\text{-}CH_3OC_6H_4CHBrCHBrCOCOOH$.—The addition of bromine to the acid was carried out in the usual way in cooled chloroform solution. The bromine was decolorized rapidly. When the product was poured out and the chloroform evaporated in a current of moist air, there was a copious evolution of hydrogen bromide; in a current of dry air there was no evidence of loss of hydrogen bromide. The oily residue gradually solidified. After washing the product with cold ligroin, a straw-colored solid remained, which melted with vigorous decomposition at about 90°. As analyses of the product, crystallized from chloroform or benzene, gave results much too high in carbon and hydrogen for the dibromide, the crude product, washed rapidly with cold ligroin, was analyzed.

Anal. Subs., 0.1589: CO_2, 0.2147; H_2O, 0.0530. Calcd. for $C_{11}H_{10}O_4Br_2$: C, 36.06; H, 2.73. Found: C, 36.84; H, 3.70.

The substance is evidently the impure dibromide. Repeated analyses of different products gave no better results. It would seem to be impossible to prepare the dibromide without loss of some hydrogen bromide.

β-Bromo-o-methoxybenzalpyruvic Acid, $o\text{-}CH_3OC_6H_4CH{=}CBrCOCOOH$ (173°).—This acid is readily obtained by warming the dibromide just described in benzene solution, boiling it with water, or heating it on a water-bath until there is no further evolution of hydrogen bromide. It crystallizes from chloroform, chloroform mixed with ligroin, or methyl alcohol in stiff, colorless needles melting at 173°.

Anal. Subs., 0.1859: CO_2, 0.3153; H_2O, 0.0581. Calcd. for $C_{11}H_9O_4Br$: C, 46.31; H, 3.15. Found: C, 46.27; H, 3.51.

By oxidation of this acid in alkaline solution with hydrogen peroxide, bromomethoxycinnamic acid (171°) was obtained in quantitative yield. Since the bromine atom lost from the dibromide is undoubtedly the one in the position ***beta*** to the ketonic group and *gamma* to the carboxyl, the oxidation product of the compound thus formed must have the bromine atom in the *alpha* position to the carboxyl group.

$$CH_3OC_6H_4CHBrCHBrCOCOOH \longrightarrow CH_3OC_6H_4CH{=}CBrCOCOOH \longrightarrow CH_3OC_6H_4CH{=}CBrCOOH$$

The acid (171°) is therefore α-bromo-*o*-methoxycinnamic acid.[4] It is described in the latest edition of Beilstein[5] as "*a* or β bromo" *o*-methoxycinnamic acid.

The Methyl Ester of β-bromo-*o*-methoxybenzalpyruvic acid can be prepared in quantitative yield by the reaction of an ethereal solution of diazomethane on the purified acid. It separates from methyl alcohol in firm clumps of colorless needles melting at 88–89°.

Anal. Subs., 0 1540: CO_2, 0.2708; H_2O, 0.0542. Calcd. for $C_{12}H_{11}O_4Br$: C, 48.16; H, 3.69. Found: C, 47.95; H, 4.00.

When the acid was treated with methyl alcohol saturated with hydrogen chloride, almost the entire amount was recovered unchanged, a behavior like that of other unsaturated a-ketonic acids. Only a minute quantity of a substance crystallizing in fine, yellow needles, melting at 86°, possibly an isomeric ester, was isolated.

By the action of bromine on the methyl ester of o-methoxybenzalpyruvic acid, neither the methyl ester of the dibromide nor of the unsaturated bromo acid was obtained. The product, crystallized from diluted methyl alcohol, was a mixture of the unsaturated bromo acid (173") and of an unsaturated bromo acid (210°) with bromine in the ring, to be described later. The reaction had evidently consisted in addition of bromine, loss of hydrogen bromide, bromination in the ring and hydrolysis of the ester.

Reaction with Excess of Bromine

5-Bromo-o-methoxybenzalpynrvic Acid Dibromide, (2)-CH_3O-(5)-BrC_6H_3CHBr-$CHBrCOCOOH$.—*o*-Methoxybenzalpyruvic acid was dissolved in chilled chloroform, one gram molecular proportion of bromine added slowly, then a second gram molecular proportion of bromine added and the mixture was allowed to stand in the ice chest from three to four days. The product, after evaporation of the chloroform in a current of dry air, was a straw-colored solid melting with vigorous decomposition at 95–100°. It is soluble in the usual organic solvents except ligroin. That the substance contained bromine in the ring was proved by its oxidation with a hot solution of potassium permanganate to 5-bromo-2-methoxybenzoic acid. Analyses of the substance washed with cold ligroin gave results consistently high in carbon and hydrogen and low in bromine for a tribromo compound, showing loss of hydrogen bromide during the manipulation. When the crude product of bromination was stirred for a few minutes with cold methyl alcohol it was changed to a colorless solid which proved to be the methyl ester of the tribromo acid. The substance separates from hot methyl alcohol in clear, firm crystals melting at 103–106°. Analyses of the substance as in the case of the acid gave results about 1% high in carbon and hydrogen for a tribromo ester, showing loss of hydrogen bromide. The same product was obtained in no purer form by the action of diazomethane on the tribromo acid.

p-Bromo-5-bromo-2-methoxybenzalpyruvic Acid, (2)-CH_3O-(5)-$BrC_6H_3CH{=}CBr$-$COCOOH$, (colorless, 210°).—This acid was prepared in practically quantitative yield by boiling the tribromo acid just described in 40% acetic acid, from which it separated in fine, colorless needles melting with vigorous decomposition at 210°.

Anal. Subs., 5.928 mg.; CO_2, 7.97 mg.; H_2O, 1.31 mg. Calcd. for $C_{11}H_8O_4Br_2$: C, 36.26; H, 2.19. Found: C, 36.67; H, 2.47.

On oxidation with cold potassium permanganate 5-bromo-2-methoxybenzoic acid was obtained. Treatment with hydrogen peroxide in alkaline solution gave α-bromo-2-methoxycinnamic acid (221°).[4]

The Methyl Ester prepared by the action of diazomethane on an ethereal solution

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[4] Reimer and Howard, THIS JOURNAL, 50, 196 (1928).

[5] Vol. X, p. 293.

of the acid is a colorless solid separating from a small volume of boiling ether in firm clumps melting at 131°.

Anal. Subs., 4.431 mg.; CO_2, 6.23 mg.; H_2O, 1.05 mg. Calcd. for $C_{12}H_{10}O_4Br_2$: C, 38.09; H, 2.65. Found: C, 38.35; H, 2.65.

When the methyl ester of 5-bromo-2-methoxybenzalpyruvicacid dibromide (103–106") was hydrolyzed an acid, isomeric with that just described, and its ester were obtained.

β-Bromo-5-bromo-2-methoxybenzalpyruvic Acid (Yellow, 210°).—The methyl ester of the tribromo acid was covered with a 2% solution of potassium in methyl alcohol and the mixture stirred. The liquid became bright lemon yellow and, as the original colorless ester went into solution, a yellow solid separated. After five minutes the mixture was filtered. A considerable portion of the yellow solid formed was soluble in water. From this solution and from the filtrates hydrochloric acid precipitated an acid which crystallized from benzene in fine needles of a deep yellow color.

Anal. Subs., 6.28 mg.; CO_2, 8.25 mg.; H_2O, 1.45 mg. Calcd. for $C_{11}H_8O_4Br_2$: C, 36.26; H, 2.19. Found: C, 35.78; H, 2.58.

On heating in a melting point tube, the yellow color fades out completely between 145 and 150° and the colorless product melts at 210°. A mixture of the yellow acid and the colorless (210°) acid melted at 210°. The yellow acid is evidently the geometrical isomer of the colorless (210°) acid with a transition temperature of about 150". On repeated crystallization from benzene and on exposure to the light the same transformation takes place.

The yellow solid formed by the action of potassium methylate on the methyl ester of the tribromo acid (103–106") which was not soluble in water was crystallized from methyl alcohol. It separates in fine, pale yellow needles melting at 143°.

Anal. Subs., 0.1238; CO_2, 0.1729; H_2O, 0.0327. Calcd. for $C_{12}H_{10}O_4Br_2$: C, 38.09; H, 2.65. Pound: C, 38.08; H, 2.91.

The analysis and the fact that the compound gives the yellow acid just described on hydrolysis with alcoholic potassium hydroxide prove it to be the methyl ester of this acid. It can be prepared in quantity by shaking the methyl ester of the tribromo acid (103–106°) with methyl alcohol and a slight excess of potassium acetate in the cold for a few minutes.

Reaction with Bromine in Methyl Alcoholic Solution

This reaction was carried out as previously described.[2] There was no addition of methyl hypobromite under varying conditions of concentration, temperature and speed of addition of bromine. When bromine vapor was passed through the diluted alcoholic solution of the acid as fast as it was decolorized, the product was an oil which gradually solidified. It was proved to be a mixture of the dibromide of o-methoxybenzalpyruvic acid and the unsaturated bromo acid (173°) formed from it by loss of hydrogen bromide. By careful manipulation of the mixture a quantitative yield of the unsaturated bromo acid was obtained.

Reaction of Benzalpyruvic Acid and its Methoxy Derivatives with Concentrated Sulfuric Acid

Two to three drops of pure, concentrated sulfuric acid were placed on a glazed porcelain plate, approximately one milligram of the substance to be tested was added and stirred into the acid. Under this treatment, cinnamic acid, its *p*- and o-methoxy derivatives and their bromine substitution products gave no color or a pale to bright yellow, fading out to colorless in a short time. The colors with the ketonic acids are shown in the following table.

TABLE I

COLORS WITH KETONIC ACIDS

Substance	Color	Color with concentrated sulfuric acid
$C_6H_5CH{=}CHCOCOOH$	Pale yellow	Deep yellow → brown
$C_6H_5CHBrCHBrCOCOOH$	Colorless	Yellow → red-brown → dark brown
$C_6H_5CH{=}CBrCOCOOH$	Colorless	Yellow → red-brown → dark brown
$C_6H_5CH{=}CBrCOCOOCH_3$	Colorless	Yellow → red-brown → dark brown
p-$CH_3OC_6H_4CH{=}CHCOCOOH$	Deep yellow	Orange
p-$CH_3OC_6H_4CHBrCHBrCOCOOH$	Cream color	Orange → brown → red-violet
p-$CH_3OC_6H_4CHBrCHBrCOCOOCH_3$	Colorless	Orange → brown → red-violet
p-$CH_3OC_6H_4CH{=}CBrCOCOOH$	Colorless	Orange → brown → red-violet
p-$CH_3OC_6H_4CH{=}CBrCOCOOCH_3$	Colorless	Orange → brown → red-violet
p-$CH_3OBrC_6H_3CH{=}CBrCOCOOH$	Pale yellow	Orange → brilliant green → blue
p-$CH_3OBrC_6H_3CH{=}CBrCOCOOCH_3$	Pale yellow	Orange → brilliant green → blue
o-$CH_3OC_6H_4CH{=}CHCOCOOH$	Orange	Deep cherry-red
o-$CH_3OC_6H_4CHBrCHBrCOCOOH$	Straw color	Yellow → red-violet
o-$CH_3OC_6H_4CH{=}CBrCOCOOH$	Colorless	Red-brown → red-violet
o-$CH_3OC_6H_4CH{=}CBrCOCOOCH_3$	Colorless	Red-brown → red-violet
o-$CH_3OBrC_6H_3CHBrCHBrCOCOOH$	Colorless	Green → deep blue
o-$CH_3OBrC_6H_3CHBrCHBrCOCOOCH_3$	Colorless	Green → deep blue
o-$CH_3OBrC_6H_3CH{=}CBrCOCOOH$	Colorless	Green → greenish-blue
o-$CH_3OBrC_6H_3CH{=}CBrCOCOOCH_3$	Colorless	Green → greenish-blue
o-$CH_3OBrC_6H_3CH{=}CBrCOCOOH$	Deep yellow	Brown → olive-green
o-$CH_3OBrC_6H_3CH{=}CBrCOCOOCH_3$	Yellow	Olive-green

These color changes are rapid and sharp. The last color given in the table for each substance persists for an hour or more, then gradually changes to brown. If bromine is in the side chain, this brown color persists for several days; if in the ring, all color fades out in two to three hours.

It is noteworthy that these changes of color with sulfuric acid: yellow in the case of benzalpyruvic acid, orange and red with *p*- and o-methoxybenzalpyruvic acids, respectively, reddish-violet with a methoxyl group together with bromine in the side chain, and blue and green with bromine also in the ring are the same and in the same order as the color changes brought about by increased numbers of systems of conjugated double linkages in unsaturated hydrocarbons when treated with concentrated sulfuric acid.[6] The accumulation of substituting groups in our compounds has, in the reaction with sulfuric acid, the same effect as an increase in the condition of unsaturation and of conjugation in these hydrocarbons.

After these experiments had been completed, a paper by Pfeiffer and Wizinger[7] appeared in which the color reactions of sulfuric acid with a, a-dianisylethylenes are described. It is striking that these substances give violet colors with sulfuric acid only when there is halogen in the side chain, as is the case with our compounds.

Summary

For the purpose of comparison with other unsaturated a-ketonic acids, o-methoxybenzalpyruvic acid and its reactions with bromine have been studied.

The color reactions of sulfuric acid with benzalpyruvic acid, *p*-methoxybenzalpyruvic acid and o-methoxybenzalpyruvic acid are described.

NEW YORK CITY

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OR NEBRASKA]

THE ACTION OF SODIUM BENZYL CYANIDE WITH CINNAMIC ESTER. II[1]

BY S. AVERY

RECEIVED JUNE 22, 1928 PUBLISHED SEPTEMBER 5, 1928

Introduction

In 1897, Walther and Schickler[2] brought together equal moles of sodium ethylate, benzyl cyanide and cinnamic ester in the presence of ether. From the products of the reaction they isolated a substance melting at 162–163°. This they believed to be cinnamplbenzyl cyanide, but as the analysis indicated the presence of one molecule more of water than this compound would call for, they regarded it as a hydrated derivative.

Three years later Erlenmeyer[3] isolated as a product resulting from the reaction of dry sodium ethylate, cinnamic ethyl ester and benzyl cyanide

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[6] Kuhn and Winterstein, *Helv. Chim. Acta,* 11, 151 (1928).

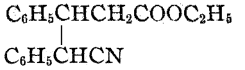
[7] Pfeiffer and Wizinger, *Ann.,* 461, 132 (1928).

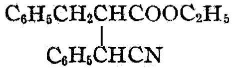
[1] Read at the meeting of the Division of Organic Chemistry, American Chemical Society, St. Louis, April 18, 1928.

[2] Walther and Schickler, J. *prakt.* Chem., [2] 55, 347 (1897).

[3] E. Erlenmeyer; Jr., *Ber.,* 33, 2006 (1900).

a substance melting at 99–100° having the composition $C_{29}H_{19}O_2N$. He suggested the following as structural possibilities.

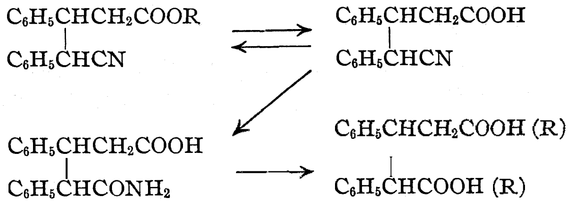
I 
$C_6H_5CHCH_2COOC_2H_5$ / C_6H_5CHCN

II 
$C_6H_5CH_2CHCOOC_2H_5$ / C_6H_5CHCN

Erlenmeyer found, further, that this substance on saponification gave the "cinnamylbenzyl cyanide" (m. p. 162–163°) of Walther and Schickler. Hence the latter could not have the structure previously ascribed to it, and Erlenmeyer suggested that it was probably the imide of diphenylglutaric acid.

In 1908 Avery and McDole[4] showed that the substance melting at 162–163° was in reality β,γ-diphenyl-γ-cyanobutyric acid. This made it evident that Erlenmeyer's formula I was correct, and eliminated II as a possibility.

The preceding is a partial summary of the published researches relating to the compounds derived from the action of benzyl cyanide (1 molecule) with cinnamic ester (1 molecule). It is the hope of the author that the present paper will supply the most important gaps in our knowledge of these compounds and of their saponification products. The following compounds of this series have been studied



Of the compounds just outlined, β,γ-diphenyl-γ-monamide glutaric acid and β,γ-diphenyl-γ-cyanobutyric methyl ester have not been previously reported. α,β-Diphenylglutaric ethyl ester is of interest as it has been prepared by Borsche[6] through the action of phenyl acetic ester on cinnamic ester thus leading to the synthesis of the α,β-diphenylglutaric acid without the use of benzyl cyanide. Further, this glutaric acid, according to the researches of Kishner,[6] and Meerwein and Dott[7] is one of two stereoisomers, which are best distinguished through a comparison of the methyl with the ethyl esters.

Turning now to the possibility of the condensation of one molecule of benzyl cyanide with two molecules of cinnamic ester, we find that Erlen-

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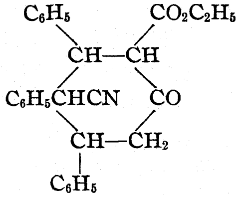
[4] Avery and McDole, THIS JOURNAL, 30, 596, 1423 (1908).

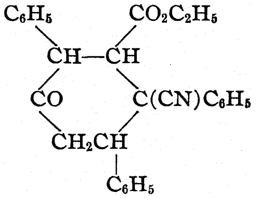
[5] Borsche, *Ber.*, 42, 4496 (1909).

[6] Kishner, J. *Russ. Phys.-Chem. Soc.*, 47, 1819–1848 (1915); J. Chem. *Soc.*, 110, I, 292 (1916).

[7] Meerwein and Dott, J. *prakt. Chem.*, 97, 264–268 (1918).

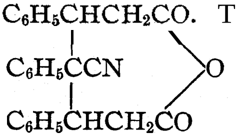
meyer,[8] at the temperature of the steam-bath, obtained a body melting at 206–207°, having the empirical formula $C_{28}H_{25}O_3N$, representing the direct union of benzyl cyanide with two molecules of cinnamic ester minus one molecule of the corresponding alcohol. For the structure of the substance, he suggests the following possibilities

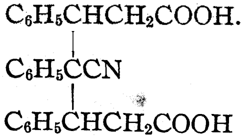
I


II


Formula I shows condensation as effected in the @-position in relation to the two carboxyl groups. Formula II shows condensation as effected in the a-position toward one and in the @-position toward the other carboxyl group. Both formulas show secondary ring formation. The experimental part of this paper shows that the substance under consideration may also **be** prepared by the action of sodium **β,γ-diphenyl-γ-cyanobutyric** ester on cinnamic ester. It is hardly probable that benzyl cyanide in condensing with first one and then with a second molecule of cinnamic ester should form first a *β*- and then an a-condensation product. Finally, the work of Dieckmann, referred to later, shows that ring formation in the case of dibasic esters takes place with elimination of alcohol in the a-position in relation to the unchanged ester group. For these reasons we may regard Formula II as excluded. This confirms Formula I excepting only the typographical error of one excess H atom.

Using methods similar to those employed by Erlenmeyer, Avery and McDole isolated a substance melting at 231–232° (uncorr.) for which they suggested "only tentatively" the formula $C_6H_5CHCH_2CO$. The experimental part of this communication shows this to have been incorrect, and that the substance was really 2-keto-4,5,6-triphenyl-5-cyanohexahydrobenzoic methyl ester. They gave, however, to the acid obtained by hydrolyzing this product the correct formula, namely, $C_6H_5CHCH_2COOH$.





$$\begin{array}{l} C_6H_5CHCH_2COOH \\ \quad | \\ C_6H_5CCN \\ \quad | \\ C_6H_5CHCH_2COOH \end{array}$$

The course of the reactions when one molecule of benzyl cyanide reacts with two of cinnamic ester is as follows.

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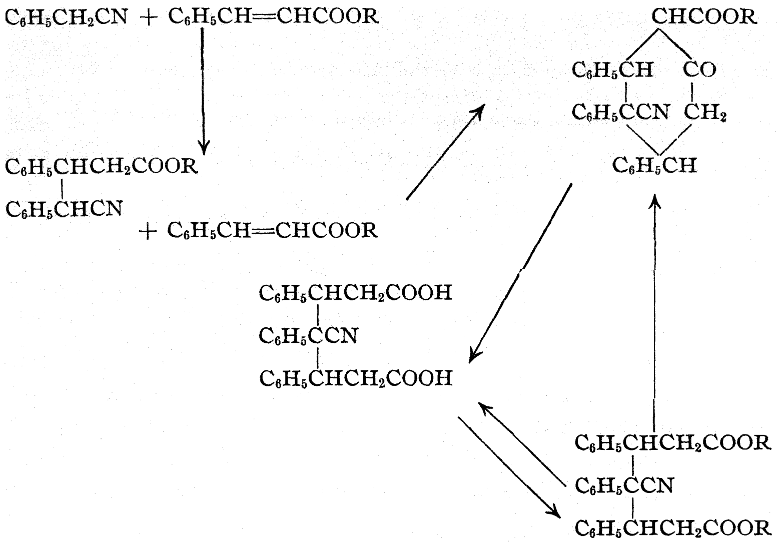
[8] E. Erlenmeyer, Jr., *Ber.*, **33**, 2009–2010 (1900).



The reactions just outlined may be explained by assuming that the β,γ-diphenyl-γ-cyanobutyric ester first formed reacts further with cinnamic ester to form an ester of the pimelic series, but that in the presence of the condensing agent it immediately gives off alcohol, forming an ester of the hexahydrobenzoic series. This latter reaction is to be expected in the light of Dieckmann's[9] investigations on ring formation with dibasic esters. As in the case of less complex 2-keto-hydrobenzoic esters, this ester hydrolyzes to an acid of the pimelic series from which the pimelic esters may be obtained.

Experimental Part

β,γ-Diphenyl-γ-cyanobutyric Methyl Ester.—Five g. of sodium dissolved with heating in a small excess of methyl alcohol was added to 25.5 g. of benzyl cyanide and the mixture was cooled to approximately 20°; 35.7 g. of melted methyl cinnamate was then added, the mixture well shaken and placed in a bath at 0° for approximately five hours, then allowed to stand at 20 to 25° for several days. A crystalline mass gradually formed. This was macerated with a strong aqueous solution of ammonium chloride, filtered and washed. The yield including the substance recovered from filtrates after twice crystallizing amounted to 41–42 g. or 67% of the theoretical. The crystals are long, transparent needles, soluble in benzene, chloroform, acetic ether and hot alcohol, difficultly soluble in petroleum ether. A sample recrystallized to constant melting point melted sharply at 106.5" (corr.).

Anal. Calcd. for $C_{18}H_{17}O_2N$: C, 77.4; H, 6.1; N, 5. Found: C, 77.7; H, 6.1; N, 5.

This compound is also formed when benzyl cyanide is condensed with ethyl cinnamate using sodium methylate as a condensing agent; also when β,γ-diphenyl-γ-cyanobutyric acid is treated with methyl alcohol and hydrogen chloride gas. The latter

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[9] Dieckmann, *Ber.*, 27, 103 (1894); *Ann.*, 317, 100 (1901).

reaction shows it as the methyl ester of an acid, the structure of which was previously determined by Avery and McDole. The procedure just described is similar to that followed by Erlenmeyer in working with the corresponding ethyl compounds.

β,γ-Diphenyl-γ-cyanobutyric Ethyl Ester.—The synthesis of this coinpound corresponds exactly to that of the methyl ester, except that ethyl derivatives are used throughout. A *50%* yield was obtained; melting point, *101*.5° (corr.); crystalline form and solubility similar to the methyl ester.

Anal. Calcd. for $C_{19}H_{19}O_2N$: C, *77.8;* H, *6.5;* *N*, *4.8.* Found: *C*, *77.9;* H, *6.6;* *N*, 4.8.

The sharp melting point (slightly higher than found by previous investigators) and the closely checking analysis indicate a high degree of purity in the preparation. On saponification it gives the corresponding acid, thus clearly indicating its composition.

β,γ-Diphenyl-γ-cyanobutyric Acid.--Some difficulty is encountered in preparing this compound in a pure condition. Contamination with the ester resulting from incomplete saponification, and contamination with the corresponding monamide acid due to the saponification proceeding too far, are equally to be avoided.

Five g. of the pure ester (methyl or ethyl) was dissolved in *50* cc. of *95%* ethyl alcohol, *1*.5 g. of potassium hydroxide in solution added, and the solution digested on the steam-bath. Water was added from time to time until the total volume equaled about *80* cc. Heating was continued for about fifteen minutes after a drop no longer became turbid with water. Then strong acetic acid was added in excess. On cooling and diluting little by little a granular precipitate formed. Care is to be taken not to cool and dilute so rapidly as to form a milky emulsion. Ultimately a large excess of water is added. The yield is about 90% of the theoretical.

The ester may also be saponified by dissolving in strong acetic acid and boiling, while gradually diluting with hydrochloric acid; melting point, 163.5–165° (corr.) according to rate of temperature increase. It partially decomposes on melting. Benzene was found to be the best solvent for separating the acid in a pure condition from the more soluble esters and from the less soluble monamide glutaric acid.

β,γ-Diphenyl-γ-monamide Glutaric Acid.—A compound melting from 200–205° had been noted in previous investigations but no definite suggestions were made in regard to its composition or structure. It is readily formed when @,?-diphenyl-y-cyanobutyric acid or a corresponding ester is boiled with strong alcoholic potash, evaporated with the addition of small amounts of water and finally brought to a temperature of *100"*. On dissolving the salt-like mass and acidifying, a milky or resinous substance forms which becomes crystalline on standing. Recrystallized from alcohol or, better, from acetic acid it forms glistening, transparent flakes. It melts at 200–205° with the evolution of ammonia. It is nearly insoluble in ligroin, difficultly soluble in benzene or chloroform and readily in hot alcohol or acetic acid.

Anal. Calcd. for $C_{17}H_{17}O_3N$: C, *72.0;* H, *6.05;* *N*, 4.9. Found: C, *71.8;* H, *6.05;* N, 4.9. Titration: *6.85* cc. of *N*/10 NaOH neutralized *0.1928* g. Calcd.: *6.8* cc.

α,β-Diphenylglutaric Acid and Esters.—The acid may be prepared by hydrolyzing β,γ-diphenyl-γ-monamide glutaric acid, β,γ-diphenyl-γ-cyanobutyric acid, or its esters, with concentrated hydrochloric acid solution under pressure. Three hours' heating at *150"* gave satisfactory results. When the temperature of the melting point apparatus is increased at the rate of about 1° per minute, the reading is 225–228° (corr.); melting point of ethyl ester, **93.3**" (corr.); methyl ester, *143.0"* (corr.). The methyl ester made by the method of Borsche melted at the same temperature as the methyl ester made from the pure acid by the action of methyl alcohol and hydrochloric acid, and not 7° lower as found by Meerwein and Dott,[10] and cited by them as an evidence of the presence of an admixture of a stereoisomer. It appears, therefore, that only the "fumaroid" form, to follow Kishner's designation, is found in the synthesis of α,β-diphenylglutaric acid by the method of Avery and McDole or by the method of Borsche.

2-Keto-4,5,6-triphenyl-5-cyanohexahydrobenzoic Ethyl Ester.—The following is a modification of Erlenmeyer's method: **3** g. of sodium as sodium ethylate, nearly free from ethyl alcohol, was mixed with **7.5** g. of benzyl cyanide and **22.5** g. of ethyl cinnamate was added. To the mixture **75** cc. of toluene was added and the whole boiled with a return flow condenser for three hours. After cooling, glacial acetic acid was added in a quantity sufficient to neutralize the sodium, then ligroin in excess and the solids were filtered under pressure. The cake formed was digested with **95%** alcohol, cooled and filtered, washed with alcohol and finally with water; yield, 15.5 g., which on recrystallizing from **95%** alcohol gave **13** g. of nearly pure white crystals.

Almost equally good results can be obtained by heating the mixture of cyanide, sodium ethylate and ester over a hot-plate to **101°**, stirring constantly. On cooling, a resinous product is formed which on acidifying with acetic acid and digesting with 95% alcohol gives a light yellow, crystalline residue. This is filtered off and washed first with alcohol, then with water and recrystallized from alcohol.

The ester is purified as follows. After dissolving in a small quantity of chloroform, butyl or amyl alcohol is added. The solution is then concentrated to crystallization on the steam-bath; melting point, **208–209°** (corr.).

This substance can also be prepared by heating at 100° equal moles of β,γ-diphenyl-β-cyanobutyric ethyl ester, ethyl cinnamate and sodium ethylate. A yield of approximately 50% of the theoretical has been obtained. Finally, the same substance is obtained when β,γ,δ-triphenyl-γ-cyanopimelic ester is treated with sodium ethylate. These reactions leave no doubt in regard to the structure of the compound.

2-Keto-4,5,6-triphenyl-5-cyanohexahydrobenzoic Methyl Ester.—This substance was prepared by Bessie F. Whitney using the methods described under the ethyl ester. It crystallizes in beautiful beveled plates; melting point, 242–244° (corr.); more difficultly soluble in alcohol, benzene, chloroform, etc., than the ethyl ester.

Anal. Calcd. for $C_{27}H_{23}O_3N$: C, **79;** H, **5.7;** N, 3.4. Found: C, 79; H, **5.8;** **N, 3.3.**

The ester was also prepared as follows: **0.39** g. of potassium in 5 cc. of absolute methyl alcohol was mixed with **2.79** g. of β,γ-diphenyl-γ-cyanobutyric methyl ester and **1.62** g. of methyl cinnamate. The mixture was stirred with a thermometer and then heated in an oil-bath until the thermometer read above **100'**. One cc. of acetic acid and **25** cc. of chloroform were added and the resinous mass was brought into solution by heating and stirring. The nearly clear, straw-colored solution was concentrated to **15** cc., **15** cc. of butyl alcohol was added and the solution again concentrated to about **15** cc., when crystals began to form. After cooling these were washed first with butyl alcohol and then with water. The white, glistening crystals weighed **2.5** g., 59% of the theoretical yield. Recrystallized once, the substance melted at 242–244° (corr.).

Finally, the ester under consideration was prepared as follows: **0.88** g. of β,γ,δ-triphenyl-γ-cyanopimelic methyl ester was dissolved in ether and a drop of absolute methyl alcohol added; **0.08** g. of potassium was added and when nearly dissolved **2** cc. of absolute methyl alcohol also, and the solution was warmed and acidified with acetic acid. Water was added and the mixture warmed to drive off the ether, crystals gradually forming. It was then cooled, filtered and washed. The crystalline mass

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[10] Meerwein and Dott, **J. prakt. Chem., 97, 269 (1918).**

was recrystallized and found to melt at 242–244° (corr.) The crystalline form was identical with that of the substance prepared by other methods.

β,γ,δ-Triphenyl-γ-cyanopimelic Acid.—This compound is to be expected as the result of saponifying an ester of 2-keto-4,5,6-triphenyl-5-cyanohexahydrobenzoic acid. Ten g. of the ethyl ester was placed in a flask, 50 cc. of 95% alcohol added and 5 cc. of a 50% solution of potassium hydroxide. The mixture was heated on the steam-bath for about ten minutes, then transferred to an evaporator, 25 cc. of water added and evaporated nearly to dryness. The residue was again treated with strong, alcoholic potassium hydroxide, again evaporated nearly to dryness, diluted and filtered. The filtrate was acidified strongly with hydrochloric acid, yielding a wax-like solid and a milky liquid, the former gradually passing into a crystalline mass and the latter into loose crystals. The snowy white, well washed and dried substance weighed 9.8 g. It is most easily purified by dissolving in ether, evaporating to a small volume, adding benzene and condensing to crystallization. It crystallizes from dilute alcohol as prisms, apparently containing alcohol of crystallization, which it loses on the steam-bath, becoming amorphous; melting point, 218–219° (corr.).

Anal. Calcd. for $C_{26}H_{23}O_4N$: C, 75.5; H, 5.6; N, 3.4. Found: C, 75.6; H, 5.6; N, 3.4.

It was found by the combustion analysis, by titration and in respect to the melting point and solubilities, to be identical with the substance isolated by Avery and McDole.

β,γ,δ-Triphenyl-γ-cyanopimelic Methyl Ester.—Ten g. of the corresponding acid was placed in a flask with 50 cc. of absolute methyl alcohol and hydrogen chloride was passed in to saturation. The acid dissolved and a granular precipitate gradually formed. On refluxing and cooling, an almost solid mass of white crystals formed. The mother liquor was filtered off, the crystals were washed with cold methyl alcohol, and then recrystallized from hot methyl alcohol; yield, about 90% of the theoretical; melting point, 108.2° (corr.). It crystallized from methyl alcohol in needles or spikes depending on the rate of cooling.

Anal. Calcd. for $C_{28}H_{27}O_4N$: C, 76.2; H, 6.2. Found: C, 76.2; H, 6.3.

On saponifying the ester, the corresponding pimelic acid is formed. On treating the ester with methyl alcohol the corresponding hexahydrobenzoic methyl ester is formed.

β,γ,δ-Triphenyl-γ-cyanopimelic Ethyl Ester.—This substance was made exactly as the methyl ester except that ethyl alcohol was used; melting point, 102.5° (corr.). Solubilities and crystalline form were similar to those of the methyl ester. On saponification, the corresponding pimelic acid is regenerated.

Anal. Calcd. for $C_{30}H_{31}O_4N$: C, 76.9; H, 6.7; N, 3. Found: C, 77.0; H, 6.9; N, 3.

Composition of the Compound Tentatively Designated as an "Anhydride" of a Dibasic Acid by Avery and McDole[11]

This substance was first prepared by the action of sodium methylate on a mixture of ethyl cinnamate and benzyl cyanide. (At that time the migration of ester radicals had been studied only slightly.) A body was obtained melting not very sharply at 231–232° (236–237°, corr.). The analytical data corresponded fairly well to the theoretical composition of such a body, namely, $C_{26}H_{21}O_3N$. It corresponds equally well to $C_{27}H_{23}O_3N$, which it really is.

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[11] Avery and McDole, THIS JOURNAL, 30, 599 (1908).

When the work of Avery and McDole was repeated recently, using, however, methyl instead of ethyl cinnamate, the same results were obtained except that the product melted at 242–244' (corr.). When, however, ethyl ester and alcohol were used, the product melted at 208–209° (con.). The "supposed anhydride" is therefore 2-keto-4,5,6-triphenyl-5-cyanohexahydrobenzoic methyl ester, synthesized from the ethyl ester through the migration of methyl group from the sodium methylate used in the reaction and probably containing small amounts of the ethyl ester, as shown by the lower melting point.

Summary

The compounds resulting from the union of one molecule of sodium benzyl cyanide with one of the cinnamic ester, and also the compounds resulting from the union of one molecule of sodium benzyl cyanide with two molecules of cinnamic ester, have been prepared and studied.

The reaction of benzyl cyanide with cinnamic ester in the cold with moisture carefully excluded has been found to be exactly analogous to Michael's reaction in the classic example of sodium malonic ester. Complete hydrolysis leads to compounds of the glutaric series.

At higher temperatures the first condensation product of benzyl cyanide with cinnamic ester unites with a second molecule of cinnamic ester and forms derivatives leading by hydrolysis to the pimelic series. The reactions in passing from the ketohexahydrobenzoic ester to the pimelic esters are reversible.

In so far as appears to be possible, all compounds of both series have been hydrolyzed in successive stages. Methyl and ethyl esters have been made not only by direct synthesis but also by esterifying the free acids.

Through the preparation of a number of new compounds both series are now fairly complete. These explain more fully than heretofore the nature of the reactions involved. Errors in the literature of the subject have been corrected.

LINCOLN, NEBRASKA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF IOWA STATE COLLEGE]

THE RELATIVE REACTIVITIES OF NORMAL BUTYL BROMIDE AND BROMOBENZENE TOWARD MAGNESIUM IN ETHER

BY HENRY GILMAN AND E. A. ZOELLNER

RECEIVED JUNE 22, 1928 PUBLISHED SEPTEMBER 5, 1928

Several explanations have been proposed for the orienting influences of various elements and groups in substitution reactions of benzene and other aromatic types. The Fliirscheim hypothesis has been criticized because of the implicit assumption that some bonds are strong and others weak. The following extract is from a recent text.[1] "Silver nitrate will remove bromine from methyl bromide much more readily than from bromobenzene, which appears to support Flürscheim's ideas, since it suggests that the strength of the bonds joining bromine to carbon is different in the two organic molecules. But in the formation of the Grignard reagent it is found that magnesium acts with ***equal***[2] ease upon methyl bromide and bromobenzene; so that no difference in reactivity is noticeable."

Several studies in this Laboratory indicated that alkyl halides, in general, react more readily than the corresponding aryl halides with magnesium in ether to form the respective Grignard reagents. The results of the present studies support this view. First, in some semi-quantitative investigations on the effect of negative catalysts[3] on the formation of organomagnesium halides, it has been shown that n-butyl bromide reacts with magnesium in ether distinctly more readily than does bromobenzene to form the respective Grignard reagents.[4] Second, the yields of n-butylmagnesium bromide and phenylmagnesium bromide as quantitatively determined, under corresponding conditions, at several time intervals showed that larger amounts of the alkylmagnesium bromide were formed in a given time.

It should be remembered here that the reaction between an RX com-

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[1] "Recent Advances in Organic Chemistry" by Alfred W. Stewart, fifth edition, Vol. I, p. 338, 1927, published by Longmans, Green and Co., Ltd. The particular criticism in this and in other texts may possibly have its origin in Holleman's "Die direkte Einführung von Substituenten in den Benzolkern," p. 212–213, published by Veit and Co., Leipzig, in 1910. One of the statements made there is the following: "However, one observes that in ethereal solution the halogen in the benzene ring is just as easily replaced by magnesium as that in alkyl halides." No measurements of this were made (private communication from Dr. Holleman), but the observation is understandable in view of the comparative readiness with which bromobenzene reacts with magnesium in ether.

[2] The italics are ours.

[3] Studies by R. J. VanderWal.

[4] The color test described by Gilman and Schulze was used in these experiments, THIS JOURNAL, 47,2002 (1925), and Bull. *soc. chim.*, 41,1279 (1927).

pound and magnesium to form a Grignard reagent is accompanied by other reactions, such as the Würtz-Fittig reaction which is probably preceded by the formation of free radicals and disproportionation.[5] Furthermore, the positive color test[4] for the Grignard reagent, despite its high sensitivity, must wait on the formation of an amount of the RMgX compound in excess of that required to react with any incidental moisture and impurities in the ether such as peroxides. Attention should be directed, in connection with these studies, to a recent paper by Rudd and Turner[6] on the competitive interaction of alkyl and aryl halides with magnesium. These authors allowed a mixture of two different halides (one mole of each) to compete for one atom of magnesium, and the product was analyzed for halogen after complete dissolution of the metal. Obviously their results do not represent the exact quantities of Grignard reagent formed, and there is the possibility that one RMgX compound may have affected the rate of formation of the other.' Both of these points were mentioned by them. The pairs of halides they allowed to compete for magnesium had *different* halogens.

Experimental Part

The quantitative experiments were made under the general conditions and in the special apparatus used by Gilman and co-authors in earlier studies on the quantitative estimation[s] of the Grignard reagent and on the yields[g] of some RMgX compounds.

The halides were very carefully dried and then distilled prior to use. Commercial magnesium was used and the particles (after crushing in a mortar and sieving) were essentially uniform. In each run **0.05** mole of halide, **0.054** atom of magnesium and 30 cc. of dry ether were used.

The magnesium was first covered with **6.5** cc. of ether and then, after having added a crystal of iodine, **30** drops (or its equivalent) of the halide was added and the mixture was heated for ten minutes without stirring in a bath kept at 45°. This insured the start of reaction prior to the addition of the main quantity of halide. The remainder of the halide and ether was then added rapidly with stirring (the time of addition here was ten seconds) and from this point was taken the time given in Table I.

At the end of a given time interval (forty-five or ninety seconds) the reaction flask

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[5] **A** preliminary account of this study was made at the St. Louis Meeting of the American Chemical Society, April 17, **1928,** by Gilman, Fothergill, Kirby and Heck. The final results will be published shortly.

[6] Rudd and Turner, *J. Chem. Soc.,* **133,686 (1928).**

[7] An indication of this is found in some competitive studies of halides, such as n-butyl bromide and bromobenzene, toward magnesium. The yields of derivatives of these two Grignard reagents (formed at the same time with an insufficient amount of magnesium) differ frotn the acid titration values.

[8] Gilman, Wilkinson, Fishel and Meyers, THIS JOURNAL, **45, 150 (1923)**; Gilman and Meyers, *Rec. trav. chim.,* **45, 314 (1926).**

[9] Gilman and Meyers, THIS JOURNAL, **45, 159 (1923);** Gilman and McCracken, *ibid.,* **45, 2462 (1923);** ***Rec. trav. chim.,*** **46, 463 (1927);** Gilman and Zoellner, THIS JOURNAI,,50,425 (1928).

was chilled in a bath of ice and water. Experiments showed that the reaction was virtually stopped by such chilling, for the yield of RMgX at the beginning of the chilling period was only about **2.5%** less than that determined at the end of one-half hour of chilling. Three aliquots were removed for analysis at the beginning of the chilling period. After removing the aliquots the mixture was allowed to react at room temperature for forty-five minutes and then two aliquots were removed for analysis.

The analyses of these final two aliquots have no essential bearing on the relative reactivities of the halides since the reaction was complete at that time.[9] However, they did serve, first, as an additional check on the technique and, second, to call attention to marked differences in the respective total quantities of Grignard reagents at the end of each experiment. For when runs were made with both halides, under the general conditions followed in the ninety seconds experiments but *without* removal of the three aliquots, the yield of phenylmagnesium bromide (92.7%) and that of n-butylmagnesium bromide (79.7%) checked those in the reactivity runs when interruptions were made for the removal of aliquots. Under the conditions usually employed for the preparation of the Grignard reagent (slow addition, etc.)[9] the yield of phenylmagnesium bromide is 96.2% and that of n-butylmagnesium bromide, 94%.[10] This marked drop in the yield of n-butylmagnesium as a consequence of rapid addition is of particular significance. It emphasizes a reactivity of n-butyl bromide that is distinctly greater than that shown by the respective quantities of Grignard reagent actually determined (see Table I) inasmuch as the drop in yield (from 94 to 79.7%) very probably resulted, in large part,[11] from n-butylmagnesium bromide being used up in side reactions.[5]

Table I includes the averages of several runs where aliquots were removed at two different time intervals. The aliquots from a given experiment agreed within the experimental error for such work, namely, about one per cent.[8,9] The average values for analyses made of duplicate runs of a given halide after ninety seconds of reaction agreed within 2.7%; and

TABLE I

RESULTS OF ANALYSES

Halide	Moles	Time of reaction, secs.	Yield of corresponding RMgX, %
Bromobenzene	**0.05**	**45**	**36.9**
n-Butyl bromide	**.05**	**45**	**53.7**
Bromobenzene	**.05**	**90**	**51.7**
n-Butyl bromide	**.05**	**90**	**65.4**

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[10] Other studies in progress on the effect of rapid addition of halide on the yield of Grignard reagent show no apparent correlation as yet with the type of RX compound used.

[11] In so far as the immediate purpose of this paper is concerned it does not matter how much of this drop is due to Grignard reagent that has disappeared as a result of side reactions. The significant thing is that the n-butyl bromide has reacted more rapidly than the bromobenzene toward magnesium.

those after forty-five seconds of reaction agreed within 6.5%. Quite probably these average errors can be significantly reduced with a more refined technique such as, for example, the use of a definite quantity of iodine instead of the somewhat arbitrary "crystal of iodine." The rates of some other halides are being measured under more exact conditions.

The authors wish to acknowledge help in some of these experiments from J. B. Dickey.

Summary

n-Butyl bromide reacts more rapidly than bromobenzene with magnesium in ether. This result is of direct value in connection with some theories proposed to account for orientation in the benzene nucleus.

AMES, IOWA

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

OXIDATION IN THE BENZENE SERIES BY GASEOUS OXYGEN. IV. MECHANISM OF THE SLOW OXIDATION OF SATURATED HYDROCARBONS

BY H. N. STEPHENS

RECEIVED JUNE 25, 1928 PUBLISHED SEPTEMBER 5, 1928

Previous papers by the writer[1] have shown that alkyl benzenes are oxidized slowly by gaseous oxygen at a temperature of about 100°. Methylbenzenes yielded mono-aldehydes and the corresponding acids, while hydrocarbons containing two or more carbon atoms in the side chain were attacked only at the a-carbon atom, yielding ketones. When alkyl substituents replaced all of the hydrogen on the a-carbon atom, no oxidation took place under the conditions employed; therefore we must conclude that the linkages between this particular carbon atom and its hydrogen are the points of weakness which are attacked by oxygen.

In studying some of these oxidations it was found that the water formed by the reactions exerted a retarding effect and later, when excess water was used with the hydrocarbons, complete inhibition of oxidation resulted. Important exceptions to this behavior were noted in hydrocarbons which have only one hydrogen atom attached to the a-carbon atom, in which cases no inhibitory action was noted.

In seeking an explanation of the inhibitory action of water, it did not seem to us sufficient merely to classify it under the vague and unsatisfactory term "anticatalysis." Neither did it seem possible to account for the phenomenon on the basis of a protective action in which the water molecules might be assumed to attach themselves loosely to the hydrocarbon molecules, preventing ready access of oxygen to the vulnerable

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[1] Stephens, THIS JOURNAL, 48, 1824, 2920 (1926).

point. The exceptions to the inhibitory action, which have just been noted, seem to preclude this possibility, as there is no apparent reason why cumene or cymene should not be protected as well as other hydrocarbons.

As has been suggested in previous papers, the simplest and most reasonable explanation seems to lie in the assumption of a reversible stage in the oxidation which involves the elimination of water. In the oxidation of the *iso*propyl group, however, in which only one hydrogen is attached to the α-carbon atom, it has been assumed that the elements of methyl alcohol, instead of the elements of water, tend to be eliminated.

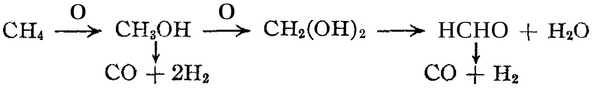
In order to justify such an assumption it was necessary, of course, to obtain additional information about the mechanism of oxidation, the most important problem being to determine the nature of the earlier stages. During the past few years there seems to have been a growing tendency to assume that the oxidation of saturated hydrocarbons passes through all the possible intermediate stages, starting with the alcohol. This view owes its origin chiefly to the work of Bone and his collaborators, which has given rise to the well-known "hydroxylation" theory.

As far as the writer is aware, only one case is on record in which an alcohol has actually been identified as a product of oxidation of a saturated hydrocarbon and in this case the oxidizing agent was ozone.[2] However, this lack of experimental evidence has not been considered a serious drawback to the "hydroxylation" theory, as Bone and Stockings[3] have shown that ethyl alcohol is much more readily oxidized than ethane. Thus it is considered that the alcohol, assumed to be the primary oxidation product, is oxidized further, as rapidly as it is formed.

Another important line of evidence in favor of intermediate formation of alcohols[4] lies in the fact that when methane is exploded with an insufficient supply of oxygen, an increase in the initial pressure of the gases causes a decrease in the proportion of water formed. The interpretation of this fact by Bone and Townsend involves the assumption that at higher pressures the tendency of methane to decompose

$$CH_4 \text{ (1 vol.)} \longrightarrow C + 2H_2 \text{ (2 vols.)}$$

would be repressed; that is, the loosening of the carbon to hydrogen valences which it is necessary to assume in their "hydroxylation" scheme, would be less pronounced. Therefore, in the series of reactions postulated by Bone's theory



$$\begin{array}{ccccccc} CH_4 & \xrightarrow{O} & CH_3OH & \xrightarrow{O} & CH_2(OH)_2 & \longrightarrow & HCHO + H_2O \\ & & \downarrow & & & & \downarrow \\ & & CO + 2H_2 & & & & CO + H_2 \end{array}$$

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[2] Bone and Drugman, *Proc.* Chem. *Soc.,* 20, 127 (1904).

[3] Bone and Stockings, *ibid.,* 20, 106 (1904).

[4] Townsend, *Proc.* Roy. *Soc., London,* **116A,** 652 (1927).

although it is assumed that normally (that is, at ordinary pressures) there is a tendency toward a "non-stop" oxidation of CH_4 to $CH_2(OH)_2$; under the influence of higher pressures greater difficulty is experienced in introducing the second atom of oxygen and there is more tendency for the oxidation to stop at the alcohol stage. Then, as methyl alcohol has been shown to decompose into CO and H_2, the total amount of water formed would be decreased. In passing, it might be pointed out that it is not clear why the introduction of the second oxygen atom should be disfavored rather than the first, as this is not in accord with the fact that ethyl alcohol is oxidized more readily than ethane.

As the assumptions made by the writes to account for the inhibitory action of water do not definitely provide a place for the alcohol stage, it seemed desirable to find out, if possible, whether or not the alcohol stage was an intermediate one in the production of aldehydes and ketones. With this end in view a study of the oxidation of several a-phenyl carbinols was made[5] and it was found, with one exception (that of *iso*propylphenyl carbinol), that a small amount of ketone was formed at 100". However, in this study and in some later experirnents, other evidence was found which argues very strongly against the alcohol stage being an intermediate one in the oxidation of hydrocarbons. Assembling material both from papers already published and from the present paper we may present the following arguments.

1. The main products obtained from alcohols at 100° were high boiling liquids, which were presumably ethers. Also benzoic acid was formed in the oxidation of all secondary alcohols. None of these products was detected in the oxidation of hydrocarbons.

2. Oxidations of xylene and ethylbenzene were carried out in the presence of acetic anhydride in an attempt to get an ester of the intermediate alcohol but in neither case was any ester detected. To eliminate the possibility of the ester being oxidized, xylyl acetate was treated with oxygen under the usual conditions but no toluic aldehyde was formed. The only effect of acetic anhydride was to increase the rate of oxidation, due to the removal of water.

3. Water inhibits the oxidation of all of the alcohols studied. In the hydrocarbons containing normal alkyl groups, the oxidation of which is completely inhibited by water, we must, therefore, assume that the oxidation of hydrocarbon to alcohol is inhibited. In the oxidation of cumene, however, water does not inhibit the reaction, although the oxidation of the corresponding alcohol, dimethylphenyl carbinol, is completely inhibited. In this case, then, it would be expected that the alcohol, if it is an intermediate product, would accumulate and that no acetophenone would be formed. As it has been shown that cumene is oxidized

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[5] Stephens, THIS JOURNAL, **50**, 186 (1928).

directly to acetophenone in the presence of water, with no formation of dimethylphenyl carbinol, the assumption that the alcohol is an intermediate stage seems unjustifiable.

4. Finally, it has been shown that, using equimolecular amounts of ethylbenzene and phenylmethyl carbinol, a much greater yield of acetophenone is obtained in a given time from the hydrocarbon than from the alcohol. In this particular case, then, the non-existence of alcohol in the final products from the hydrocarbon cannot be explained on the basis of the more rapid oxidation of the alcohol. On the contrary, the alcohol would be expected to accumulate, if it were an intermediate oxidation product.

In the face of the above arguments, it seems impossible to grant that the alcohol stage is an intermediate one in the oxidation of alkyl benzenes to aldehydes or ketones and if this is true for alkyl benzenes, there seems no reason why it should not be true for paraffin hydrocarbons. The retarding action of water on the oxidation of ethane at 415 and 440° has been noted by Bone and Andrews[6] and thus one point of similarity is definitely established. The writer takes the view that the benzene nucleus merely exerts a directive influence without affecting, in any fundamental way, the mechanism of oxidation. Granting this, any theory of the mechanism of oxidation ought to be able to explain oxidations in both classes of hydrocarbons. As Bone's theory assumes the existence of the alcohol stage, which, apparently, is not justifiable and also provides no explanation for the inhibitory action of water, the following scheme is submitted in the belief that it is capable of explaining satisfactorily all of the known facts

$$\text{Hydrocarbon} + O_2 \rightleftharpoons \text{Complex} \rightleftharpoons H_2O + \underset{\substack{\downarrow \\ \text{Aldehyde or ketone}}}{\text{unsaturated residue}}$$

In the oxidation of the alkyl benzenes, it is believed, although not definitely proved, that the reaction takes place chiefly, if not exclusively, in the vapor phase; therefore, the first stage may be considered as a homogeneous gas reaction in which one molecule of hydrocarbon associates with one molecule of oxygen. To call the bimolecular aggregate thus formed a molecular compound might possibly be misleading, as it is considered as being extremely unstable and, consequently, short-lived. On account of the slowness of these oxidations it must be assumed that the majority of these temporary associations are followed by dissociation into the original molecules; that is, the first stage is strictly reversible. It might be mentioned, in passing, that it seems much more reasonable to consider molecular oxygen as the oxidizing agent rather than atomic, as assumed by Bone and his co-workers. At explosion temperatures, the presence of atomic oxygen will be granted, but as the "hydroxylation"

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[6] Bone and Andrews, *J. Chem. Soc.*, **89**, 659 (1906)

theory is applied to slow oxidations as well as to rapid combustions, the existence of appreciable concentrations of oxygen atoms at 100° would have to be assumed, which is apparently contrary to fact.

The Inhibitory Action of Water

Although the majority of the bimolecular aggregates just dealt with are assumed to dissociate again, a small proportion might be expected to decompose, as shown in the second stage of oxidation, with elimination of the elements of water and formation of an "unsaturated residue." Now, if this reaction is reversible, the extremely interesting phenomenon of the inhibitory action of water can be explained in a very simple way. On the other hand, it seems impossible, on the basis of the hydroxylation theory, to devise any simple explanation of this behavior. It will be seen readily that, if this stage is reversed, no permanent oxidation product can be formed.

The final stage of this series of reactions involves a rearrangement, or orientation, of the "unsaturated residue" into the stable form of an aldehyde or ketone and this reaction could hardly be thought of as other than an irreversible one. On this account, the oxidation as a whole would be irreversible and the action of water on an aldehyde or ketone could not be expected to yield the corresponding hydrocarbon and oxygen.

It might be mentioned that the purpose of introducing the "unsaturated residue" is twofold; first, to account for the irreversibility of the reaction as a whole and, second, to take cognizance of the fact that it must take a finite time, however short, for an unsaturated fragment from the decomposition of a molecule or aggregate to orientate itself into a stable configuration. Then, if this residue has a definite life period, the presence of a sufficient concentration of water vapor could cause the second stage of the oxidation to be reversed.

In the oxidation of the isopropyl group in cumene, or cymene, the series of reactions shown above would be the same except for the elimination of the elements of methyl alcohol instead of water. In this case, it would be expected that oxidation would accompany, or immediately follow, this elimination and actually the product that is obtained is not methyl alcohol but formic acid. As was anticipated, the presence of methyl alcohol in excess did not inhibit the oxidation of cumene and other work is at present under way to attempt to throw more light on this reaction.

To return once more to the oxidation of methane under high pressure and with a small proportion of oxygen present,[4] it seems quite possible, in accord with the above theory, to grant the correctness of the assumption that some methyl alcohol was formed. Under ordinary conditions (ordinary pressures arid with a sufficient supply of oxygen) it seems reasonable to assume that the simplest possible type of reaction will take place, that is, a bimolecular one. However, if the concentration of methane were very high, with respect to that of oxygen, there seems every possibility of two molecules of methane associating with one molecule of oxygen. That is, according to the widely accepted view of Trautz and Schleuter,[7] there would be ample opportunity for a second methane molecule to encounter a bimolecular oxygen–methane aggregate, while the two molecules were still under their mutual sphere of influence. Now, the decomposition of this trimolecular aggregate would be most simply represented by the equation

$$CH_4 \cdot O_2 \cdot CH_4 \longrightarrow 2CH_3OH$$

Thus, under these special conditions, the formation of an alcohol from a hydrocarbon seems quite possible. It must be pointed out, however, that the alcohol thus formed is a by-product and not an intermediate in the oxidation of the hydrocarbon.

Finally, we might turn to the only case on record in which an alcohol has been detected as an oxidation product of a saturated hydrocarbon, that of the production of ethyl alcohol from ethane by means of ozone.[3] If we assume the same type of reaction as in the case of oxygen, we should expect the bimolecular aggregate thus formed to decompose, giving ethyl alcohol and oxygen.

$$C_2H_6 \cdot O_3 \longrightarrow C_2H_5OH + O_2$$

Ozone, then, cannot be compared too strictly with oxygen, as the former can give an alcohol through bimolecular impacts, while the latter cannot. One other possibility might be mentioned in this connection. In the work of Bone and Drugman a large excess of ethane was employed and it is conceivable that some trimolecular impacts might occur under these conditions. If this does take place, the resulting aggregates might decompose according to the scheme

$$C_2H_6\,O_3 \cdot C_2H_6 \longrightarrow C_2H_5OH + CH_3CHO + H_2O$$

also yielding ethyl alcohol.

To sum up very briefly, the normal primary reaction between a saturated hydrocarbon and oxygen is assumed to depend on bimolecular impacts. Under exceptional conditions, as has just been indicated, trimolecular collisions may take place to some extent. Only in this latter event can any alcohol be formed and the alcohol would thus be considered as a by-product rather than an intermediate oxidation product.

Experimental Part

A. Oxidation in the Presence of Acetic Anhydride

Xylene.—Twenty g. of xylene and 20 g. of acetic anhydride oxidized at 102–104° for twenty-one days yielded 7.85 g. of crude toluic aldehyde, b. p. 78–81° (10 mm.); previously reported, 1.9 g. of aldehyde from 90 g. of xylene in 30 days at 100°.

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[7] Trautz and Schleuter, *Z. anorg Chem* , 136, 1 (1924).

Ethylbenzene.—Twenty-five g. of ethylbenzene and 25 g. of acetic anhydride oxidized for eleven days at 102–104° yielded 9.0 g. of crude acetophenone; previously reported, 9.5 g. of acetophenone from 50 g. of ethylbenzene in twenty-four days at 110–115°.

Xylyl Acetate.—Twelve g. of xylyl acetate, b. p. 103–106° (10 mm.), oxidized for eleven days at 102–104°, yielded no tolnic aldehyde.

B. Parallel Oxidation of Ethylbenzene and Phenylmethyl Carbinol

Twenty-five g. of phenylrnethyl carbinol, oxidized for eleven days at 122–124° yielded 0.85 g. of acetophenone, isolated as semicarbazone.

Twenty-one g. of ethylbenzene, oxidized as above for eleven days, yielded **6.3** g. of crude acetophenone, b. p. 77–83° (8mm.).

Summary

A new mechanism of the oxidation of saturated hydrocarbons by gaseous oxygen is proposed, which accounts for the inhibitory action of water in oxidations studied by the writer.

It is shown that the oxidation of a hydrocarbon to aldehyde or ketone does not go through the alcohol stage.

MINNEAPOLIS, MINNESOTA

[CONTRIBUTION PROM THE DEPARTMENT OP CHEMISTRY: COLUMBIA UNIVERSITY, No. 578]

THE INTERRELATION OF HYDROGEN-ION ACTIVITY AND CONCENTRATION OF SALT IN THE ACTIVATION OF PANCREATIC AMYLASE[1]

BY H. C. SHERMAN, M. L. CALDWELL AND M. ADAMS

RECEIVED JUNE 28, 1928 PUBLISHED SEPTEMBER 5, 1928

It has long been known that the presence of electrolyte is essential to the activity of pancreatic amylase, but quantitative data obtained under sufficiently controlled conditions have not been available to afford satisfactory explanations of this influence or to permit strictly quantitative comparisons of different electrolytes.

In view of this fact and of the theoretical and practical importance of the subject, series of investigations to obtain quantitative and comparable data concerning the influence of various electrolytes upon the activity of pancreatic amylase have been carried out in which the influence of the other factors involved has been recognized and eliminated as completely as possible. In this way it was hoped that the magnitude of the influence, if any, exerted by each salt might be quantitatively established, that other interrelated factors might be recognized, that more light might be thrown upon the way in which such influences are exerted and that

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[1] We are greatlv indebted to the Carnegie Institution of Washington for grants in aid of this investigation.

thus more knowledge of the nature and mode of action of the enzyme itself might be obtained.

The study should also be of value in establishing and making it possible to maintain the most favorable conditions for future measurements of enzymic activity.

The results of one series of experiments in which several typical "buffer" salts were studied have already been published.[2] These results led to the conclusion that the influence upon the activity of pancreatic amylase which had hitherto been attributed to such salts as the phosphates, citrates and borates of sodium is mainly if not entirely due to the influence which they exert upon the hydrogen-ion activities of the systems. This explanation would, however, not apply to all electrolytes and the study has, therefore, been extended to include several representative neutral salts.

In the many previous investigations on the influence of neutral salts on the activity of pancreatic amylase, it has generally been assumed that the optimal hydrogen-ion activity for the enzyme as determined in the presence of one concentration of a salt is also the optimal hydrogen-ion activity for that enzyme in the presence of any other concentration of the salt under consideration. Moreover, when there has been any attempt to compare the influence of different salts on the activity of pancreatic amylase there has been no attempt to determine the optimal concentration for each of the salts studied.

Recent investigations[3] have indicated a need for investigating these assumptions as it has been shown that the factors which influence enzymic activity are much more dependent upon one another than has heretofore been generally recognized.

Experimental

The experimental work may be divided into three parts. (1) A study of each salt was made first to determine the influence of changes in its concentration on the optimal hydrogen-ion activity for the hydrolysis of starch by pancreatic amylase. (2) The optimal concentration of each salt was then ascertained by comparing the hydrolysis of starch by pancreatic amylase in the presence of different concentrations of the salt, the enzymic activity being measured at the optimal hydrogen-ion activity in each case. (3) It was then possible to make direct comparisons of the hydrolysis of starch by pancreatic amylase in the presence of each of these salts with the starch in each case adjusted to the hydrogen-ion activity and to the concentration of salt which is most favorable for pancreatic

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[2] Sherman, Caldwell and Dale, THIS JOURNAL, 49, 2596 (1927).

[3] (a) Hahn and co-workers, *Z. Biol.*, 71, 286, 302 (1920); (b) 73, 10 (1921); (c) 74, 217 (1922); (d) 76, 227 (1922); (e) Myrback, *Z. physiol. Chem.*, 149, 1 (1926); (f) Sherman, Caldwell and Adams, THIS JOURNAL, 49, 2000 (1927).

amylase activity. The results of the first phase of this work will be reported briefly in this paper while the other phases will be treated more fully later.

This first series of experiments, therefore, was undertaken to determine the interrelation of hydrogen-ion activity and concentration of salt in the activation of pancreatic amylase. This was accomplished by making parallel measurements of the enzymic activity in the presence of systematically graded hydrogen-ion activities for each concentration of each salt studied.

The salts studied were sodium, potassium and lithium chlorides, and the bromide, fluoride, nitrate, chlorate, sulfocyanate and sulfate of sodium. These were carefully purified by recrystallization.

Because of the difficulties involved in obtaining sodium iodide free from traces of iodine, this salt was omitted from the present series. In our opinion it is impossible at present to separate the influence upon enzymic activity which may be attributable to the iodide ion from that of the traces of free iodine also present in solutions of sodium iodide.

Three preparations of pancreatic amylase were used for these investigations: a commercial pancreatin of high amylase activity obtained by the courtesy of Parke, Davis and Company in 1922, and two purified preparations, one prepared according to the method of Sherman and Schlesinger,[4] the other according to the same method except that the addition of maltose before dialysis was omitted and the final alcohol solution was dialyzed for twelve to fourteen hours instead of forty hours. The activities of these preparations expressed on the Sherman and Kendall[5] scale were 280, 940 and 1130, respectively.

The method of measuring the amylase activity was by the gravimetric determination of the reducing sugar produced from the starch by the enzyme, as shown by the reduction of Fehling's solution and the formation of cuprous oxide. The details of this method have been described in previous publications from this Laboratory.[6] The concentration of each enzyme preparation was kept constant throughout the series of experiments, the solutions being made up immediately before use in ice-cold water containing **0.0005** M disodium phosphate.

Selection of a Suitable Buffer.—In order to make a quantitative study of the influence of these neutral salts it was desirable to have present some buffer salt which would not itself influence the enzymic activity but by means of which it would be possible to control accurately the hydrogen-ion activities of the substrates. Mixtures of the phosphates of sodium had been found, as shown above,[2] to answer these requirements. This finding, that phosphate has no influence upon the activity of pancreatic amylase in half-hour hydrolyses of 2% starch at 40°, has been confirmed and extended.

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[4] Sherman and Schlesinger, THIS JOURNAL, **33, 1196 (1911); 34, 1104 (1912).**

[5] Sherman, Kendall and Clark, ibid., **32,1093 (1910).**

[6] Sherman and Walker, ibid., 41, 1866 **(1919);** Adams, *Dissertation,* Columbia University, 1927.

In the absence of any neutral salt but in the presence of a total phosphate concentration of 0.01 M, the enzyme solutions in the concentrations in which they were used throughout this investigation produced no measurable hydrolysis of starch. An unfavorable hydrogen-ion activity^{3} of the system was not a factor here as the measurements of enzymic activity were made in the presence of systematically graded differences in hydrogen-ion activities from *PH 5.7* to **PH** 7.7.

When the concentration of the commercial pancreatin was doubled, there was evidence of slight enzymic activity. This was greatest in solutions corresponding in hydrogen-ion activity to **PH** *5.3* but was very slight at best and was evidently due to the small amount of electrolyte impurities present in the commercial pancreatin, because, under similar conditions, the purified enzyme preparations produced no measurable hydrolysis of starch. These results justified the use of 0.01 M phosphate buffer mixtures throughout this investigation.

The total phosphate concentration was held constant in all the starch solutions but the relative amounts of primary and secondary phosphates were varied in order to obtain the desired hydrogen-ion activities. The hydrogen-ion activities were measured electrometrically for each starch solution used.

Results **with** Individual Salts.—The results with sodium chloride are shown graphically in Fig. 1. It is seen from these results that the optimal hydrogen-ion activity for pancreatic amylase activity in the presence of sodium chloride **is** different for each concentration of sodium chloride as this is increased from 0.0005 to 0.01 *M*. Above 0.01 M, the optimal *PH* is the same (PH 7.1 – 7.2) with increasing concentrations of sodium chloride.

TABLE I

A SUMMARY OF RESULTS WITH DIFFERENT SALTS SHOWING THE INTERRELATIONSHIP BETWEEN CONCENTRATION OF SALT AND HYDROGEN-ION ACTIVITY (EXPRESSED AS PH) IN THEIR INFLUENCE UPON THE ACTIVITY OF PANCREATIC AMYLASE[a]

Concn. of salt, *M*	Most favorable hydrogen-ion activity for pancreatic amylase in the presence of different concentrations of each of the following salts, *PH*					
	NaCl	KCl	NaBr	$NaNO_3$	$NaClO_3$	NaSCN	NaF
0.0005	6.5	.....	...	.....	.....	.....	.....
.001	6.7	.....	...	.....	.....	.....	.....
.0025	6.9	.....	...	.....	.....	.....	.....
.005	7.0	7.0–7.1	...	6.6–6.8	6.5	.....	.....
.01	7.1	7.1–7.2	7.1	6.9–7.1	.....	.....	.....
.02	7.1	.....	...	.....	.....	.....	.....
.03	7.1	7.1–7.2	...	.....	.....	.....	.....
.05	7.1	7.1–7.2	7.1	7.0–7.2	6.9–7.1	6.5	.....
.10	7.1	.....	7.1	.....	.....	6.7–6.8	6.3–6.7
.15	...	.....	...	.....	.....	6.7–6.8	.....
.20	...	.....	7.1	7.1–7.2	6.9–7.1	6.7–6.8	6.6–6.8
.30	...	.....	...	.....	.....	.....	6.6–6.8

[a] Mixtures of acid and alkaline sodium phosphates corresponding to a total concentration of 0.01 M phosphate were present in all cases.

As shown in Table I, the results obtained with the other salts studied were similar, but the concentration of the salt at which the optimal hydrogen-ion activity for the enzymic activity ceases to be appreciably influenced depends upon the salt.

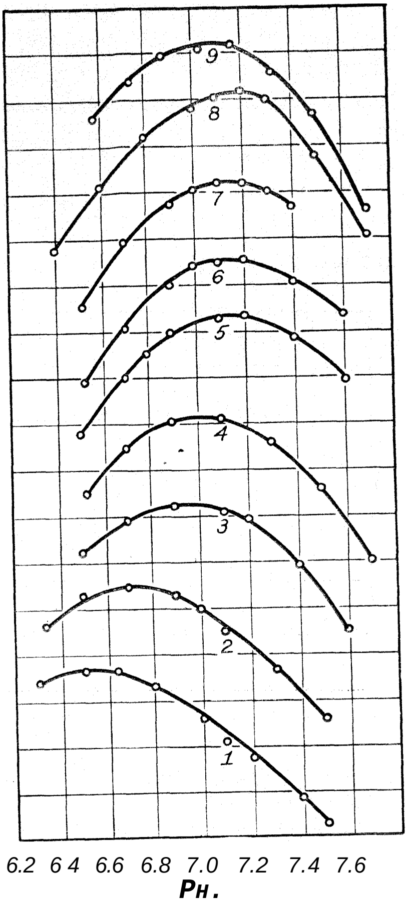
Thus this concentration was found to be 0.01 *M* for sodium chloride, potassium chloride or sodium bromide; 0.05 *M* for sodium nitrate or sodium chlorate; 0.10 *M* for sodium sulfocyanate and 0.20 *M* for sodium fluoride. In each case as the concentration of the salt is decreased below these concentrations, the enzyme is most active in increasingly more acid solutions.

A comparison of the results given in Table I also shows that the optimal hydrogen-ion activity for pancreatic amylase is somewhat different in the presence of these different salts, even when enough of each salt is present to eliminate the influence of changes in its concentration.

Sodium sulfate was found to be without influence upon the activity of pancreatic amylase even when the hydrogen-ion activities of the solutions were varied at graded intervals from PH 5.7 to PH 7.7 and the concentrations of the salt from 0.01 to 0.10 M.

Because of the insolubility of lithium phosphate it was not possible to study lithium chloride in the same way in which the other salts were investigated and the results with this salt will be given in a later paper.

Conditions for the Enzymic Activity in the Presence of More than One Salt.—Experiments similar to those just described were also carried out with mixtures of two salts. In previous investigations[7] dealing with the influence



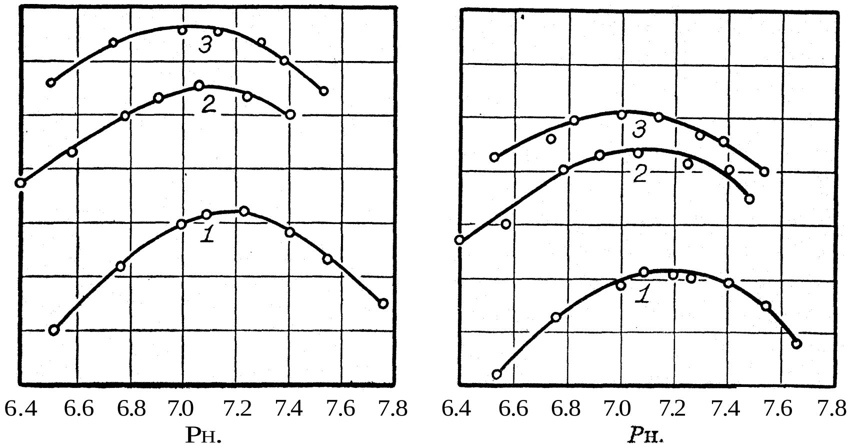
Pancreatin (power 280). 1—0.0005 M NaCl; 2—0.001 M NaCl; 3—0.0025 *M* NaCl; 4—0.005 *M* NaCl; 5—0.01 *M* NaCl; 6—0.02 *M* NaCl; 7—0.03 *M* NaCl; 8—0.05 M NaCl; 9—0.10 *M* NaCl.

Fig. 1.—Influence of the concentration of sodium chloride upon the activity of pancreatic amylase at different hydrogen-ion activities. All the points on any one curve are comparable but the curves are not placed to indicate relative activity of the enzyme in the presence of different concentrations of salt. This is true of the curves in all subsequent figures.

[7] Michaelis and Pechstein, *Biochem. Z.*, 59, 77 (1914); Hahn and Harpuder, *Z. Biol*, 71, 286, 302 (1920).

of more than one salt upon the activity of pancreatic amylase no attempt has been made first to establish quantitatively the optimal conditions for the activity of pancreatic amylase in the presence of mixtures of these salts. In the present experiments the activity of the enzyme was measured in the presence of 0.02 M sodium chloride with additions of 0.01 to 0.20 M sodium nitrate or 0.01 to 0.10 *M* sodium sulfate.

Pig. 2 shows the results obtained with mixtures of sodium chloride and sodium nitrate. The results with mixtures of sodium chloride and sodium sulfate were similar. The optimal hydrogen-ion activity for the enzyme in the presence of mixtures of 0.02 *M* sodium chloride and sodium sulfate was PH 7.1–7.2 when the sodium sulfate was present in total concentrations of 0.01 to 0.05 M, and *PH* 6.9 when the concentration of sulfate present was increased to 0.10 *M*. It was found that as the concentration of sodium nitrate or sodium sulfate was increased the enzymic activity was favored by solutions of greater hydrogen-ion activity, that is, by more acid solutions.



Pancreatin (power 280).
1—0.01 M $NaNO_3$ + 0.02 M NaCl;
2—0.10 M $NaNO_3$ + 0.02 M NaCl;
3—0.20 M $NaNO_3$ + 0.02 M NaCl.

Purified preparation (power 1130).
1—0.01 M $NaNO_3$ + 0.02 M NaCl;
2—0.10 M $NaNO_3$ + 0.02 M NaCl;
3—0.20 M $NaNO_3$ + 0.02 M NaCl.

Fig. 2.—Influence of the concentration of sodium nitrate upon the activity of pancreatic amylase at different hydrogen-ion activities in the presence of 0.02 M sodium chloride.

Summary

The optimal hydrogen-ion activity for pancreatic amylase in the presence of different concentrations of sodium or potassium chlorides or of sodium bromide, fluoride, nitrate, chlorate, sulfocyanate or sulfate has been quantitatively investigated.

The optimal hydrogen-ion activity for pancreatic amylase is dependent both upon the kind and concentration of salt present.

In the presence of each of the salts investigated here, the optimal hydrogen-ion activity for pancreatic amylase decreases with increasing concentration of the salt up to a certain salt concentration, beyond which it ceases to he appreciably influenced.

The concentration of salt at which the optimal hydrogen-ion activity for the enzymic activity ceases to be appreciably influenced depends on the salt.

In the presence of more than one of these salts the optimal hydrogen-ion activity depends upon the concentration of the salts present.

Sodium sulfate and sodium phosphate were found to be without influence on the activity of pancreatic amylase.

NEW YORK CITY

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY, No. 5791

THE INFLUENCE OF CONCENTRATION OF NEUTRAL SALT ON THE ACTIVATION OF PANCREATIC AMYLASE[1]

BY H. C. SHERMAN, M. L. CALDWELL AND M. ADAMS

RECEIVED JUNE 28, 1928 PUBLISHED SEPTEMBER 5, 1928

In a previous paper[2] the optimal hydrogen-ion activity for pancreatic amylase in the presence of different concentrations of each of a series of neutral salts has been reported. These having been established, it was possible to continue the investigation and to determine the optimal concentration of each salt for the activity of the enzyme. The results of this phase of the work will be reported briefly in this paper.

Experimental

A series of parallel hydrolyses of starch by pancreatic amylase was carried out in the presence of different concentrations of each salt with the hydrogen-ion activity in each case adjusted to that previously found to be optimal[2] for the enzyme in the presence of the concentration of salt being studied. The conditions for making up solutions and measuring enzymic activity as there described[2] were maintained throughout. Fig. 1 shows the results obtained from a direct comparison of the activity of pancreatic amylase in the presence of from 0.005 to 0.10 M sodium chloride. The enzyme was found to exert its optimal activity in the presence of from 0.02 to 0.05 M sodium chloride.

With potassium chloride the concentrations investigated were 0.01,

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[1] We are greatly indebted to the Carnegie Institution of Washington for grants in aid of this investigation

[2] Sherman, Caldwell and Adams, THIS JOURNAL, 50, 2529 (1928).

0.02, 0.03 and 0.05 *M*, and 0.03 to 0.05 *M* potassium chloride solutions were found to permit optimal enzymic activity. From a direct comparison of the activity of pancreatic amylase in the presence of 0.01, 0.03, 0.05, 0.10 and 0.20 *M* sodium bromide it was found that 0.03 to 0.20 *M* was the most favorable concentration.

Measurements of the activity of pancreatic amylase in the presence of 0.03, 0.05, 0.10, 0.15 and 0.20 *M* sodium nitrate showed that 0.10 to 0.20 *M* was the most favorable concentration of sodium nitrate.

The results obtained in the presence of 0.05, 0.10, 0.15 and 0.20 *M* sodium chlorate solutions were similar to those obtained with sodium nitrate.

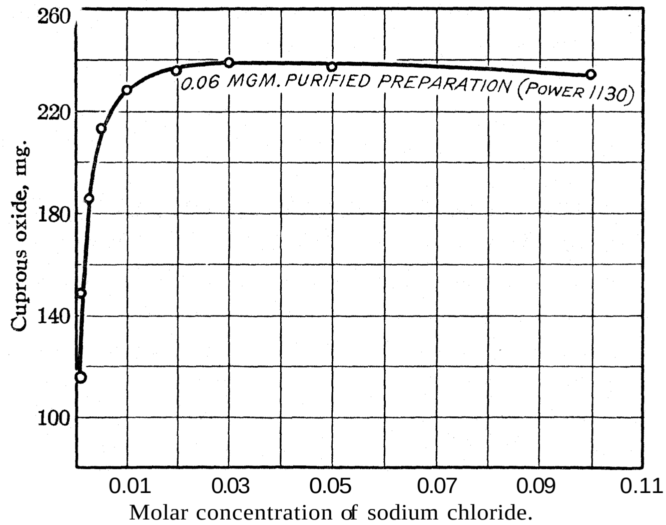

Fig. 1—Influence of concentration of sodium chloride on the activity of pancreatic amylase.

Comparisons of the activity of pancreatic amylase in the presence of 0.10, 0.15, 0.175 and 0.20 *M* sodium sulfocyanate or in the presence of 0.10, 0.15, 0.175, 0.20, 0.25 and 0.30 *M* sodium fluoride showed that a concentration of from 0.15 to 0.20 *M* sodium sulfocyanate or 0.20 to 0.30 *M* sodium fluoride was sufficient for the maximum activation which these salts are capable of producing.

An examination of the data summarized in Table I shows that the concentration of salt necessary for maximum activation of pancreatic amylase depends upon the individual salt present.

There is an increase in the enzymic activity as the concentration of salt is increased up to a maximum activity of the enzyme in the presence of each salt. Within the limits of concentration investigated here, further increases in the concentration of salt had practically no influence on the

TABLE I

THE OPTIMAL CONCENTRATIONS OF CERTAIN SALTS WITH THE CORRESPONDING OPTIMAL HYDROGEN-ION ACTIVITIES FOR THE ACTIVITY OF PANCREATIC AMYLASE[a]

Salt	Optimal concn., *M*	Optimal P_H
Sodium chloride	0.02–0.05[b]	7.1–7.2
Potassium chloride	03– .05	7.1–7.2
Sodium bromide	.03– .20	7.1
Sodium nitrate	.10– .20	7.1
Sodium chlorate	.10– .20	6.9–7.1
Sodium sulfocyanate	.15– .20	6.7–6.8
Sodium fluoride	20– .30	6.7–6.8

[a] Mixtures of acid and alkaline sodium phosphates corresponding to a total concentration of 0.01 M phosphate were present in all cases.

[b] The practically constant activity obtained within the limits of concentration considered here would indicate that there is enough of the salt present fully to activate the enzyme in each case.

activity of the enzyme or on the hydrogen-ion activity which is optimal for the enzyme in its presence. In the presence of insufficient salt to produce maximum activation, as the concentration of salt is decreased, the enzyme exerts its optimal activity in increasingly more acid solutions. Pancreatic amylase exerts its optimal activity in more acid solutions in the presence of those salts which require higher concentrations for complete activation. All of these results emphasize again the need of carefully standardizing and controlling the conditions for measuring enzymic activity.

Summary

The concentration of sodium or potassium chloride or of sodium bromide, nitrate, chlorate, sulfocyanate or fluoride most favorable (in each case) to the activation of pancreatic amylase has been quantitatively established.

The optimal concentration (in terms of molarity) is found to be different for different neutral salts.

The activity of pancreatic amylase is favored by more acid solutions in the presence of those salts of which higher concentrations are required for its complete activation.

NEW YORK CITY

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY,
No. 580]

A QUANTITATIVE COMPARISON OF THE INFLUENCE OF NEUTRAL SALTS ON THE ACTIVITY OF PANCREATIC AMYLASE[1]

BY H. C. SHERMAN, M. L. CALDWELL AND M. ADAMS

RECEIVED JUNE 28, 1928 PUBLISHED SEPTEMBER 5, 1928

In previous papers[2] the optimal hydrogen-ion activities and concentrations of salts for pancreatic amylase in the presence of different salts have been reported. With these conditions established it was possible to continue the investigation and obtain direct comparisons of the influence of these salts (each under its own optimal conditions) on the activity of the enzyme. The salts studied were the chlorides of sodium, potassium and lithium and the bromide, nitrate, chlorate, sulfocyanate, fluoride, sulfate and phosphate of sodium. Mixtures of sodium chloride with either sodium nitrate or sulfate were also studied.

Experimental

The results for the individual salts are summarized in Table I, and are given in terms of the effect of sodium chloride, taken as 100, because this salt was found to have the most favorable influence upon the enzyme.

TABLE I

COMPARISON OF THE ACTIVITY OF PANCREATIC AMYLASE IN THE PRESENCE OF VARIOUS NEUTRAL SALTS EACH AT ITS OPTIMAL HYDROGEN-ION ACTIVITY AND CONCENTRATION[a]

	Activity, compared to that obtained in the presence of 0.03 M NaCl		
Salt	Pancreatin, power 280	Purified preparation, power 940	Purified preparation, power 1130
Sodium chloride	100	100	100
Potassium chloride	100	100	100
Lithium chloride[b]	80–90	..	80–90
Sodium bromide	77	77	77
Sodium nitrate	41	40	40
Sodium chlorate	29	27	27
Sodium sulfocyanate	29	..	28
Sodium fluoride	24	..	21
Sodium sulfate	0	0	0
Sodium phosphate	0	0	0

[a] Mixtures of acid and alkaline sodium phosphates corresponding to a total concentration of **0.01** M phosphate were present in all cases.

[b] As described in the text the procedure was slightly different with this salt.

Because of the insolubility of lithium phosphate it was necessary to follow a different procedure in determining the influence of lithium chloride on the activity of pancreatic amylase than that followed with the other

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[1] We are greatly indebted to the Carnegie Institution of Washington for grants in aid of this investigation.

[2] Sherman, Caldwell and Adams, THIS JOURNAL, 50, 2529, 2535 (1928)

salts.[2] Sodium hydroxide, 0.01 *M*, was used instead of mixtures of sodium phosphate to adjust the solutions to different hydrogen-ion activities. It was not possible to measure experimentally the hydrogen-ion activities of these unbuffered, nearly neutral, solutions or to plan to reproduce any one of them exactly for use in comparisons. However, by planning parallel and overlapping determinations of enzymic activity, it was possible to eliminate the influence of hydrogen-ion activity and to obtain relative values for the optimal activity of the enzyme in the presence of different concentrations of lithium chloride, which were comparable with each other and with the optimal activity of the enzyme in the presence of sodium chloride. Thus 0.005, 0.02, 0.03 and 0.05 M lithium chloride solutions were studied and it was found that the optimal activity of the enzyme in the presence of 0.02 or 0.05 *M* lithium chloride was 80 to 90% of the optimal activity of the enzyme in the presence of sodium chloride. This was found to be true whether the hydrogen-ion activities of the sodium chloride solutions were adjusted with mixtures of sodium phosphates or with sodium hydroxide. This would indicate that the lower activity of the enzyme in the presence of lithium chloride was not due to the absence of phosphate in the case of lithium chloride.

From the results summarized in Table I, it would seem that, of the ions considered here, the anions are by far the most important in their influence upon this enzyme. Pancreatic amylase may be activated to the same extent by potassium or sodium chlorides but the concentration of potassium chloride necessary fully to activate pancreatic amylase is slightly greater than the concentration of sodium chloride needed. Lithium chloride activates pancreatic amylase but even when optimal concentrations are used the activity obtained is not equal to that obtained in the presence of either sodium or potassium chlorides. The cations, therefore, seem to have some slight influence.

Of the anions studied, chloride is the most efficient ion and the salts considered here may be placed in the following order in their influence on the hydrolysis of starch by pancreatic amylase: sodium and potassium chlorides, lithium chloride, sodium bromide, sodium nitrate, sodium chlorate and sodium sulfocyanate, sodium fluoride. The results obtained with the purified and the commercial enzyme preparations have been found to be similar throughout these experiments.

A Study of the Possible Interrelation of the Influence of Different Neutral Salts.—The next series of experiments was planned to study the influence on the activity of pancreatic amylase of the presence of more than one of these salts. The activity of the enzyme was measured in the presence of 0.02 *M* sodium chloride with additions of 0.01 to 0.20 *M* sodium nitrate or 0.01 to 0.10 M sodium sulfate. Direct comparisons of the activity of the enzyme in the presence of each combination of salts were made with the activity of the enzyme in the presence of 0.02 M sodium chloride alone. In these series of experiments 0.02 *M* sodium chloride solutions were used instead of 0.03 M as in the previous experiments in order to reduce the sodium chloride concentration to the minimum capable of producing complete activation of the enzyme. Each solution was adjusted to the hydrogen-ion activity previously found[2] to be most favorable under the conditions maintained in this investigation. The results are summarized in Table II and are given in terms of the effect of sodium chloride taken as 100.

TABLE II

INFLUENCE OF THE CONCENTRATION OF SODIUM SULFATE OR SODIUM NITRATE ON THE ACTIVITY OF PANCREATIC AMYLASE IN THE PRESENCE OF SODIUM CHLORIDE[a]

Concentration of sodium nitrate, *M*	Activity compared to that obtained in the presence of NaCl Purified preparation, power 1130	Pancreatin, power 280
0.01	91	92
.10	66	68
.20	55	54
Concentration of sodium sulfate, *M*		
0.01	100	100
.05	93	94
.10	90	92

[a] Mixtures of acid and alkaline sodium phosphates corresponding to a total concentration of 0.01 M phosphate were present in all cases.

From the data given in Table II it is seen that as the concentration of sodium nitrate or sulfate is increased the activity of pancreatic amylase decreases. The addition of sodium nitrate has a much more noticeable effect in decreasing the activity of the enzyme than additions of sodium sulfate. The activity of pancreatic amylase in the presence of 0.02 *M* sodium chloride is reduced by the addition of sodium nitrate even when the concentration of sodium nitrate present is much lower than the concentration of sodium chloride.

Possible Explanations of the Influence of Neutral Salts upon Enzymic Activity.—The results of these investigations show that there is some decided specific influence of these salts on the activity of pancreatic amylase but how this influence is exerted is not yet known.

Several previous investigators[3] have reported indications of a relation between the concentration of enzyme and the concentration of sodium chloride necessary to activate it. For this reason a series of experiments was carried out to see whether decreasing the concentration of enzyme to one-half that previously used would change the results obtained. A series of starch solutions containing graded concentrations of sodium

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[3] Starkenstein, *Biochem.* Z., 24, 210 (1910); 47, 300 (1912); Norris, *ibid.*, 7, 622 (1913).

chloride from 0.005 to 0.05 *M*, each adjusted to the optimal hydrogen-ion activity previously determined, were hydrolyzed in parallel using for every 100 cc. of 2% starch 0.03 instead of 0.06 mg. of the purified preparation which had a power of 1130. The optimal activity of the enzyme was found to occur in the presence of 0.02 to 0.05 *M* sodium chloride, iust as had been observed in the presence of the more concentrated enzyme solutions.

Other investigators[4,5] state that the concentration of starch influences the amount of salt that is essential. Experiments with 4% instead of 2% starch were therefore also carried out.

The optimal hydrogen-ion activity for the activity of pancreatic amylase in the presence of 4% starch solutions containing 0.01 to 0.05 M sodium chloride was first determined and was found to be PH 6.8 to 7.2, which is similar to the optimal PH 7.1 to 7.2 observed[2] for the enzyme in the presence of 2% starch. The concentration of sodium chloride permitting the optimal activity of pancreatic amylase was found to be 0.02 to 0.05 M, which is the same as that found for the enzyme in the presence of 2% starch.

These results do riot necessarily indicate that there is no relation between concentration of starch, enzyme and salt, because there is already present in 2% starch solutions a large excess of starch and further increase in the concentration of starch would not necessarily call for further increase in the concentration of sodium chloride. It is evident, however, that for the conditions regularly used in determining amylase activity in this Laboratory, solutions of 0.02 to 0.05 *M* sodium chloride and hydrogen-ion activities corresponding to PH 7.0 to 7.2 will permit optimal enzymic activity when the substrate is 2 to 4% starch and when the concentration of enzyme is such that the activity is within the limits usually maintained here, the formation of 100 to 240 mg. of maltose in thirty minutes at 40°.

There are several possible explanations of the influence of neutral salts on the activity of pancreatic amylase but the experimental evidence substantiating most of these expianations is not conclusive.

It is possible that the influence of neutral salts on the activity of pancreatic amylase may be due to some influence on the colloidal state of the enzyme. Sherman, Thomas and Caldwell[6] found that the isoelectric point of malt amylase coincides with the optimal hydrogen-ion activity for the enzymic activity of malt amylase. This would indicate that malt amylase is most active in a state in which it is least soluble and most readily salted out.

If the optimal hydrogen-ion activity and the isoelectric point also coin-

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[4] Kubel, *Pflüger's Arch.*, 76, 276 (1899).

[5] Ambard, Pellois and Bricka, *Bull. soc. chim. biol.*, 2, 42 (1920).

[6] Sherman, Thomas and Caldwell, THIS JOURNAL, 46, 1711 (1924).

cide for pancreatic amylase, as has been indicated,[7] it would be expected that those neutral salts which are most effective in precipitating it would have the most favorable influence on its activity. When the anions which have been considered in this investigation are arranged in the order of their favorable effect upon the hydrolysis of starch by pancreatic amylase, the following order results: chloride, bromide, nitrate, chlorate and sulfocyanate, fluoride. Except for sulfate, which was found to exert no influence on the activity of pancreatic amylase, this is the same order that has been observed in the influence of neutral salts on the precipitation of proteins and other neutral substances and the reverse of that obtained by Pfeiffer and Wurgler[8] on the influence of these anions on the solubility of amino acids. This salting out factor which depends upon the specific properties of the ions is generally observed in more concentrated solutions of salt than we are considering in this investigation. In the lower concentrations of salt with which we are concerned here, the influence exerted by different ions as determined by freezing point and solubility measurements depends upon the valence type of the salt. This does not seem to hold here as the activity of pancreatic amylase is very different in the presence of salts of the same valence type and appears to be uninfluenced by the divalent sulfate ion. Moreover, the cations do not seem to fall into the order expected if their influence is one of salting out the enzyme. The order of their favorable influence upon enzymic activity is sodium and potassium, lithium, instead of lithium, sodium, potassium.

This makes it seem probable that we are dealing with some specific reaction between the enzyme, and the salt or substrate, or both, rather than merely with an influence of salt on the total ionic strength and activity of the solution.

Summary

The influence of sodium, potassium and lithium chlorides and of the bromide, fluoride, nitrate, chlorate, sulfocyanate and sulfate of sodium upon the activity of pancreatic amylase has been quantitatively investigated and compared.

The influence of neutral salts on the activity of pancreatic amylase was found to be the same for the purified preparations of the enzyme and for commercial pancreatin and seems therefore, to he a property of the enzyme itself rather than of any impurities that may be present.

The salts which are less favorable to the activity of pancreatic amylase are required in higher concentration and in turn exert their most favorable influence in solutions of higher hydrogen-ion activities than do those salts which are more efficient activators.

The activity of pancreatic amylase in the presence of two anions which

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[7] Sherman, Caldwell and Adams, THIS JOURNAL, 48,2947 (1926).

[8] Pfeiffer and Wurgler, *Z. Physiol*, 97, 128 (1916).

exert a specific influence on its activity, such as the nitrate and chloride ions, is intermediate between the activity of the enzyme in the presence of each taken separately. The activity of the enzyme in the presence of such a mixture of salts is dependent on the relative concentrations of the ions. Anions which alone do not influence the activity of the enzyme seem to have comparatively small influence on the activity of the enzyme in the presence of anions which exert a decidedly specific influence.

Reducing the concentration of enzyme by one-half or using 4% instead of 2% starch does not appreciably influence the concentration of sodium chloride necessary for complete activation of the enzyme or the optimal hydrogen-ion activity.

The presence of neutral salt is essential to the activity of pancreatic amylase. The influence exerted by different salts appears to be very specific.

The anion is far more influential than the cation, although the latter seems to have some slight influence on the activity of the enzyme.

Of the ions studied, chloride is the most efficient ion and the salts may be placed in the following order in their influence on the hydrolysis of starch by pancreatic amylase: sodium and potassium chlorides, lithium chloride, sodium bromide, sodium nitrate, sodium chlorate and sodium sulfocyanate, sodium fluoride. Sodium sulfate and phosphate were found to be without influence on the activity of pancreatic amylase.

A consideration of the influence of the different anions on the activity of pancreatic amylase indicates that these have specific effects on the enzyme or substrate.

NEW YORK CITY

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

THE MECHANISM OF CARBOHYDRATE OXIDATION. X. (a) THE ACTION OF POTASSIUM HYDROXIDE ON MANNOSE. (b) A COMPARISON WITH THAT OF GLUCOSE AND FRUCTOSE

BY WILLIAM LLOYD EVANS AND DAVID CHARLES O'DONNELL[1]

RECEIVED JUNE 29, 1928 PUBLISHED SEPTEMBER 5, 1928

It has been shown[2] that glucose, fructose, mannose and galactose may be oxidized with alkaline potassium permanganate solutions into carbon dioxide, oxalic acid and small amounts of acetic acid. At lower alkali normalities and at a temperature of 25°, it was observed that the oxalic acid–carbon dioxide ratios obtained from both glucose and galactose were not of the same value. However, as the normality of the alkali was in-

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[1] Read at the Detroit Meeting of the American Chemical Society, September 6, 1927.

[2] (a) Evans and co-workers, THIS JOURNAL, 47, 3085 (1925); (b) Evans and Buehler, *ibid*, 47, 3008 (1925)

creased in both cases, there seemed to be a tendency for the amounts of oxalic acid and carbon dioxide derived from these two carbohydrates to become more nearly the same. As the temperature of these oxidations was increased, this tendency toward identical yields became so marked that at 75° it was found that the amounts of these reaction products were practically the same. In the case of glucose, mannose and fructose at 50°, and at the lower alkali normalities, there were observable differences in the oxalic acid-carbon dioxide ratios, but these differences tended to disappear in the region of higher alkali normalities. At 75°, the yields of reaction products from glucose, fructose and galactose were practically the same. It has been suggested that alkaline solutions of the carbohydrates contain equilibrated systems which are easily influenced by a change in these experimental factors—a condition which ought to give rise to the differences observed in the amounts of the reaction products obtained in these oxidations.

By reason of this suggestion, it has become of much interest to study the behavior of these carbohydrates toward aqueous solutions of potassium hydroxide of various concentrations and at different temperatures for the purpose of observing whether the same general tendencies observed in the presence of oxidizing agents would also be observed in their absence. The general methods employed in this phase of the problem have been given in much detail in previous papers from this Laboratory. Because the earlier results on glucose and galactose and the more recent ones on fructose[3] have been reported, the two principal purposes in this study were these: *(a)* to learn if the behavior of mannose toward changes in alkali concentration and temperature were the same as those to be expected on the basis of the above suggestion; *(b)* to make a comparative summary of the results obtained by us and other workers[4] in this Laboratory to see if, by reason of the structural relations, certain predicted similarities in the behavior of the mannose–glucose–fructose group of hexose sugars could be detected.

Experimental Part

Chemicals.—The same precautions were taken with reference to the degree of purity of all reagents and chemicals used throughout this work as were observed in the previously reported experiments in this series of carbohydrate studies.'

Treatment of Mannose with Potassium Hydroxide.—The procedure adopted in the treatment of mannose with aqueous solutions of potassium hydroxide of appropriate normality was exactly the same as that used by Evans and Hass[5] in their work on glyceric aldehyde.

The amount of hexose sugar used in each experiment was 2.25 g. This was dissolved in 25 cc. of potassium hydroxide solution of the desired normality.

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[3] Evans and Hutchman, THIS JOURNAL, 50, 1496 (1928).

[4] Evans, Edgar and Hoff, *ibid.*, 48, 2665 (1926).

[5] Evans and Hass, ibid., 48,2703 (1926).

Determination of Formic, Acetic and Lactic Acids.—Formic, acetic and lactic acids were identified and determined by methods previously described. By reason of some later work on fructose, we redetermined the amount of lactic acid obtained from glucose and potassium hydroxide solutions.

Determination of Pyruvic Aldehyde Osazone.—Owing to the fact that mannose differs from the sugars previously studied in this series, in that it forms an insoluble phenylhydrazone, the method for determining the amounts of pyruvic aldehyde osazone had to be modified as follows. The general procedure used in the case of fructose by Evans and Hutchman[3] was followed in every detail in our experiments with both mannose and glucose. It was found necessary to separate the pyruvic aldehyde osazone from the insoluble mannose phenylhydrazone by treating the mixture with acetone, a reagent in which the pyruvic aldehyde osazone was found to be completely soluble. The acetone solution was evaporated to dryness, the residue being washed with 30% alcohol, dried in a vacuum oven at 65° and then weighed. The osazone thus obtained was identified by its melting point (144–146°) and by the color test with sulfuric acid, a reagent which causes it to give an olive green color, which changed into a slate blue and finally to a violet.

Qualitative Reactions.—The reaction mixtures were qualitatively examined at appropriate places during the progress of a given experiment for hydroxy acids, acetol and pyruvic acid.[4]

Our quantitative data have been expressed in the form of graphs.

Theoretical Part

Mannose and Potassium Hydroxide.—The views[2a,4] which have been used in the interpretation of the results obtained from the alkaline oxidation of certain carbohydrates and also those resulting from the behavior of aqueous solutions of potassium hydroxide toward these same sugars are summarized at this point. (a) The classical experiments of Lobry de Bruyn and Alberda van Ekenstein[6] show that mannose, as well as either glucose or fructose, gives rise to an equilibrated system which may be represented by the following

$$d\text{-Mannose} \rightleftarrows d\text{-Glucose} \rightleftarrows d\text{-Fructose} \rightleftarrows d\text{-Pseudo-fructose} \rightleftarrows d\text{-}\alpha\text{-Glucose} \rightleftarrows d\text{-}\beta\text{-Glucose}$$

The equilibria arising from the use of each of these three sugars taken individually are not quantitatively identical.[6,7] (b) Through an elaboration of the views of Wohl and Neuberg,[8] and Fischer,[9] Nef[10] concluded from the results of oxidation experiments that mannose would yield a system of enediols in alkaline solutions which he represented by the following reaction.

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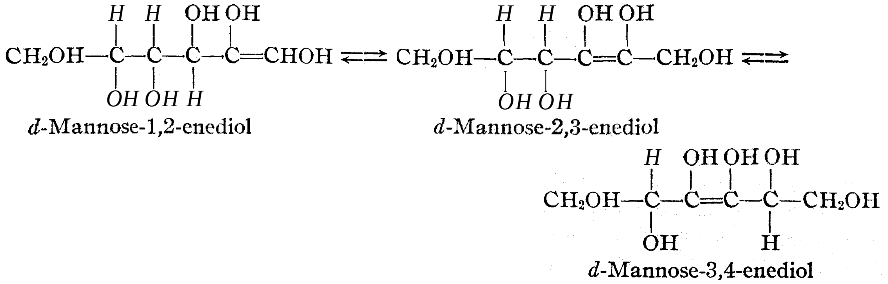
[6] de Bruyn and van Ekenstein, (a) *Rec. trav. chim.*, 14, 164 (1895); (b) 14, 203, 214 (1895); (c) 16,257 (1896); (d) compare Nef, *Ann.*, 403,239, note (1914).

[7] Powell, J. *Chem. Soc.*, 107, 1335 (1915).

[8] Wohl and Neuberg, *Ber.*, 33, 3099 (1900).

[9] Fischer, *Ber.*, 28, 1149 (1895)

[10] Nef, *Ann.*, 403,208–213 (1914).



$$CH_2OH-\underset{OH}{\overset{H}{C}}-\underset{OH}{\overset{H}{C}}-\underset{H}{\overset{OH}{C}}-\overset{OH}{C}=CHOH \rightleftarrows CH_2OH-\underset{OH}{\overset{H}{C}}-\underset{OH}{\overset{H}{C}}-\overset{OH}{C}=\overset{OH}{C}-CH_2OH \rightleftarrows$$

d-Mannose-1,2-enediol *d*-Mannose-2,3-enediol

$$CH_2OH-\underset{OH}{\overset{H}{C}}-\overset{OH}{C}=\overset{OH}{C}-\underset{H}{\overset{OH}{C}}-CH_2OH$$

d-Mannose-3,4-enediol

It is clear that glucose and fructose should also yield the same enediols as does mannose. When these enediols are ruptured at their respective double bonds, the resulting systems will still be qualitatively identical. The fission products of such an action will give rise to an extension of the above system through the formation of other enediols containing a smaller number of carbon atoms. In the presence of appropriate oxidizing agents, these bivalent carbon atom intermediates will be oxidized to their respective acids. Therefore, it follows that the alkaline oxidation of mannose, glucose and fructose should yield products which are *qualitatively* the same but not necessarily *quantitatively* so. This point of view is supported by the literature in this field of investigation. (*c*) In offering an explanation for the quantitative differences observed in the oxidation of these well-known carbohydrates in alkaline potassium permanganate solutions, the suggestion was made that these reactions are best understood when it is assumed that a more general equilibrium, consisting of reactions (a) and (b), is present in the alkaline solutions of these sugars. Changes in the experimental factors, such as concentration of alkali and temperature, should give rise to changes in an equilibrium of this kind which, in the presence of oxidizing agents, would become evident through a variation in the *amounts* of the reaction products formed. Furthermore, it was pointed out that should these alkaline solutions give rise to irreversible equilibria, then it is probable that the speed of the slowest reaction in the series of changes taking place must be the factor that is influenced by the two experimental conditions, temperature and alkali concentration.

Mannose-1,2-enediol. Formic Acid.—When mannose-1,2-enediol is ruptured at the double bond, the active forms of formaldehyde and arabinose are produced. Formic acid should be found in alkaline solutions in which such an action takes place. Our results are shown in Fig. 1. It is obvious that the amounts of formic acid are a function of the alkali normality and the temperature employed. This behavior of mannose is in complete accord with that of glucose and fructose when these carbohydrates are studied under exactly the same experimental conditions. Upson[11]

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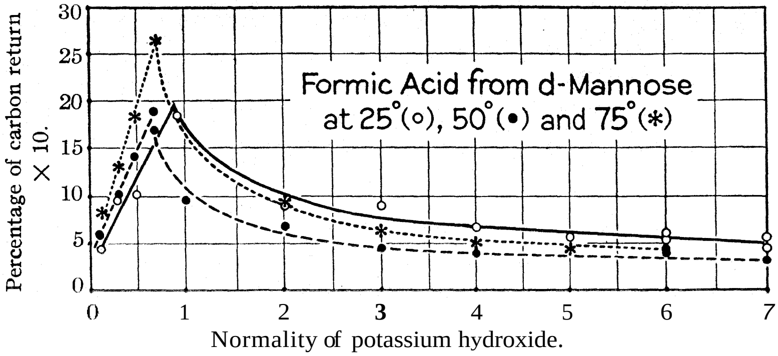
[11] (a) Power and Upson, THIS JOURNAL, 48, 195 (1926); (b) Jensen and Upson, *ibid.*, 47, 3019 (1925).

and his collaborators found that formic acid is a product of the oxidation of glucose in the presence of calcium hydxoxide and also when Soldiani's reagent is used. These investigators also isolated the arabonic derivatives in each case. Gustus and Lewis[12] have shown that 2,3,4,6-tetramethyl-d-glucose yields formic acid when it is oxidized with alkaline hydrogen peroxide solutions. There are many similar cases in the literature.[13]

Mannose-3,4-enediol. (a) Pyruvic Aldehyde.—(I) When one molecule of the 3,4-enediol common to mannose, glucose and fructose is ruptured at its double bond, two molecules of the active form of glyceric adehyde are produced. In the absence of oxidizing agents, the glyceric aldehyde so formed will then give rise to the equilibrated system represented by the following reaction.



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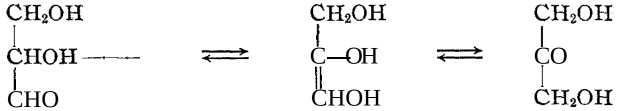

$$\begin{matrix} CH_2OH \\ | \\ CHOH \\ | \\ CHO \end{matrix} \rightleftharpoons \begin{matrix} CH_2OH \\ | \\ C{-}OH \\ \| \\ CHOH \end{matrix} \rightleftharpoons \begin{matrix} CH_2OH \\ | \\ CO \\ | \\ CH_2OH \end{matrix}$$

Glyceric aldehyde Triose enediol Dihydroxy-acetone

It has been shown previously that pyruvic aldehyde is formed when glyceric aldehyde and dihydroxy-acetone are treated with aqueous solutions of potassium hydroxide. The amounts of the aldehyde thus formed are a function of the alkali concentration, the temperature and the speed with which it is converted into lactic acid. If glyceric aldehyde is present as a fission product in alkaline solutions of mannose and glucose, then it follows that these two carbohydrates should also give rise to pyruvic aldehyde whose amounts would be dependent upon the same factors as those

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[12] Gustus with Lewis, THIS JOURNAL, **49,** 1512 (1927).

[13] (a) Cross, Bevan and Smith, J. *Chem. Soc.,* **73, 463** (1898); (b) Meisenheimer, *Ber., 41, 1009* (1908); (c) McLeod, *Am. Chem. J.,* **37,** 20 (1907); (d) Anderson, *ibid.,* **42,** 401 (1909); (e) Spoehr, *ibid.,* **43,** 227 (1910); (f) Glattfeld, *ibid.,* **50,** 163 (1913).

observed when the aldehyde is obtained from either glyceric aldehyde or dihydroxy-acetone. This was found to be the case. Our results are shown in Figs. 2 and 3. (II) According to the demands of the theory, alkaline solutions of all the hexose sugars should show exactly the same qualitative behavior as that of the trioses in this respect because the active form of glyceric aldehyde is a fission product of the 3,4-enediol, a tautomer which is common to all of this series of carbohydrates. In addition to the pyruvic aldehyde data which we have obtained from mannose and glucose in these experiments, we have assembled for the purposes of comparative study all similar data obtained in this Laboratory that have a

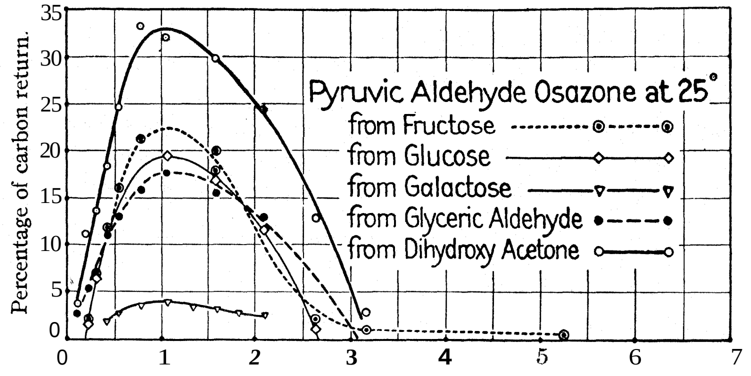


Fig. 2.

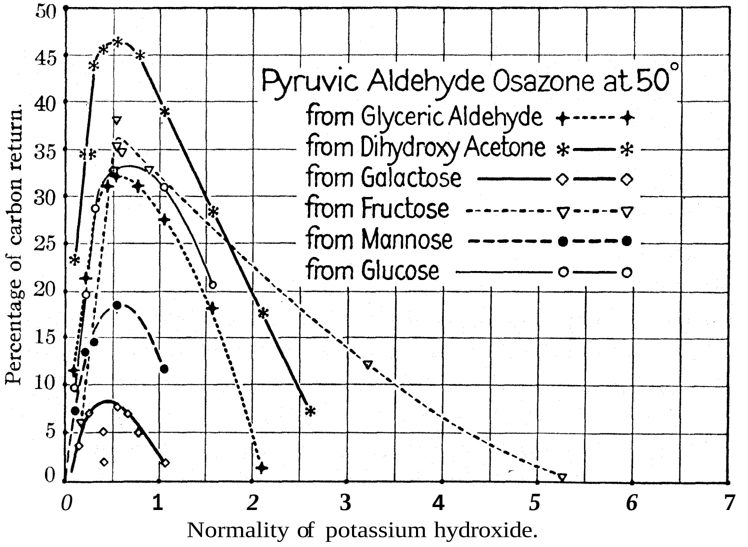


Fig. 3.

bearing on this point in carbohydrate chemistry, It has been shown previously that alkaline solutions of fructose and galactose, during a period of forty-eight hours as well as glucose for ninety-six hours, give rise to the formation of pyruvic aldehyde. (111) Owing to the fact that glucose. mannose and fructose do not form identical equilibria at the temperatures used, it was to have been expected that the yields of pyruvic aldehyde osazone from this series of sugars should not be the same. It does not follow from this fact, however, that there may not be experimental conditions under which this might not be true. At the only temperature beyond 50°, namely, 75°, at which work on this point has been carried out, it has been found that tarry materials seriously interfere with the demands of precise work. From the data in Figs. 2 and 3, it is seen that the maximum yields of pyruvic aldehyde osazone derived from the glucose, fructose and mannose at 25° (except mannose) and 50°, occur at approximately 1.0 *N* and 0.50 N alkali, respectively. This is also true for galactose. It is a very significant fact that both glyceric aldehyde and dihydroxy-acetone also yield their maximum return of pyruvic aldehyde osazone at these two temperatures and at practically the same alkali normality as do these hexose sugars—an observation which seems to us to be most convincing evidence for the theoretical views expressed above to the effect that the hexose carbohydrates in alkaline solutions of appropriate

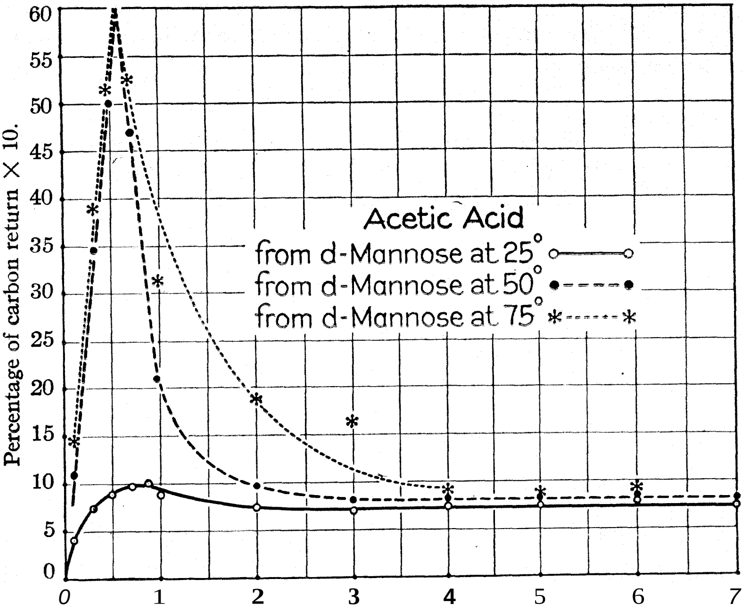


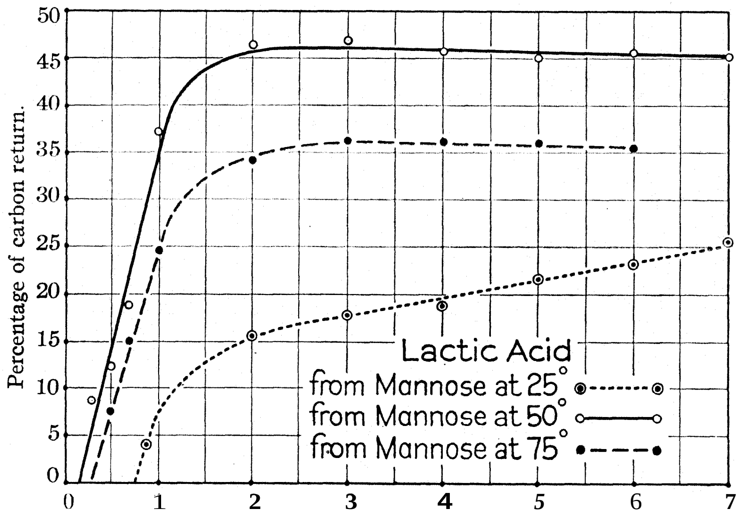
Fig. 4.'

normality will give rise to glyceric aldehyde as an intermediate compound in the formation of pyruvic aldehyde, which, in turn, is converted into lactic acid. Although we had no other hexose sugars at our disposal, it may be safely predicted that the other carbohydrates of this series will also show the same behavior. (Dr. D. C. O'Donnell and Karl B. Nordstroni of this Laboratory are at present studying the pentose sugars from this point of view.)

(b) Acetic Acid.—In previous papers it was pointed out that the acetic acid and a portion of the formic acid obtained from the carbohydrates thus far studied must arise from the action of the potassium hydroxide on the dissociation products of pyruvic aldehyde shown in the following reaction

$$CH_3COCHO \longrightarrow CH_3CHO + CO$$

The results obtained with mannose (Fig. 4) are of the same general character as those obtained previously with glucose and fructose.



Normality of potassium hydroxide.

Fig. 5.

(c) Lactic Acid.—In the action of aqueous solutions of potassium hydroxide on mannose, as well as its action on fructose and glucose, it has been observed that a maximum point of production was found for both acetic and formic acids. As previously pointed out,[4] this must be due to the fact that pyruvic aldehyde at that alkali normality and temperature is rearranging to lactic acid with the same speed that it is dissociating after the manner of the above equation. When the speed of rearrangement of the aldehyde to lactic acid becomes greater with the increased alkali normality, the yields of acetic and formic acids should decrease accordingly and that of the lactic acid should increase. Our results on lactic acid from mannose and glucose are shown in Figs. 5 and 6, respectively. They are essentially of the same general character as those obtained

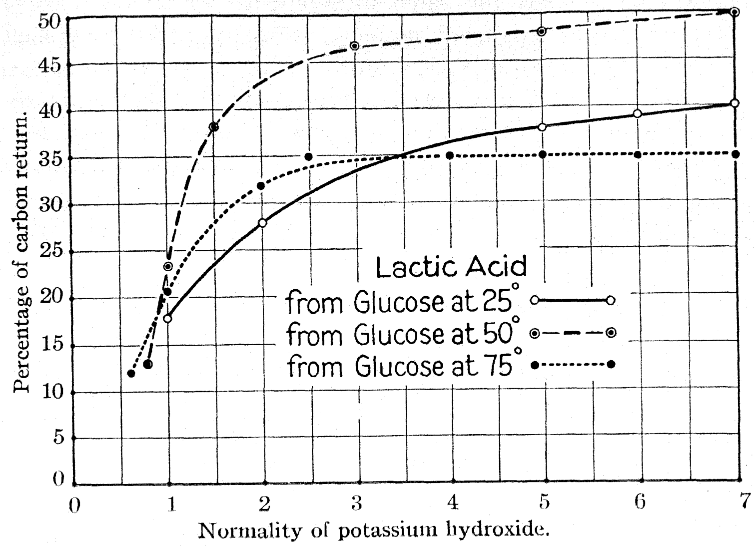


Fig. 6.

previously with fructose. In all three cases the amounts of lactic acid obtained at 75° are less than those obtained at 50°, a fact which is probably due to the pronounced tar formation at the higher temperature. In

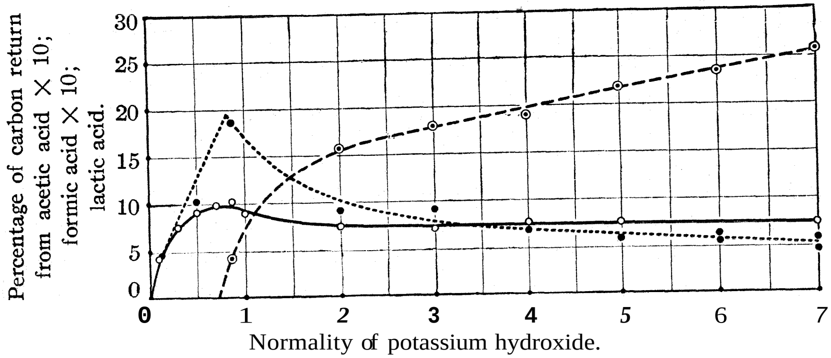


Fig. 7.—Production relation of acetic acid, ○; formic acid, ●; and lactic acid, ⊙ from mannose at 25°.

this connection it should be noted that we did not examine these tars for the presence of saccharinic acids.

In the pyruvic aldehyde osazone curves (Figs. 2 and 3), the maximum yield in each case is regarded as the point at which the velocity of rearrangement of pyruvic aldehyde to lactic acid is just equal to that of the osazone formation at that temperature and alkali concentration. According to the explanation given above for the sources of pyruvic aldehyde, acetic, formic and lactic acids, the same interdependence should exist in the yields of these compounds from mannose as was observed previously with fructose.[3] This is shown in Figs. 7 and 8. For the purposes of this comparative study we have assembled in Figs. 9 and 10 our lactic acid and pyruvic aldehyde osazone results from glucose and also those for acetic and formic acids obtained by Evans, Edgar and Hoff from the same carbohydrate. It is thus seen that this same interdependence is found in this sugar also. The fact that this same interdependence which is common to mannose, glucose and fructose is also present in the trioses, seems to us most convincing evidence for the point of view expressed above with reference to the important role played by pyruvic aldehyde when these three carbohydrates are acted upon with aqueous solutions of potassium hydroxide. It may be safely predicted that all the hexose sugars will show this important interdependence in the yields of pyruvic aldehyde, lactic, acetic and formic acids.

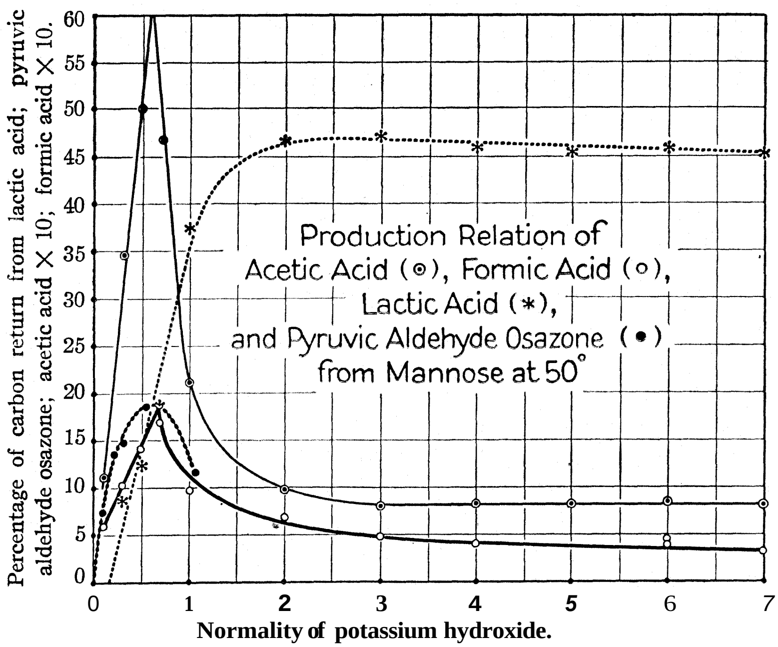


Fig. 8.

Influence of Alkali Concentration and Temperature on Mannose, Glucose and Fructose.—It has been shown that the temperature and the alkali concentration exercise a marked effect on the products obtained in the oxidation of these carbohydrates with potassium permanganate. The quantitative differences observed at the lower alkali normalities and at the lower temperatures have been attributed to the fact that these three sugars taken individually do not give rise to identical equilibria. However, in the alkaline oxidation of fructose and glucose with potassium permanganate at 75°, it was found that the amounts of oxalic acid and carbon dioxide obtained from these two carbohydrates were practically the same. This must have been due to the fact that both experimental factors, the alkali concentration and the temperature (or some temperature between that and 50°) influenced the general equilibrium in each case to

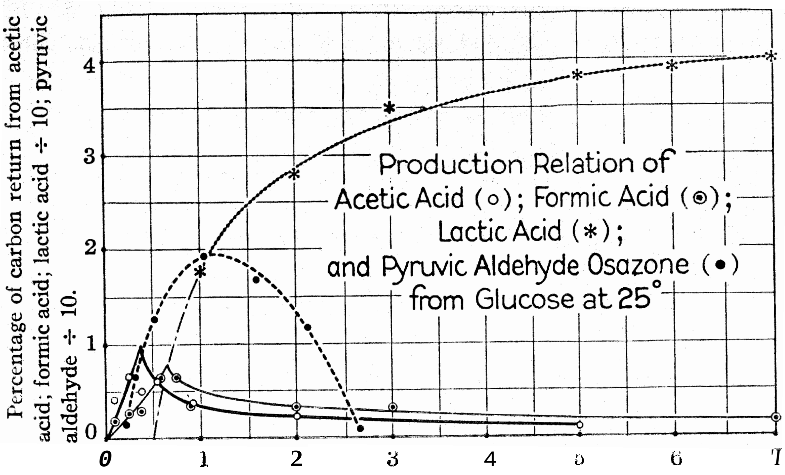
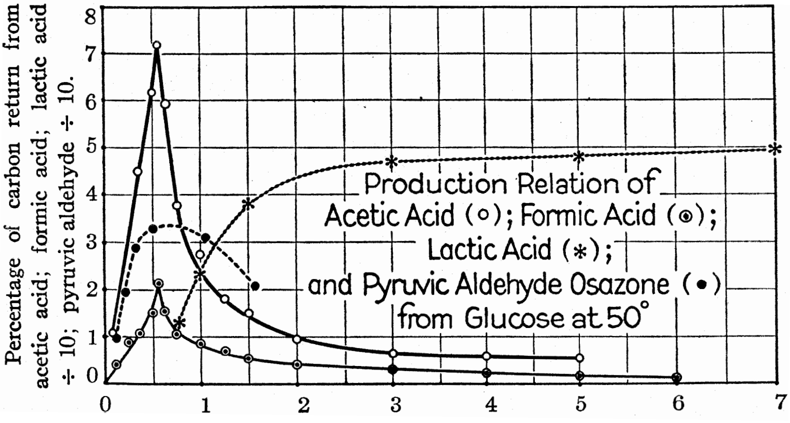


Fig. 9.



Pig. 10.

such an extent that the resulting solutions had become practically identical both qualitatively and quantitatively. If this is so, then the amounts of lactic acid obtained by the action of alkalies, in the absence of potassium permanganate, on mannose, glucose and fructose should also be the same in each case. In Fig. 11 we have shown that within the limits of experimental error this is true. In this connection it is of much interest to note that Nef[14] obtained closely agreeing results when he oxidized mannose, glucose and fructose with copper hydroxide in the presence of sodium hydroxide, a fact which undoubtedly depended on the close relationship existing between the equilibria in the alkaline solution of each of these carbohydrates. In a recent study of the methods for determining the copper number of glucose, Amick[15] came to the important conclusion that the amount of oxidation is dependent on the alkalinity of the solution.

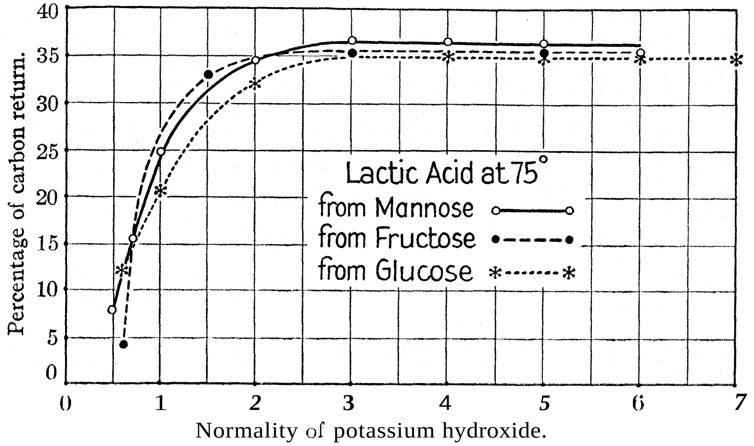


Fig. 11.

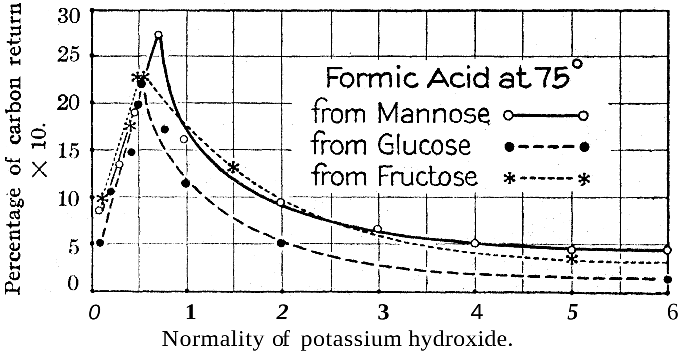


Fig. 12.

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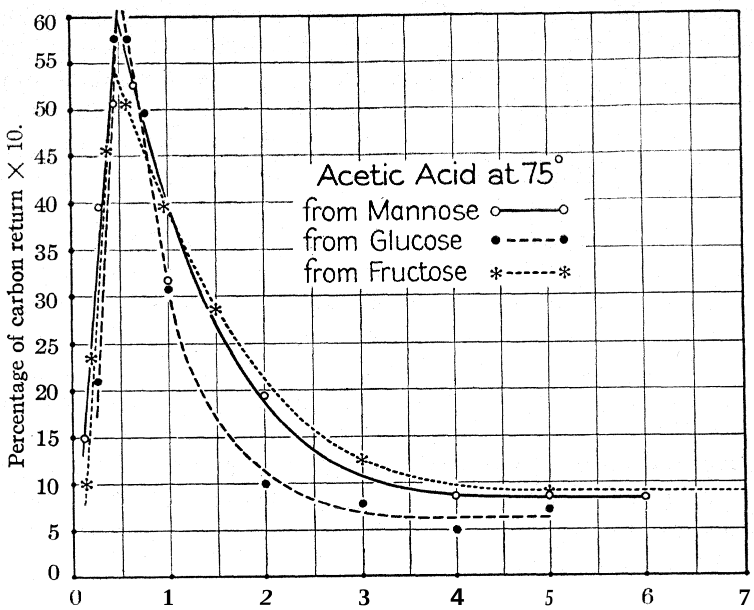
[14] Nef, *Ann.*, 357, 271, 277, 282 (1907).

[15] Amick, *J. Phys Chem* , **31**, 1476 (1927).

Finally, the yields of formic and acetic acids obtained from these three sugars at 75° are shown in Figs. 12 and 13 to be practically the same. Since the amounts of these two acids are relatively small, it has been necessary to multiply our results by 10 in order to show this point. This has magnified the experimental errors of our quantitative methods, which already in themselves have inherent errors. However, the comparison of the data for these two acids at 75° seems to be in complete harmony with the views set forth above with reference to the general condition of the equilibrium existing in alkaline solutions of these three well-known carbohydrates. On the basis of one of the statements above, it may be safely assumed that the relationship of the yields of acetic and formic acids obtained from the other hexose sugars will be approximately the same as that shown here for the mannose–glucose–fructose group.[16]



Normality of potassium hydroxide.

Fig. 13.

Summary

1. The action of aqueous solutions of potassium hydroxide of various concentrations on mannose was studied at 25, 50 and 75° in order to ascertain whether this hexose, like fructose and glucose, reacts in accordance with the suggestion that the alkaline solutions of these well-known carbohydrates contain an equilibrated system which can be disturbed by changes in the experimental conditions, temperature and alkali normality.

[16] Ref. 4, p 2672-2673.

2. The reaction mixtures were examined quantitatively for pyruvic aldelyde, lactic, acetic and formic acids. Changes in temperature and alkali concentration produced changes in the yields of these compounds which were of the same general character as those obtained under exactly the same conditions from fructose and glucose.

3. The interdependence of the reactions producing pyruvic aldehyde, lactic, acetic and formic acids in alkaline solutions of glyceric aldehyde and dihydroxy-acetone is also found to exist between the reactions producing these same products when they are obtained from alkaline solutions of mannose, glucose and fructose under the same experimental conditions. This fact is regarded as evidence for the assumption that the formation of glyceric aldehyde, a fission product of 3,4-hexose enediols, is an intermediate step in the production of these compounds from the hexose sugars. It is predicted that this interdependence will be found to exist in the products of the interaction of aqueous solutions of potassium hydroxide and of all those hexose sugars which are not available for laboratory experimentation at the present time,

4. At the lower temperatures and the lower alkali normalities, the amounts of reaction products obtained from mannose, glucose and fructose are not the same. This is understood on the ground that the equilibria formed in each individual case with the hexose and the alkali are not quantitatively identical.

5. At 75° the amounts of lactic, acetic and formic acids obtained from mannose, glucose and fructose are practically the same in each case. These facts seem to support the view that the equilibrated systems in the alkaline solutions of these hexose sugars are identical at this temperature.

COLUMBUS, OHIO

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE STATE UNIVERSITY OF IOWA]

NEW BROMINE SUBSTITUTION PRODUCTS OF VANILLIN AND SOME OF THEIR DERIVATIVES[1]

BY L. CHAS. RAIFORD AND W. C. STOESSER

RECEIVED JUNE 30, 1928 PUBLISHED SEPTEMBER 5, 1928

One purpose of this work was to complete the list of possible bromine substitution products of vanillin and to use these compounds in studying the effect of the ortho substituents of an aldehyde in its reaction with an amino compound. Kauffmann and Franck[2] were unable to convert 2-aminoresorcinoldimethyl ether into either a thiocarbanilide or a benzyli-

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[1] Condensed from a portion of the thesis submitted by W. C. Stoesser to the faculty of the Graduate College of the State University of Iowa in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Kauffmann and Franck, Brr , 40,3999 (1907)

dene derivative. Sachs and Appenzeller[3] failed to prepare both the oxime and the hydrazone from tetramethyl-2,4-diaminobenzaldehyde. In apparent opposition to this Blanksma[4] condensed 2,4,6-trinitrobenzaldehyde with aniline, but reported no yield, while Lowy and collaborators[5] obtained good yields of benzal derivatives from 2,4-dinitro- and 2,4,6-trinitrobenzaldehydes with various aromatic amines, though they studied no aldehyde containing a substituent other than the nitro radical.[6] These differences suggested further study of the question.

In previous reports[7] from this Laboratory one dibromo and two new monobromo compounds of vanillin were described. Each of these products was characterized by the preparation of several derivatives, especially those obtainable by reaction with amino compounds, but it was recognized that their activities as aldehydes should be studied further. In our previous work retardation due to the presence of ortho substituents was noted in a few cases only, though the work included no instance in which both ortho positions were substituted. It seemed necessary to test that point further because the work on record included too few radicals. Tabular summaries of the present work (see experimental part) will show that when only one ortho position is substituted the hindrance is not noticeable in the cases studied, and that when both are involved the retardation is less pronounced than might have been expected.

A second purpose in this study was to test further the extent to which substituents in the benzene nucleus may determine the positions taken by new groups. When Pschorr and Sumuleanu[8] nitrated acetylvanillin they obtained a 2-nitro derivative; later Raiford and Stoesser[7] found that bromination of the same starting material gives a 6-bromo compound exclusively, which shows that the acetoxy radical directs to the meta position, but to a different one in the instances cited, which suggests that the directive influence of this radical may depend on the specific character of the entering substituent. But in an unsymmetrical structure[9] like vanillin, it is not to be expected that positions 2 and 6 will be equally favored in substitution even by the same entering group. In fact, in a repetition of Pschorr and Sumuleanu's nitration, using a larger amount

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[3] Sachs and Appenzeller, *Ber.*, 41, 98 (1908).

[4] Blanksma, *Chem. Weekblad*, 9,865 (1912).

[5] Lowy and others, THIS JOURNAL, 43, 1961 (1921).

[6] The results of Meyer [*Z. physik. Chem.*, *24*, 219 (1897)], Fischer and Giebe [*Ber.*, 31, 546 (1898)] and Baly and Collie [*J. Chem. Soc.*, *87*, 1340 (1905)] tend to indicate that the effect of the nitro radical is not typical of the behavior of benzene substituents under the conditions of these experiments.

[7] (a) Raiford and Stoesser, THIS JOURNAL, 49, 1077 (1927); (b) Raiford and Hilman, *ibid.*, 49, 1571 (1927).

[8] Pschorr and Sumuleanu, *Ber.*, 32,3408 (1899).

[9] The directive influence of the acetoxy radical in symmetrical structures is being studied by Mr. McCormack in this Laboratory.

of starting material, it was found that if the total mass of acetylnitro product is hydrolyzed before an attempt is made to purify it, two compounds may be isolated: 80% of the 2-nitro derivative, m. p. 136°, described by the authors named, and about 5% of another mononitro product, m. p. 212°, which should be the 6-derivative.[10]

A third purpose in this study was to test further the observations of Brady and Dunn[11] that "no evidence of the existence of a second isomeride has been obtained in the case of any of the hydroxybenzaldoximes," but that "certain negative substituents in the benzene ring seem to favor the existence of two isomeric oximes." In the work described below one oxime, probably the *anti* form, was readily obtained from every bromine derivative of vanillin. Attempts to obtain the isomeride by Goldschmidt's[12] method caused the loss of the methyl radical and the formation of the oxime of the corresponding bromoprotocatechuic aldehyde.[13] Treatment of the available forms with gaseous hydrogen chloride for the purpose of transmutation[14] failed also.

Experimental Part

Derivatives of 6-Bromovanillin

Acetate[15] of the Oxime of 6-Bromovanillin.—Ten g. of the oxime[7a] was mixed with 20 cc. of acetic anhydride, allowed to remain for one hour with occasional stirring and the solid filtered off; yield, 98%. Repeated crystallization from benzene gave nearly colorless needles, m. p. 149–151°.[16]

Anal. Subs., 0.2248: 7.79 cc. of 0.1 *N* $AgNO_3$. Calcd. for $C_{10}H_{10}O_4NBr$: Br, 27.78. Found: 27.72.

The Oxime of Acetyl-6-bromovanillin.—A mixture of 5 g. of the acetyl derivative, 1.58 g. of hydroxylamine hydrochloride, an equal weight of sodium acetate and 15 cc. of alcohol was refluxed for half an hour. Addition of water precipitated a yield of 89%. Crystallization from alcohol gave colorless needles; m. p. 150–152°. A mixture of this and its isomer, just described, melted between 122 and 130°.

Anal. Subs., 0.2163: 7.43 cc. of 0.1 N $AgNO_3$. Calcd. for $C_{10}H_{10}O_4NBr$: Br, 27.78. Found: 27.48.

Acetate of the Oxime of Acetyl-6-bromovanillin.—Four g. of the acetyl derivative just described and 8 cc. of acetic anhydride were heated to the boiling point and allowed

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[10] The other one demanded by theory melts at 176° [Bentley, *Am. Chem. J.*, *24*, 173 (1900)] and was proved by Vogel [*Monatsh.*, *20*, 383 (1899)] to have the nitro radical in position 5.

[11] Brady and Dunn, *J. Chem. Soc.*, *105*, 824 (1914); *107*, 1859 (1915)

[12] Goldschmidt, *Ber.*, **16**, 2176 (1883).

[13] *Anal.* Subs., 0.2111: 9.15 cc. of 0.1 *N* $AgNO_3$. Calcd. for $C_7H_6O_3NBr$: Br, 34.48. Found: 34.68.

[14] Luxmore, *J. Chem. Soc.*, *69*, 181 (1896).

[15] The acetyl group has here replaced the hydrogen of the oxime radical.

[16] In about six months this had dropped to 140–141°, which accords with the observations of Janny [*Ber.*, *15*, 2782 (1882)], Gabriel [*Ber.*, 16, 520 (1883)] and Holleman, [*Rec. trav. chim.*, 13, 429 (1894)].

to cool and crystallize. Removal of the solid and treatment of the filtrate with water gave additional product; total yield, **87%.** Recrystallization from alcohol gave colorless diamond-shaped plates; m. p. 153–154". This product was also obtained by warming a mixture of the acetate of the oxime, acetic anhydride and one drop of sulfuric acid until all was dissolved and allowing it to crystallize.

Anal. Subs., **0.2399: 7.25** cc. of **0.1** *N* $AgNO_3$. Calcd. for $C_{12}H_{12}O_5NBr$: Br, 24.24. Found: **24.18.**

3-Methoxy-4-acetoxy-6-bromobenzonitrile.—This was obtained in nearly quantitative yield by boiling **5** g. of the acetate of the oxime with 10 cc. of acetic anhydride for an hour and then adding water. Repeated crystallization from alcohol gave nearly colorless masses that appeared like cotton; m. p. 148–149°.

Anal. Subs ,0 2044: AgBr,0 1422. Calcd for $C_{10}H_8O_3NBr$: Br, 29.63. Found: 29.60.

6-Bromovanillic Acid.—Ten g. of the above-described nitrite and 100 cc. of 6 *N* potassium hydroxide solution were refluxed for three and one-half hours and then acidified with hydrochloric acid; yield, 98%. Repeated crystallization from dilute alcohol gave irregular masses that, after drying at 110°, melted at **190–191°.**

Anal. Subs , 0.2101: AgBr, **0.1595.** Calcd. for $C_8H_7O_4Br$: Br, **32.39.** Found: 32.31.

Dibromo and Tribromovanillin Derivatives

Nitration of **Acetylvanillin.**—One hundred g. of acetylvanillin was rapidly added to **400** g. of fuming nitric acid which was kept between 2 and 6°, and the clear red solution was poured into 1.5 liters of ice and water. **The** product separated as a green oil which solidified after a brief period. When this was hydrolyzed by boiling with potassium hydroxide solution, and the clear but very d&-colored liquid was poured into excess of concentrated hydrochloric acid, a mixture of two nitro compounds was precipitated. Extraction of the dry material with cold alcohol removed 2-nitrovanillin; m. p. 136°. Crystallization of the residue from acetic acid gave vellow plates of the isomeric 6-nitro derivative; m. p. 212°. The latter was analyzed.

Anal. Subs., 0.4834: **31.8** cc. of N_2 at 21° and **730** mm. Calcd. for $C_8H_7O_5N$: **N, 7.11.** Found: **7.3.**

Acetyl-2-nitro-5-bromovanillin—Ten g. of acetyl-5-bromovanillin[17] was added to **40** g. of fuming nitric acid, the mixture held between **25** and 30° and stirred until clear, and the solution then poured into ice and water. The oil which separated at first solidified after a short time; yield, 80%. It was repeatedly crystallized by treatment of its hot benzene solution with ligroin (b. p. 60–70°) and was obtained in nearly colorless granules that became yellow on exposure to light; m. p. **128".**

Anal. Subs, **0.4090, 0.2446: 17.5** cc. of N_2 at 25° and **729** mm.; AgBr, **0.1439.** Calcd. lor $C_{10}H_8O_6NBr$: N, **4.40;** Br, **25.16.** Found: N, **4.7,** Br, **25.04.**

2-Nitro-5-bromovanillin.—This was obtained by hydrolysis of the above-described acetyl derivative and also by bromination of 2-nitrovanillin. Sixty g. of the nitro compound and 1 g. of iodine were added to a solution of **16.5** cc. of bromine in **200** cc. of acetic acid, the mixture warmed until all was dissolved and allowed to stand overnight. When the solution was poured into water the bromine derivative was precipi-

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[17] This was obtained in 90% yield by slowly adding acetyl chloride to a cold 40% solution of 5-bromovanillin in pyridine, allowing the mixture to stand overnight and then pouring it into an excess of dilute sulfuric acid.

tated in 95% yield. Crystallization from benzene gave nearly colorless prisms, m. p. 150–151°.

Anal. Subs., 0.2326: 8.39 cc. of 0.1 *N* $AgNO_3$. Calcd. for $C_8H_6O_5NBr$: Br, 28.99. Found: 28.86.

2-Amino-5-bromovanillin.—Ferrous hydroxide was prepared by treatment of a solution of 300 g. of ferrous sulfate in 1 liter of water with 400 cc. of concentrated ammonia water, and to this hot mixture was slowly added 35 g. of the above-described nitro compound. This was boiled for fifteen minutes, 600 cc. of boiling water was added and the mixture filtered hot. The residue was extracted with hot water and the combined filtrates acidified with dilute sulfuric acid, yield, 96.8%. Crystallization from dilute acetone gave long tan-colored needles; m. p. 139–140°.

Anal. Subs., 0.5598, 0.2498: 29 cc. of N_2 at 22" and 731 mm., 10.17 cc. of 0.1 N $AgNO_3$. Calcd. for $C_8H_8O_3NBr$: N, 5.69; Br, 32.52. Found: N, 5.8; Br, 32.57.

2,5-Dibromovanillin.—A smooth paste was made by mixing 33.1 g. of the above-described finely powdered amino compound, 60 cc. of constant boiling hydrobromic acid and 20 cc. of water. This was cooled below 0°, diazotized by adding 9.5 g. of sodium nitrite in small portions and then 15 g. of cuprous bromide in 60 cc. of hydrobromic acid was poured in. After heating on a water-bath for one and one-half hours, an equal volume of dilute hydrochloric acid (1:1) was added and the dibromo compound filtered out, yield, 79%. Crystallization from acetic acid gave colorless needles, m. p. 189°.

Anal. Subs., 0.2018: AgBr, 0.2454. Calcd. for $C_8H_6O_3Br_2$: Br, 51.61. Found: 51.75.

2,5-Dibromo-3-methoxy-4-acetoxybenzal Diacetate.—Ten g. of the dibromo compound just described was suspended in 20 cc. of acetic anhydride and one drop of concentrated sulfuric acid added. When all of the solid had dissolved, the liquid was warmed gently for about two minutes. Addition of water to decompose excess of anhydride precipitated the diacetate in 97% yield. Repeated crystallization from alcohol gave colorless plates, m. p. 157–158°. After drying at 120° it was analyzed for bromine.

Anal. Subs., 0 3046: 13.38 cc. of 0.1 *N* $AgNO_3$. Calcd. for $C_{14}H_{14}O_7Br_2$: Br, 35.24. Found: 35.14.

Hydrolysis of the diacetate with potassium hydroxide solution gave a 98% yield of 2,5-dibromovanillin.

Acetyl-2,5-dibromovanillin.—Ten g. of the dibromo compound, an equal weight of sodium bisulfite[18] and 20 cc. of acetic anhydride were mixed and warmed until the dibromovanillin had dissolved. The bisulfite appeared thus far to be unchanged. Fifty cc. of water was added, the mixture stirred and warmed until nearly all was in solution and then filtered hot. The bisulfite addition product that crystallized on cooling was removed, decomposed by sodium carbonate solution and the acetyl derivative separated; yield 74%. Recrystallization from alcohol gave colorless prisms; m. p. 68–70°.

Anal. Subs., 0.3962: 22.46 cc. of 0.1 N $AgNO_3$. Calcd. for $C_{10}H_8O_4Br_2$: Br, 45.46. Found: 45.35.

This dibromovanillin was further characterized by the study of the derivatives indicated in Table I.

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[18] Attempts to prepare the acetyl derivative by the usual methods failed to give a pure product. One of the impurities was the benzal diacetate described above. Its formation under the conditions was prevented by the bisulfite.

TABLE IA

DERIVATIVES OF 2,5-DIBROMOVANILLIN

No.	Compound	Solvent	Crystal form	Yield, %
1	*p*-Nitrophenylhydrazone	Dil. pyridine	Yellow needles	99
2	Semicarbazone[a]	Dil. acetic acid	Fine colorless needles	95
3	*bis*-Benzidine[b]	Pyridine	Bright orange granules	..
4	Oxime	Benzene	Nearly colorless needles	97
5	Acetate of oxime	...	Uncrystallizable	93
6	Acetate of acetyloxime	Ligroin (140–150)	Colorless needles	72
7	Acetoxynitrile	Dil. acetic acid	Colorless needles	90
8	Dibromovanillic acid	Acetic acid	Colorless needles	91

[a] Drying over potassium hydroxide under partial pressure at room temperature for several days caused loss of some acetic acid of crystallization. *Anal.* Subs., 0.2300: loss in wt. at 120°, 0.0376. Calcd for 2 moles of $C_2H_4O_2$: 24.64. Found: 16.35.

[b] Product changed color and lost pyridine of crystallization when heated at 120°, but the amount was not determined.

TABLE IB

DERIVATIVES OF 2,5-DIBROMOVANILLIN

No	Formula	M. p., °C.	Subs., g	Cc. of 0.1 *N* $AgNO_3$ or wt of AgBr	Halogen, % Calcd.	Halogen, % Found
1	$C_{14}H_{11}O_4N_3Br_2$	249"	0.2034	0.1717 g.	35.96	35.92
2	$C_9H_9O_3N_3Br_2$	233–234	.3085	16.91 cc.	43.60	43.85
3	$(C_{14}H_{10}O_2NBr_2)_2$	<350	.3089	16.16 cc.	41.67	41.85
4	$C_8H_7O_3NBr_2$	154–155	.1784	0.2071 g.	49.23	49.40
5	$C_{10}H_9O_4NBr_2$	184–185	.3299	18.05 cc.	43.60	43.77
6	$C_{12}H_{11}O_5NBr_2$	137–139	.4034	19.85 cc.	39.12	39.36
7	$C_{10}H_7O_3NBr_2$	89–90	.2996	17.20 cc.	45.85	45.93
8	$C_8H_6O_4Br_2$	179–180	.3376[b]	20.60 cc.	49.08	48.82

[a] After removal of pyridine of crystallization. **Anal.** Subs., 0.2099: loss in wt. at 120°, 0.0319. Calcd. for 1 mole of C_5H_5N: 15.08. Found: 15.20.

[b] After removal of acetic acid of crystallization. *Anal* Subs., 1.0023: loss in wt. at 120°, 0.1447 Calcd. for 1 mole of $C_2H_4O_2$: 15.54. Found: 14.44.

2-Nitro-6-bromovanillin.—Fifty g. of acetyl-6-bromovanillin[19] was gradually added with stirring to 200 g. of fuming nitric acid which was kept between 0 and 6°. When the clear red solution so obtained was poured into ice and water, the oil that separated became solid on standing, The product was heated with potassium hydroxide solution to remove the acetyl group and the free nitro compound was precipitated in 78% yield by the addition of hydrochloric acid. Repeated crystallization from dilute acetic acid gave cream-colored needles that melted at 168–170°, which seemed to be constant.

Anal. Subs, 0.5231: 18.81 cc. of 0.1 *N* $AgNO_3$. Calcd. for $C_8H_6O_5NBr$: Br, 28.99. Found: 28.77.

2-Amino-6-bromovanillin.—The above-described nitro compound was reduced by ferrous hydroxide as previously explained, except that an additional 50 cc. of concentrated ammonia water was added just before filtration. The amino compound was obtained in 94% yield. Recrystallization from alcohol gave yellow needles that shrink at 210° and melt at 217–218°.

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[19] Ref. 7a, p. 1079

Anal. Subs., **0.5205: 21.16 *cc.*** of 0.1 *N* $AgNO_3$. Calcd. for $C_8H_8O_3NBr$: Br, **32.52.** Found: **32.52.**

2,6-Dibromovanillin.—To a solution containing 30 cc of sulfuric acid and **10** cc. of water, 9.8 g. of the above-described amino compound was added and the mixture stirred into a smooth paste. Four g. of solid sodium nitrite was slowly added with continual stirring, while the temperature was kept between **10** and 15° by standing the container in a cooling bath. Five g. of ice was slowly added to the reaction mixture every fifteen minutes during one and one-fourth hours. This was then poured into a solution containing **9** g. of cuprous bromide in 50 cc. of constant boiling hydrobromic acid, the whole heated for some time on a water-bath, **100 cc.** of hydrochloric acid (1:1) added and the mixture filtered. The yield was **85%.** After purification by extraction with benzene, which left a small portion of insoluble material, repeated crystallization from dilute alcohol gave nearly colorless needles; m. p. **155–156°.** The substance was further identified by study of the derivatives indicated in Table II.

Anal. Subs., **0.3378:** 21.86 cc **of** 0 1 **N** $AgNO_3$. Calcd. for $C_8H_6O_3Br_2$: **Br, 51.61.** Found: **51.77**

TABLE IIA

DERIVATIVES OF 2,6-DIBROMOVANILLIN

No	Compound	Solvent	Crystal form	Yield, %
1	Oxime	Benzene	Colorless needles	73
2	*p*-Bromophenylhydrazone	Dil. acetic acid	Flesh-colored needles	56
3	Semicarbazone[a]	Acetic acid	Colorless needles	73
4	*bis*-Benzidine[b]	Pyridine	Yellowish-brown plates	**74**

[a] Drying under partial vacuum over potassium hydroxide for several hours probably caused loss of some acetic acid of crystallization. **Anal.** Subs., **0.3671:** loss in wt. at 120°, **0.0865.** Calcd. for **2** moles of $C_2H_4O_2$: **24.64.** Found: **23.56.**

[b] ***Anal.*** Subs., **0.4141:** loss in wt., **0.0718.** Calcd. for **2** moles of C_5H_5N: **17 06.** Found: **17.34.**

TABLE IIB

DERIVATIVES OF 2,6-DIBROMOVANILLIN

No	Formula	M p, °C.	Subs, g	0 1 *N* $AgNO_3$, cc	Halogen, % Calcd.	Halogen, % Found
1	$C_8H_7O_3NBr_2$	**144–145**	**0 3618**	**22.26**	**49.23**	**49.22**
2	$C_{14}H_{11}O_2N_2Br_3$	168–170	.3061	19.26	**50.10**	**50 34**
3	$C_9H_9O_3N_3Br_2$	**216–217"**	.2806	**15.32**	**43.60**	**43 68**
4	$(C_{14}H_{10}O_2NBr_2)_2$	238–239[b]	.3423	**17.87**	**41.67**	**41** 76

[a] After heating at 120° to remove acetic acid.

[b] After removal of pyridine of crvstallization

2,5,6-Tribromovanillin.—A mixture of **12** g. of 2,6-dibromovanillin, 4 ***g.*** of sodium acetate and 40 cc. of acetic acid was warmed until all was in solution, after which **2** 4 cc. of bromine was added and the liquid allowed to stand for a short time The red color disappeared almost immediately. When water was added a 95% yield of the tribromo compound was precipitated. Crystallization from acetic acid gave fine, colorless needles; m. p. 177–178°. The product was further characterized by the preparation of the derivatives indicated in Table III.

Anal. Subs, 0 3150 **24** 25 cc of 0.1 *N* $AgNO_3$. Calcd. for $C_8H_5O_3Br_3$: Br, 61 70. Found 61.59.

TABLE IIIA

DERIVATIVES OF 2,5,6-TRIBROMOVANILLIN

No	Compound	Solvent	Crystal form	Yield %
1	Oxime	*Iso*butyl alcohol	Small, nearly colorless needles	98
2	*p*-Bromophenylhydrazone	Acetic acid	Almost colorless needles	Quant.
3	Semicarbazone[a]	Dilute pyridine	Almost colorless needles	96
4	*bis*-Benzidine[b]	Pyridine	Brown granules	84

[a] Anal. Subs., 0.3274: loss in wt , 0 0489. Calcd. for 1 mole of C_5H_5N: 15.05. Found: 14 94.

[b] Anal. Subs , 0.3382. loss in wt., 0.0535. Calcd. for 2 moles of C_5H_5N: 14.58 Found: 15.82.

TABLE IIIB

DERIVATIVES OF 2,5,6-TRIBROMOVANILLIN

No	Formula	M. p , °C	Subs , g	0.1 *N* AgNO₃, cc	Halogen. % Calcd.	Halogen. % Found
1	$C_8H_6O_3NBr_3$	192	0 3164	23 45	69.41	59 29
2	$C_{14}H_{10}O_2N_2Br_4$	169 -170	.2953	21 20	57 85	67.43
3	$C_9H_8O_3N_3Br_3$	222–223[a]	.2785	18.83	53.81	54.09
4	$(C_{14}H_9O_2NBr_3)_2$	<330	2847	18.36	51.84	51.59

[a] After heating at 120° to remove pyridine.

Summary and Conclusions

1. Nitration of acetylvanillin as directed by Pschorr and Sumuleanu gives mainly the 2-nitro derivative described by them and a small portion of another nitro compound not hitherto recorded, which probably has the nitro group in Position 6.

3. The list of possible bromine substittition products of vanillin has been completed. Each new one has been characterized by the study of several derivatives.

3. In the reactions which involved the aldehyde radical, the presence of one ortho substituent caused no noticeable hindrance; when both these positions were substituted the yields of products were lower but the effect was less pronounced than expected.

4. The hydroxyl and acetoxyl radicals, respectively, as substituents in a benzene derivative may direct entering groups to different positions. This result may depend, in part, on the chemical character of the entering substituent.

5. In no case was there obtained more than one of the oximes demanded by theory. The one obtained, probably the anti form, could not be transmuted by hydrogen chloride, and an attempt to prepare the isomeride from the 6-bromo compound by the Goldschmidt method caused the loss of the methyl radical and the formation of the oxime of the corresponding protocatechuic aldehyde. Thus far the results agree with Brady and Dunn's observations.

6. Further work is in progress in this Laboratory.

IOWA CITY, IOWA

THE ACTION OF ACETYLENE ON ARYL HYDROCARBONS IN THE PRESENCE OF A MERCURY CATALYST. II

BY J. A. REILLY AND J. A. NIEUWLAND

RECEIVED JULY 5, 1928 PUBLISHED SEPTEMBER 5, 1928

The preparation of unsymmetrical diphenylethane and other hydrocarbons of the type $CH_3CH(C_6H_4R)_2$ from acetylene and the appropriate aryl hydrocarbons has already been described by Reichert and Nieuwland.[1] The same compounds had been obtained by Fischer[2] by the action of paraldehyde and concentrated sulfuric acid. Toluene, so treated, formed the ditolyl derivative where the methyl is supposed to be para to the ethylidene group. These were made in other ways by Anschütz[3] and Haiss.[4] The place of the entering ethylidene group with respect to the alkyl of the nucleus has never been definitely proved by any of the authors mentioned, although it has been assumed that it is in the para position. Condensation is brought about by passing acetylene into the hydrocarbon in the presence of sulfuric acid and mercuric oxide or mercuric sulfate when a reaction represented by the following equation takes place

$$CH{\equiv}CH + 2C_6H_5R \longrightarrow CH_3CH(C_6H_4R)_2$$

In the present paper this series of compounds has been extended by application of the above reaction to several benzene homologs and to other aryl hydrocarbons. Acetylene gives ethylidene hydrocarbons of the above type with normal and isopropylbenzenes, normal and tertiary butylbenzenes, methyl and ethylphenylmethane, methyl*iso*propylphenylmethane, and tetrahydronaphthalene.

Ethylidene-*bis-tert.*-butylbenzene is a white, crystalline solid. The other ethylidene compounds have the general properties of unsymmetrical diphenylethane. They are viscous, amber colored liquids of high boiling points and are better distilled under reduced pressure. They are non-volatile in steam.

Several multinuclear hydrocarbons were subjected to the action of acetylene but no reaction occurred with triphenylmethane, diphenyl, diphenylmethane or dibenzyl. There seemed to be some connection between the character of the substituents in the benzene ring and the facility with which acetylene reacts. Toluene gave a yield of over 40%; benzene somewhat less of the ethylidene compounds.[1] The xylenes, with practically the same molecular weight as ethylbenzene, gave very much higher yields than the latter, while mesitylene with three substitutions in the ring gave 18 to 20% yields and the propylbenzenes were

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[1] Reichert and Nieuwland, THIS JOURNAL, 45, 3090 (1923)

[2] Fischer, *Ber.*, 7, 119 (1874).

[3] Anschütz, Ann., 235, 215 (1886).

[4] Haiss, *Ber.*, 15, 1476 (1882).

found to give less than 10% yields. Of hydrocarbons having about the same molecular weight, the di- and trisubstituted ones reacted with greater ease, probably because of the greater compactness and symmetry of the resulting ethylidene compounds. The formation of ring diethylidene compounds was found to occur to a small extent with diphenylethane and ditolylethane giving dimethylanthracene hydride and tetramethylanthracene hydride. None of the hydrocarbons described here, which were all distilled under reduced pressure, was accompanied by such a product except tetrahydronaphthalene.

Naphthalene resembled most benzene derivatives with unsaturation in the side chain in that it did not react with acetylene. But if one of the rings is saturated as it is in tetrahydronaphthalene, condensation readily occurs, with the formation of ethylidene-*bis*-tetrahydronaphthalene. The tetrahydronaphthalene then showed the same behavior as would have been expected of a dialkyl benzene.

Experimental Part

Ethylidene-*bis*-*n*-propylbenzene was prepared from n-propylbenzene obtained by the Fittig reaction from propyl bromide and bromobenzene. Acetylene was passed into a mixture of 130 g. of n-propylbenzene, 25 g. of concentrated sulfuric acid and 5 g. of mercuric oxide, the mixture being kept below 10°. When three-fourths of the theoretical quantity of acetylene had been absorbed the contents of the flask was neutralized with sodium hydroxide solution and was steam distilled until all the unchanged propylbenzene had come off. The ethylidene compound was extracted with ether from the residue, a plastic, grayish brown solid. The ether was evaporated and the residue distilled under reduced pressure; b. p. 192–194" at 42 mm. Anal. Calcd.: C, 89.7; H, 10.27. Found: C, 89.9; H, 9.8.

The solid referred to above was isolated and dried. It is amorphous and insoluble in water and the common organic solvents. When heated

TABLE I

BOILING POINTS OF HYDROCARBONS

Hydrocarbon	B. p., °C.	Pressure, mm.
$CH_3CH(C_6H_4CH_2CH_2CH_3)_2$	192–194	42
$CH_3CH[C_6H_4CH(CH_3)_2]_2$	240–245	15
$CH_3CH(C_6H_4CH_2CH_2CH_3)_2$	244248	37
$CH_3CH[C_6H_4CH(CH_3)CH_2CH_3]_2$	250–252	11
$CH_3CH[C_6H_4C(CH_3)_3]_2$	212–214"	16
$CH_3CH[C_6H_4CH(C_2H_5)_2]_2$	234–236	29
$CH_3CH[C_6H_4CH(CH_3)CH(CH_3)_2]_2$[b]	225–228	13
$CH_3CH(C_{10}H_{12})_2$	261–263"	16

[a] M. p. 94°.

[b] *Anal.* Calcd.: C, 88.6; H, 11.42. Found: C, 87.7; H, 10.55.

[c] B. p. 384, atm. pressure by pyrometer and thermometer.

it decomposed without melting. It seemed, therefore, useless to examine it further for the present.

The other ethylidene compounds were prepared in a similar manner. Ethylidene-*bis-tert.*-butylbenzene was separated from the small amount of an oily impurity accompanying it in the distillate by solution with alcohol in which it was less soluble than the oil. It was recrystallized from 95% alcohol.

The boiling points of the new hydrocarbons prepared are given in the accompanying table.

Summary

1. Ethylidene hydrocarbons of the general formula $CH_3CH(C_6H_4R)_2$ have been prepared from acetylene in the presence of concentrated H_2SO_4 and HgO from the following benzene derivatives: propyl- and *iso*propylbenzenes, n-butylbenzene, *tert.*-butylbenzene, methylethylphenylmethane, methylisopropylphenylmethane, diethylphenylmethane. These are all viscous, amber colored liquids of high boiling points, excepting ethylidene-*bis-tert.*-butylbenzene which is a white crystalline solid.

2. Tetrahydronaphthalene gives with acetylene ethylidene-*bis*-tetrahydronaphthalene and also a six-ringed compound in small quantities.

3. Polynuclear hydrocarbons such, for example, as diphenyl, diphenylmethane, dibenzyl, triphenylmethane and naphthalene do not react with acetylene.

NOTRE DAME, INDIANA

[CONTRIBUTION FROM THE RESEARCH LABORATORIES, UNIVERSITY OF NOTRE DAME]

THE CATALYTIC CONDENSATION OF ACETYLENE WITH PHENOLS. II. RESORCINOL

BY S. AQUINAS FLOOD AND J. A. NIEUWLAND

RECEIVED JULY 5, 1928 PUBLISHED SEPTEMBER 5, 1928

Introduction

In 1923 Wenzke and Nieuwland[1] reported the condensation of acetylene with resorcinol in the presence of sulfuric acid and mercury salts. The product was not separated from the alcoholic reaction mixture until it had undergone a dehydration. This second reaction was induced by diluting with water, whereupon a fine yellow precipitate slowly formed. On oxidation with stannic chloride this precipitate yielded hydroxymethylfluorone (II), indicating that the yellow compound was dihydroxymethylxanthene **(IV).** It was thought desirable, however, to make a more complete study of the reaction in an attempt to secure the primary product in the pure state, and to discover if this reaction resembled other acetylene reactions in giving the same products as acetaldehyde.

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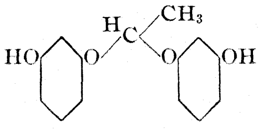
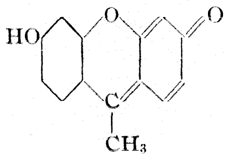
[1] Wenzke and Nieuwland, THIS JOURNAL, **46,** 179 (1924).

The literature on the reaction of acetaldehyde with resorcinol shows considerable difference of opinion. In 1894 Causse[2] reported the product as being the acetal of resorcinol (I), basing his conclusion largely on analysis and reaction of the diacetate. In the same year Möhlau and Koch[3] stated that resorcinol and aldehyde combined in different proportions at the same time—two moles of resorcinol to one of aldehyde, and two to two (one to one?). The oxidation of the first of these gave hydroxymethylfluorone (II), from which these investigators concluded that the aldehyde residue had been attached to nuclear carbons. Mohlau and Koch came to no conclusion regarding the constitution of the second resorcinol aldehyde compound.



I



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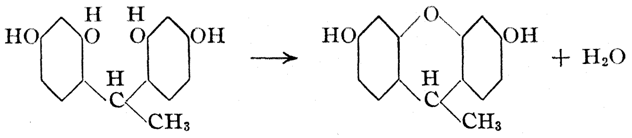

In 1900 Fosse and Ettlinger[4] attempted to make the acetal of resorcinol by the action of ethylidene chloride on the potassium salt of resorcinol. They found that while their product seemed to be identical with that of Causse, it could not be "saponified" with sulfuric acid as other acetals could be. They concluded that some rearrangement had taken place, that the ethylidene group had become attached to nuclear carbons and that elimination of water had taken place giving dihydroxymethylxanthene (IV). They likewise secured a crystalline acetate which gave practically the same analysis as that of Causse.

Comparison of the products as described and of the methods of procedure shows that while Mohlau and Koch secured a white, microscopically crystalline product from acetaldehyde and resorcinol in aqueous solution acidified with hydrochloric acid, Causse and Fosse and Ettlinger describe their products as being yellow, although the former did the aldehyde condensation in dilute sulfuric acid and the latter heated the ethylidine chloride, aqueous potassium hydroxide and resorcinol in a sealed tube,

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[2] Causse, *Ann. chim* , 1, 96 (1894).

[3] Möhlau and Koch, ***Ber.***, 27, 2891 (1894).

[4] Fosse and Ettlinger, *Bull soc. chim.*, **23**, 518 (1900)

Nieuwland[5] used ethyl alcohol acidified with sulfuric acid as a solvent for the resorcinol and aldehyde mixture, which on the addition of water slowly precipitated a yellow substance, identical with that obtained from acetylene reactions.

Many solvents for the acetylene reaction mixture were tried in an effort to secure the primary product in a definitely crystalline form. Methyl alcohol finally was found to give the desired result.

Experimental

Fifty-five grams of resorcinol was dissolved in 400 cc. of methyl alcohol to which the mercury catalyst had been added. After the flask had been tared, washed and dried acetylene was passed in from a gasometer until 13 g. had been absorbed. The solution, originally almost colorless, became reddish brown, while the catalyst darkened and settled on standing. The liquid was decanted from the catalyst and its volume reduced about one-third by evaporation on a water-bath. The flask was tightly stoppered to prevent access of air, cooled and allowed to stand for several hours. In a short time white, needle-like crystals formed in considerable quantity. They were collected on a filter, washed with methyl alcohol and dried at room temperature in the air or in a vacuum desiccator. In some cases it was necessary to recrystallize from hot methyl alcohol in order to remove the last traces of the catalyst. The filtrate and washings were processed a second and a third time, after which they were diluted with water until a slight cloudiness showed and were then allowed to stand. Microscopic yellow crystals slowly precipitated. An average yield was 70 g. of the white compound (83%) and 6 g. of the yellow (10%). These yields are calculated for the formulas given below.

Discussion

Under the procedure described above the large quantity of the white compound seemed to indicate that it was the primary product. It decomposed without melting above 250°. A loss of weight was observed when the air dried crystals were heated in a current of carbon dioxide or under reduced pressure. The loss of weight was found to be constant in various samples between 18.3 and 18.8%. The evolved vapor was condensed and proved to be methyl alcohol. This indicated that alcohol of crystallization was present. Samples dried in a vacuum desiccator showed a lower, and more variable, percentage loss under similar treatment. When fresh, the crystalline product was only moderately soluble in cold alcohol, but very soluble in hot. It dissolved readily in sodium hydroxide solution with deep red coloration. In water, ether, benzene and petroleum ether it showed little solubility. The compound, however, after standing some days, became markedly less soluble even in hot alcohol. Corresponding to this loss of solubility there had been a great increase in molecular weight, as shown by determinations made at intervals of a few days. This change, apparently polymerization, took place even when the sub-

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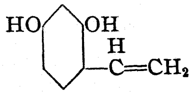
[5] Unpublished work, 1925. Read at Organic Section meeting, American Chemical Society at Los Angeles.

stance had been kept in sealed tubes, but was more rapid in the light. The crystals readily crumbled to a powder and if exposed to the air slowly became a yellowish brown. It was necessary to use fresh, air-dried crystals for the determination of the molecular weight as by the time the sample had been perfectly dried it had polymerized to such an extent as to be useless for examination. Samples of the same type were used for combustions.

Anal. Calcd. for $C_8H_8O_2 \cdot CH_3OH$: C, 64.25; H, 7.19. Pound: C, 64.37; H, 6.96. Loss **of weight** on heating. Calcd.: 18.04. Found: 18.3, 18.8 Mcl *wt.* (Ebullioscopic in methyl alcohol). Calcd.: 168. Found: 169.

These results would seem to justify at least a tentative acceptance of formula (V) for this product, vinylresorcinol



V

The polymerization of vinylresorcinol (V) is analogous to the behavior of cinnamic acid, vinylphenol and vinylcatechol, this latter compound never having been secured in the monomolecular form as far as the literature shows.

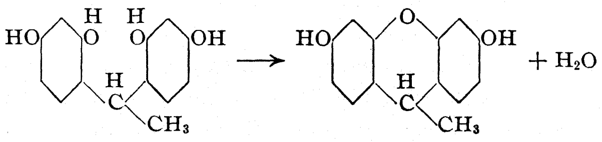
One of the great experimental difficulties encountered in the beginning of this investigation was the readiness with which the reaction mixture solidified to a crumbly, gelatinous mass insoluble in all ordinary solvents. This took place only when an excess of acetylene had been absorbed and was always accompanied by the odor of either dimethyl or diethyl acetal, according to the alcohol used as solvent. It did not occur in the case of other solvents. In order to test the assumption that the formation of this Bakelite-like mass was due to an acetal reaction, acetal was added to an alcoholic solution of resorcinol. No reaction took place until a small quantity of acid had been added, when the action became almost violent, with the formation of a clear, brittle, insoluble Bakelite closely resembling that formed in the acetylene reaction flask.

There is still doubt as to whether the yellow product has been secured in a pure state, free from vinylresorcinol. Its insolubility in water, however, and its oxidation to hydroxymethylfluorone(II) show that dihydroxymethylxanthene (IV) is present at least in considerable proportion. It is readily soluble in alcohol and ether as well as in alkali solutions and shows no tendency to polymerize.

Accordingly, the course of the acetylene-resorcinol condensation would seem to be as follows:

$$HC{\equiv}CH + (HO)_2C_6H_4 \longrightarrow \underset{(V)}{(HO)_2C_6H_3CH{=}CH_2}$$

$$\underset{\text{V}}{(HO)_2C_6H_3CH{=}CH_2} + (HO)_2C_6H_4 \rightleftarrows$$



III IV

This assumes (1) the formation of an intermediate product, ethylidenediresorcinol (III), which has not been isolated, and (2) a reaction between vinylresorcinol (V) and resorcinol. To test this latter assumption, alcoholic solutions of these compounds were mixed. At first practically colorless, the mixture soon turned reddish brown and, on dilution with water, precipitated the yellow compound (IV). Moreover, according to the reaction given above, equilibrium conditions would demand a larger amount of vinylresorcinol (V) in dilute than in concentrated solutions. This, too, was verified experimentally, the more dilute reaction mixtures always giving the higher yield of vinylresorcinol (V).

Derivatives

A. Methyl Ethers.—Attempts have been made to prepare the methyl ethers of vinylresorcinol (V) directly, but have thus far been unsuccessful. In fact, no reaction of vinylresorcinol in basic solution has been entirely satisfactory. It is probable that the base induces some sort of molecular rearrangement which is not reversible, but this point is still being investigated. Consequently the methyl ethers of resorcinol were prepared and their acetylene condensation products investigated.

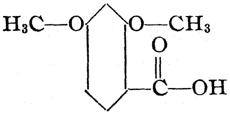
Experimental

One hundred ten grams of resorcinol was dissolved in 500 cc. of methyl alcohol, and then 46 g. of sodium gradually added, the reaction flask being kept under a reflux and frequently agitated. The solution was refluxed on a water-bath for an hour following the addition of the sodium, after which 252 g. of dimethyl sulfate was allowed to drop in slowly from a dropping funnel in the top of the condenser. It was necessary to cool the reaction flask during the addition of the first part of the dimethyl sulfate, and at the end to heat it on a water-bath. After an hour's heating, a sloution of 10 g. of sodium hydroxide was added in order to decompose the dimethyl sulfate completely and the heating was continued for another half hour. The flask was then cooled, the reaction mixture acidified and the methyl alcohol distilled off on a water-bath. Sufficient water to dissolve the salt was then added and the resorcinol ethers were extracted with ether. The ethereal solution was treated with 10% sodium hydroxide solution, which dissolved the monomethyl ether and permitted separation from the dimethyl compound The solvent ether was distilled from the dimethyl ether of resorcinol and this latter distilled. It is a clear, oily liquid boiling at 210°. The caustic solution of the monomethyl ether was acidified, extracted with ether and then treated in the same manner.

The resorcinol ethers were each dissolved in methyl alcohol and allowed to react with an equimolar quantity of acetylene in presence of the catalyst, as was resorcinol.

From the monomethyl ether only amorphous orange powders have been secured. The variable melting point and the lack of definite crystalline form would seem to indicate that the product is a mixture. Since side chain attachment to nuclear carbons of the monomethyl ether offers considerable opportunity for isomer formation, the condition described above was to have been expected, but not in the case of acetal linkage. moreover, the complete solubility of the product in dilute alkali gave evidence that the hydroxyl group was still free.

From the dimethyl ether a pale yellow oil boiling with decomposition at 235° was formed. This was oxidized by boiling with dilute nitric acid and also with dilute potassium permanganate. In both cases beautiful monoclinic crystals were formed from a hot water solution. The compound proved to be a monobasic acid melting sharply at 108°. It was identified as the dimethyl ether of β-resorcylic acid (VI); therefore the acetylene condensation product was undoubtedly the dimethyl ether of vinylresorcinol (VII). This is a further corroboration of previous experience that the side chain is attached ortho and para, respectively, to the hydroxyl groups, whether these he free or substituted.



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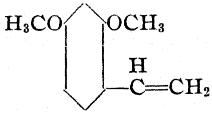

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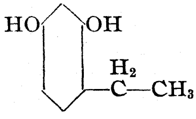


VIII

B. **Ethyl Resorcinol.**—Owing to the slight solubility of vinylresorcinol and to its rapid polymerization, considerable difficulty was experienced in reducing it. The best results were obtained from the use of tin and hydrochloric acid. The product was extracted with ether, which was then evaporated. The residue was recrystallized from boiling benzene in the form of rather large prismatic crystals, melting at 98.5–99°. This product was identified as ethylresorcinol[6] (VIII). Its synthesis from vinylresorcinol is additional evidence of the correctness of the formula assigned to this compound.

C. **Acetate.**—When acetic anhydride in excess was added to vinylresorcinol (V), solution took place accompanied by evolution of heat. On standing, after refluxing about an hour, large rhombic crystals (m. p. 285–286°) slowly formed in the somewhat reddish solution. The product was identical in all respects with that of Causse and Fosse and Ettlinger, while the percentage yield was invariably high. Naturally there is no evidence of free hydroxyls, but in view of the synthesis from vinylresorcinol (V) this cannot be taken as evidence of acetal linkage of the side chain as Causse argues. The empirical formula he assigns to it, $C_{18}H_{18}O_6$, as the diacetate of the acetal (IX), gives the same percentage composition as that of the diacetate of vinylresorcinol (X), $C_{12}H_{12}O_4$, so there is no contradiction from analysis.

$$H_3CCOOC_6H_4\text{—}O\text{—}CH(CH_3)\text{—}O\text{—}C_6H_4\text{—}O\text{—}COCH_3$$

IX

$$(H_3C\text{—}CO\text{—}O)_2{=}C_6H_3CH{=}CH_2$$

X

Aldehyde Condensation

In order to duplicate as nearly as possible the conditions under which vinylresorcinol (V) had been made from acetylene, the aldehyde condensation was tried in methyl alcohol according to the following procedure.

[6] Johnson and Hodge, THIS JOURNAL, 35, **1020** (1913).

Experimental

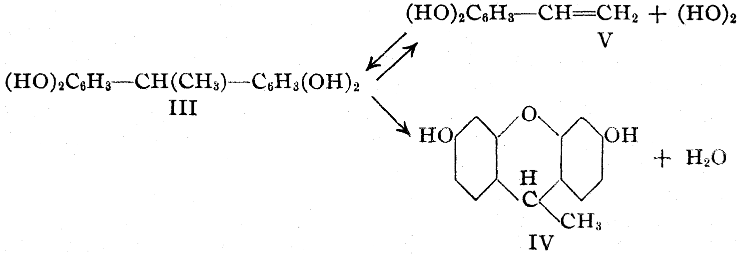
Twelve grams of dry hydrogen chloride was dissolved in 400 cc. of methyl alcohol and 110 g. of resorcinol added; 44 g. of paraldehyde was gradually added to this mixture during the two or three hours it was refluxed on a water-bath. The solution resembled the acetylene reaction mixture in all respects and on partial evaporation a copious precipitate of white, needle-like crystals formed exactly as in the acetylene reaction. Moreover, the filtrate from the third fractional crystallization gave the yellow compound (dihydroxymethylxanthene) on standing after dilution with water. Molecular weight determinations gave results agreeing with those obtained from the acetylene product, while all other properties and reactions of the white product seemed to be identical with those of vinylresorcinol (V).

Attempted oxidations of vinylresorcinol (V) from acetylene or from aldehyde have invariably failed to produce anything which gave even a trace of fluorescence, but the yellow secondary product on heating with stannic chloride gave the highly fluorescent hydroxymethylfluorone (II)

Discussion

There is little doubt but that the condensation of acetylene with resorcinol and the condensation of aldehyde with resorcinol give the same products. However, it is not as clear as to how the aldehyde reaction takes place as it is in the case of the acetylene reaction. The following equation seems the more plausible explanation.

$$2(HO)_2C_6H_4 + CH_3CHO \longrightarrow \underset{\text{III}}{(HO)_2C_6H_3{-}CH(CH_3){-}C_6H_3(OH)_2} + H_2O$$



IV

Schou,[7] however, has recently reported the presence of vinyl alcohol to the extent of $^1/_{830}$ in paraldehyde in the presence of hydrochloric acid and consequently vinylresorcinol may be formed immediately by the reaction of resorcinol with the enolized aldehyde.

Repetitions of Fosse and Ettlinger's ethylidene chloride experiments have been rather unsatisfactory. The reaction was tried in a sealed tube heated to the temperature given by these investigators, and also to much higher temperatures, but in both cases the ethylidene chloride reacted to so small an extent as to make the separation of the small quantity of product almost an impossibility. Yields proved to be equally unsatisfactory when the interacting substances were dissolved in methyl alcohol and refluxed for several hours.

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[7] Schou, *Compt.* rend., 184, **1452 (1927)**

The probable explanation of the differences of opinion expressed in the literature is that suggested by Mohlau and Koch: that the products reported have been mixtures of the products of condensation in different proportions. In this case derivatives would exhibit different properties according as the reaction with vinylresorcinol (V) or that with ethylidenediresorcinol (III) (dihydroxymethylxanthene (IV)) had predominated.

Summary

1. The primary product of the catalytic condensation of acetylene and resorcinol has been secured in crystalline form and identified as vinylresorcinol (V).
2. The dimethyl ether of vinylresorcinol (VII) has been shown to give the dimethyl ether of β-resorcylic acid on oxidation.
3. Reduction of vinylresorcinol has been effected, the product being ethylresorcinol (VIII).
4. The primary product of the condensation of aldehyde and resorcinol has been shown to be vinylresorcinol (V).
5. The work of previous investigators who showed the presence of dihydroxymethylxanthene (IV) in the products has been corroborated.
6. No evidence whatsoever in support of Causse's acetal formula (I) has been found, but a number of facts which argue against it have been observed.

NOTRE DAME, INDIANA

[CONTRIBUTION FROM THE LABORATORIES OF PHYSICAL CHEMISTRY AND AGRICULTURAL CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

THE QUANTITATIVE STUDY OF THE PHOTOCHEMICAL ACTIVATION OF STEROLS IN THE CURE OF RICKETS. II

BY STANISLAW-KAZIMIERZ KON, FARRINGTON DANIELS AND HARRY STEENBOCK

RECEIVED JULY 18, 1928 PUBLISHED SEPTEMBER 5, 1928

In an earlier paper from these Laboratories,[1] there were described experiments in which cholesterol was exposed to monochromatic light to determine the minimum number of quanta necessary to secure its antirachitic activation. This work was confined to the use of the 265 m. μ line of the mercury arc. It was followed by an extensive research by Dr. Waldemar Vanselow in which all the important lines of the quartz mercury lamp were studied under a wide variety of conditions.[2] As recent researches from several laboratories have indicated that it is ergosterol rather than cholesterol itself which produces the vitamin D upon irradiation, it seemed desirable to repeat and amplify the experiments, using ergosterol instead of cholesterol.

[1] Fosbinder, Daniels and Steenbock, THIS JOURNAL, **50,923 (1928).**

[2] Unpublished data

Fortunately, in the meantime important improvements have been made in our photochemical technique, so that it is now possible to measure directly the optical absorption as well as the curative effect on animals. In the earlier work an attempt was made to determine the percentage absorption of ultraviolet light by means of a spectrophotometer but the results were too unsatisfactory to publish. By the new technique the percentage absorption was measured directly with a thermopile and galvanometer.

Ergosterol as the Pro-Vitamin

Nearly all of the experimental evidence now available points to the conclusion that ergosterol is the mother substance of vitamin D. Windaus working in collaboratiori with Rosenheim,[3] Hess[4] and Pohl[5] found that ergosterol can be rendered active in much smaller amounts than cholesterol and that it shows exactly the same absorption bands as those considered to be characteristic of the activatable contaminant of ordinary cholesterol. It was found also by these investigators that cholesterol can be freed from the contaminant by various chemical treatments such as bromination and subsequent reduction of the'dibromide, boiling with animal charcoal, treatment with permanganate in acetone and over-irradiation. These results have been commonly interpreted as showing that ergosterol is the mother substance of vitamin D and that it is at present the only substance known to yield an antirachitic substance on irradiation.

A different point of view is held, however, by Bills, Honeywell and MacNair[6] and by Jendrassik and Kenényffi.[7] The former observers reported that highly purified cholesterol is still activatable and concluded that the residual activatability was due to something other than ergosterol. The latter assume an equilibrium between pure cholesterol and pro-vitamin D. Bills, Honeywell and MacNair used cholesterol twice purified by bromination in the laboratory of Windaus as well as cholesterol brominated three times in their laboratory. Cholesterol purified by boiling for three periods of eight hours each with Merck's blood charcoal was used also. All of these preparations after irradiation in the solid state for fifteen minutes gave positive results in feeding tests, but a level of 0.3% of the rachitogenic diet was necessary rather than the 0.01% level used in the case of the ordinary cholesterol. Spectroscopic examination showed that a concentrated solution of the purified cholesterol exhibited three absorption bands identified with ergosterol and two additional ones at 315 and 304 $m\mu$. The ergosterol bands were 150 times weaker after purification but the curative effect was only 30 times weaker.

[3] Rosenheim and Webster, *Biochem.* J.,21, 389 (1927).

[4] Windaus and Hess, *Nachr Ges. Wiss. Göttingen Math.-Phys. Klasse,* 175 (1926).

[5] Pohl, *ibid.,* 185 (1926).

[6] Bills, Honeywell and MacNair, J. *Biol. Chem.,76,* 251 (1928).

[7] Jendrassik and Kenényffi, *Biochem.* Z., 189,180 *(1927).*

This suggestion that ergosterol is not the only pro-vitamin was so important that it was necessary to put the matter to independent test before continuing with the quantum efficiency tests of the next section on ergosterol. The experiments of Bills and collaborators were repeated using twice brominated cholesterol and cholesterol purified with "Norite" charcoal and with Merck's animal charcoal. Both curative tests and preventive tests were used with several different groups of rats, and although complete cures were not obtained (save in the case of cholesterol purified with Norite of which even 0.06% proved to be active), still there was always a marked lessening of the rachitit condition, confirming the findings of Bills, Honeywell and MacNair.

The results are capable of interpretation in a different way, however. The ergosterol lines were still present in the purified cholesterol of these investigators and the difference between the absorption measurements and the rat tests (150 versus 30) might have been due to the presence of new decomposition compounds absorbing generally in the short ultraviolet, so that the results could still be explained on the assumption that the ergosterol had not been completely removed in the purification. In a recent letter to Nature, Heilbron, Morton and Sexton[8] venture the opinion that the new bands of absorption at 315 and 304 present in the specially purified cholesterol of Bills and co-workers are due to cholesterilene formed in the course of oxidation. We would completely share their opinion inasmuch as a spectrogram taken through 20 cm. of a 10% solution of our inactive cholesterol showed such a heavy absorption below 290 mμ that the presence of various oxidation products absorbing ultraviolet light, but not activatable, cannot be questioned. It must be admitted, as Bills and co-workers point out, that the stability of ergosterol is quite remarkable in the presence of cholesterol and it would be extremely interesting to find the cause of this phenomenon. It is possible that the formation of mixed crystals is effective in this respect.

It was decided to attempt a more drastic purification of cholesterol. Twenty-five grams of commercial cholesterol was dissolved in 437 cc. of boiling acetone and after the addition of 1.25 g. of powdered potassium permanganate, the solution was refluxed for one hour. The manganese dioxide was then filtered off, 1.25 g. of fresh potassium permanganate was added and the solution was refluxed for one hour again and this treatment was repeated five times. The last filtrate was diluted cautiously with water and crystallized at 0°. The crystals were carefully washed with alcohol, taken up in boiling alcohol, filtered through hardened filter paper, the solution was brought to boiling, diluted with water and crystallized; 11.5 g. of snow-white crystals of cholesterol was obtained with a melting point of 147° (uncorr.).

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[8] Heilbron, Morton and Srxton, *Nature*, **121,452 (1928).**

This material was irradiated, fed and tested as in the preceding experiments, but it was completely inactive, giving no cure and the degree of protection was so small as to be within the limit of experimental error. In the light of these experiments it seems evident that the activatable impurity left in cholesterol after bromination and after boiling with charcoal is ergosterol.

The interesting formation of antirachitic cholesterol derivatives under the action of Floridin[9] described by Bills[10] and MacDonald[11] was also studied. These preparations were made according to the method of Bills and studied in curative and protective experiments. In the protective experiment the animals were evidently stunted. There was almost no growth, though the food intake was sufficient to allow growth at a moderate rate. The development of their bones and especially of the femora and humeri seemed to be out of any proportion to the body weight—in fact the bones would be almost normal for rats of the same age, but twice the weight. The amount of ash was perfectly normal and there was no histological evidence of rickets. The results of the curative test were striking, as they presented much greater variations than is usually encountered when a single preparation is tested on standardized rats. Nearly all of them showed, however, a positive line test. In agreement with Bills and MacDonald it seems certain that the substance formed is different from vitamin D.

Having been convinced that pure cholesterol cannot be rendered antirachitic by ultraviolet irradiation and that ergosterol is at present the only substance known to be specifically activated by radiant energy, a study of the photochemical activation of ergosterol was next undertaken.

Determination of the Quantum Efficiencies

The experimental procedure was similar to that described in the earlier work,[1] but it was markedly improved by the introduction of two new features and the results reported here are more accurate.

Procedure.—The apparatus consisted of a Hilger quartz monochromator and the intensity was measured as before by means of a Coblenz vacuum thermopile and a Leeds and Northrup galvanometer. The commercial quartz mercury vapor lamp was replaced by a water-cooled capillary arc constructed in this Laboratory. A detailed description of this lamp will be published independently. The intensity of isolated lines could be increased ten times by this means over those produced by our previous lamp. A second marked improvement over the original apparatus was obtained by the use of a double absorption cell placed inside of the spectrometer tube immediately in front of the thermopile. It was arranged to slide back and forth on a rack so that either the first cell containing the solvent or the second cell containing the solution of ergosterol could be placed in the path of the light. Each compartment of the cell was 19 mm. long, 1.5

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[9] A Fuller's earth from Northern Florida possessing marked catalytic properties.

[10] Bills, *J. Biol. Chem.*, 67, 753 (1926).

[11] Bills and MacDonald, *ibid.*, 68, 821 (1926).

mm. wide and 17 mm high. This arrangement eliminated, completely, errors due to reflection from the windows and absorption by the solvent.

The degree of activation obtained in the different experiments was determined as before by the line test and the amount of calcium deposition was described as negative, positive or very positive. The smallest amount of calcium deposition accepted as a positive test was that corresponding to a condition of the bone described in this Laboratory as indication of a line, provided that the next lower test in the same series showed distinctly less and the next higher distinctly more calcification. If two subsequent members of a series showed the same lowest degree of calcification the one requiring the more energy was taken.

It should be emphasized that although this method is at present the only one which is sufficiently sensitive to detect the exceedingly minute quantities of vitamin D formed, and is far more sensitive than any chemical test, it imposes, nevertheless, limitations on the accuracy of the test. Biological variations are to be expected in all experimental animals, but the rat colony used in these experiments had been so rigorously controlled that the rats may be considered to be as highly standardized as now appears possible.

The ergosterol was prepared by a method similar to that described by Windaus and Grosskopf.[12] The ergosterol was further purified by acetylation, recrystallization of the acetate from glacial acetic acid, saponification and repeated recrystallization from absolute alcohol. The final product melted at 163° (uncorr.). It was beautifully white and crystalline The ergosterol was either irradiated in the dry state back of the slit as in the earlier work, or it was dissolved in optically pure alcohol. It was then placed in one of the compartments of the double cell in front of the thermopile. Two concentrations of the alcoholic ergosterol solution were used: 1/25% and 1/1250%. The results of the experiments carried out on different lines are tabulated below.

Discussion

It will be seen that the threshold value of activation lies for all the lines studied in the neighborhood of 700-1000 ergs (or 10×10^{13}–14×10^{13} quanta). The lower value corresponds to an amount of vitamin D equal to 6×10^{-8} g.

TABLE I

SOLID ERGOSTEROL

Subs., Irradiated, mg.	Line, mμ	Time, secs.	Defl.	Abs., %	Abs. energy, ergs	Abs. quanta	Anti-rachitic action
25	265	3	11	100	234	3.2×10^{13}	Negative
25	265	6	10	100	425	5.9×10^{13}	Negative
25	265	10	10.5	100	744	10.3×10^{13}	Positive
25	265	10	16	100	1134	15.8×10^{13}	Very positive
25	265	20	16	100	2268	31.6×10^{13}	Very positive
25	265	40	16	100	4536	63.2×10^{13}	Very positive
25	265	60	16	100	6804	94.8×10^{13}	Very positive
25	265	90	16	100	10206	142.2×10^{13}	Very positive
25	280	6	6.5	100	276	3.9×10^{13}	Negative
25	280	22	4.5	100	701	10.0×10^{13}	Positive
25	280	35	5	100	1240	17.7×10^{13}	Positive
25	280	30	7.5	100	1594	22.8×10^{13}	Very positive
25	280	60	7.5	100	3188	45.6×10^{13}	Very positive
25	280	120	7.5	100	6376	91.2×10^{13}	Very positive

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[12] Windaus and Grosskopf, *Z. physiol. Chem.*, 124, 8 (1923).

TABLE II

ALCOHOLIC SOLUTIONS OF ERGOSTEROL

Subs. irradiated	Line, mμ	Time, secs	Defl. solvent	Defl. soln	Abs., %	Abs., energy, ergs	Abs quanta	Antirachitic action
1/25%	256	15	6.5	0	100	691	9.0×10^{13}	Positive
1/25%	256	10	10	0	100	709	9.2×10^{13}	Positive
1/25%	256	22	6.5	0	100	1013	13.2×10^{13}	Positive
1/25%	256	30	6.5	0	100	1382	18.0×10^{13}	Very positive
1/25%	256	30	10	0	100	2126	27.7×10^{13}	Very positive
1/25%	256	60	10	0	100	4252	55.4×10^{13}	Very positive
1/25%	256	120	10	0	100	8504	110.8×10^{13}	Very positive
1/1250%	265	30	8.5	3.5	59	1063	14.5×10^{13}	Positive
1/1250%	265	120	8.5	3.5	59	4252	58.0×10^{13}	Very positive
1/1250%	265	600	8.5	3.5	59	21260	290.0×10^{13}	Very positive
1/25%	265	30	8.5	0	100	1807	25.1×10^{13}	Positive
1/25%	265	120	8.5	0	100	5228	100.4×10^{13}	Very positive
1/25%	265	475	8.5	0	100	28610	397.7×10^{13}	Very positive
1/1250%	280	30	5	2.5	50	531	7.6×10^{13}	Negative
1/1250%	280	120	4.5	2	56	2124	30.4×10^{13}	Positive
1/1250%	280	600	5	2.5	50	10620	157.0×10^{13}	Very positive
1/25%	280	30	5	0	100	1062	15.1×10^{13}	Positive
1/25%	280	120	5	0	100	4248	60.4×10^{13}	Very positive
1/25%	280	600	5	0	100	21240	302.0×10^{13}	Very positive
1/25%	293	20	4	0	100	567	8.5×10^{13}	Negative
1/25%	293	30	5	0	100	1063	15.8×10^{13}	Positive
1/25%	293	60	3.5	0	100	1488	23.7×10^{13}	Positive
1/25%	293	40	6.5	0	100	1842	27.5×10^{13}	Very positive
1/25%	293	65	5	0	100	2303	34.4×10^{13}	Very positive
1/25%	293	120	3.6	0	100	2976	44.4×10^{13}	Positive
1/25%	293	300	3.5	0	100	7440	111.1×10^{13}	Very positive

TABLE III

ERGOSTEROL ACETATE, ALCOHOLIC SOLUTION

Subs. irradiated	Line, mμ	Time, secs.	Defl. solv.	Defl. soln.	Abs., %	Abs. energy, ergs	Abs quanta	Antirachitic action
1/25%	265	10	6.5	0	100	461	6.4×10^{13}	Negative
1/25%	265	20	6.5	0	100	922	12.8×10^{13}	Negative
1/25%	265	30	6.5	0	100	1382	19.2×10^{13}	Very positive
1/25%	265	45	6	0	100	1913	26.6×10^{13}	Positive
1/25%	265	60	7	0	100	2976	41.4×10^{13}	Very positive
1/25%	265	90	6	0	100	3827	53.2×10^{13}	Very positive
1/25%	265	120	7	0	100	5952	82.7×10^{13}	Very positive
1/25%	265	240	6	0	100	10200	141.8×10^{13}	Very positive

The calculation is similar to that given in the previous paper,[1] and is based on the Einstein law of photochemistry and also on the assumption that vitamin D is the only product formed from ergosterol upon irradiation with monochromatic light. The slight difference in favor of the 256 mμ line when compared with the 293 mμ line is probably not sufficiently marked to be beyond the limits of experimental error. The formation of vitamin

TABLE IV

EXPERIMENTS WITH A TIME LAG

Alcoholic Solution of Ergosterol

Subs. irradiated	Line, mμ	Time, secs	Defl solv.	Defl. soln.	Abs, %	Abs. energy, ergs	Abs. quanta	Antirachitic action
1/25%	265	6	7	0	100	298	4.1×10^{13}	Negative
1/25%	265	12	7.5	0	100	638	8.9×10^{13}	Negative
1/25%	265	15	7	0	100	744	10.3×10^{13}	Positive
1/25%	265	18	9	0	100	1148	15.9×10^{13}	Positive
1/25%	265	24	8	0	100	1361	19.3×10^{13}	Positive
1/25%	265	30	7.5	0	100	1594	22.1×10^{13}	Very positive
1/25%	265	50	5	0	100	1770	24.6×10^{13}	Very positive
1/25%	265	36	7	0	100	1786	24.8×10^{13}	Very positive

TABLE V

EXPERIMENTS WITH A NARROWER SLIT

Subs irradiated	Line, mμ	Time, secs	Defl solv.	Defl soln	Abs, %	Abs, energy, ergs	Abs quanta	Antirachitic action
1/25%	265	30	2.5	0	100	531	7.4×10^{13}	Negative
1/25%	265	50	2	0	100	709	9.8×10^{13}	Negative
1/25%	265	100	2	0	100	1418	39.6×10^{13}	Positive

D from ergosterol is thus shown to be independent of the wave length over practically the whole range of selective absorption and to be only a function of the incident energy. The efficiency is also independent of the state in which ergosterol is irradiated for solid ergosterol, a concentrated solution absorbing all the incident rays and a dilute solution absorbing only about 60% of the radiation require all the same number of ergs (or quanta) for activation. When working with crystals it is necessary to use a large excess, otherwise some light passes through the interstices and a lower quantum efficiency is found. For example, 5 mg. of ergosterol placed in the small box used for the purpose (area 70 mm.^{2}) required more than 2500 ergs for activation—calculated on the basis of complete absorption.

In order to determine whether further purification of the light would result in a higher quantum efficiency, a series of irradiations was carried out with one of the slits (between the prism and the double cell) cut down to $^1/_{11}$ of its original width. This change diminished the intensity of the light 3.5 times for the 265 mμ line, but did not alter the quantum efficiency as seen in Table V. A series of irradiations was carried out with ergosterol acetate in $^1/_{25}$% alcoholic solution (prepared in the course of purification of the ergosterol, m. p. 177°, uncorr.) The quantum efficiency is the same as for ergosterol. This fact confirms the statements of other investigators[13] and shows that the hydroxyl group apparently plays no role in the process of activation.

It was thought that some information concerning the mechanism of ac-

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[13] Rosenheim and Webster, *Lancet*, *II*, 622 (1927); Windaus and Holtz, *Nachr. Ges. Wiss. Göttingen Math.-Phys Klasse*, Heft 2 (1927).

tivation could be gained by exposing ergosterol to intermittent radiation. It was, namely, possible that in the case of one of the stages of the process being a slow reaction the quantum efficiency might be altered by such means. The intermittent irradiation was carried out with a $^1/_{25}\%$ alcoholic solution of ergosterol, wave length 265 $m\mu$. The light was thrown on the cell for the duration of one second at five-second intervals. A photographic camera shutter was used for the purpose. The results are tabulated in Table IV. No change in the quantum efficiency could be detected.

The quantum efficiency of antirachitic activation of ergosterol reported in the present work is smaller than that given in the earlier paper. As already stated the present values are to be considered more accurate and this fact ought not to convey the impression that the activatability of cholesterol is due to a substance having a higher quantum efficiency than ergosterol, A large number of experiments was carried out using various preparations of cholesterol, but lack of space prevents the publication of all of the tables. It is sufficient to say that in no case did we find a higher quantum efficiency than for ergosterol, but for one preparation which had been repeatedly recrystallized and was kept in an ice chest the quantum efficiency was found to be almost the same as for ergosterol, namely 1400 ergs for the 265 line (irradiated in the solid state). Experiments with the original V-1-24 preparation (exposed to air and kept since 1925 at room temperature) showed a lower quantum efficiency—1500 ergs were negative and 5000 distinctly positive. The presence of traces of oxidation products and impurities might easily explain the smaller quantum efficiency of ordinary cholesterol. The chemically purified cholesterols described in the first part of this paper were also exposed in the solid state to monochromatic radiation with the idea that differences in the residual amount of ergosterol present might be detected. These experiments failed in so far as the highest amount of energy used, namely, 200,000 ergs, was insufficient to activate any of them.

Ergosterol was irradiated in a $^1/_{25}\%$ solution in acetone. Acetone shows selective absorption in the same region as ergosterol. The results were negative and energy up to 28,000 ergs was ineffective.

Acetone was used as a solvent also with pure cholesterol with the idea in mind that the energy absorbed by the acetone might possibly be transferred to cholesterol with the formation of vitamin D. A 1% solution of chemically purified cholesterol was used. The results were entirely negative up to 90,000 ergs.

Interesting experiments have been published by Windaus[14] on the sensitization of ergosterol to visible radiation. The products were, however, entirely inactive antirachitically.

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[14] Windaus and Brunken, *Ann.*, 460, 225 (1928); Windaus and Borgeaud, *Ann.* 460, **235** (1928).

One of us (S.-K. K.) is indebted to the International Health Board of the Rockefeller Foundation for a fellowship during the tenure of which the work here reported was carried out.

Summary

1. Repeated boiling with permanganate in acetone solution removes completely the pro-vitamin from cholesterol. Cholesterol purified in this way and irradiated is inactive antirachitically even in large doses.

2. The photochemical formation of vitamin D from ergosterol under the action of monochromatic light has been studied quantitatively for different lines.

3. The quantity of radiant energy necessary to form an amount of vitamin D sufficient to cause a demonstrable deposition of calcium in the bones of a rachitic rat has been found to be constant over a wide range of radiations, 700–1000 ergs being necessary for the 256, 265, 280 and 293 mμ lines

4. The quantum efficiency was independent of the state in which ergosterol was irradiated, the results being the same for irradiation of the solid or of solutions in alcohol of varying concentration.

5. The quantum efficiency was the same for ergosterol acetate as for ergosterol. The hydroxyl group plays no role in the process of activation.

MADISON, WISCONSIN

NEW BOOKS

Crystallographic Tables for the Determination of Minerals. BY VICTOR GOLDSCHMIDT, **Heidelberg, and** SAMUEL G. GORDON, **Philadelphia. Academy of Natural Sciences, Philadelphia,** 1928. **70** pp. **17** × 26 cm. **Price, $1.50.**

In accordance with one of the fundamental principles of crystallography, the angles of every crystallized compound are constant and, except in the cubic system, characteristic of that compound. Angle measurement should accordingly constitute a useful method for the identification of unknown substances. Owing, however, to the existence of freedom of choice as to orientation and as to the unit forms, this method has never come into general use. Previous attempts to arrange crystals in determinative tables have either covered too few compounds or have been too complicated for anyone but the author and his immediate associates to use. In the present publication an effort is made to improve upon existing tabulations (without, however, giving any credit to earlier workers), over a thousand minerals being arranged according to crystal system, with data as to crystallographic constants, composition, specific gravity, hardness and miscellaneous properties.

When any new mineralogic work appears, it is the reviewer's custom, for judging how carefully it has been prepared, to look up at once what composition is given for bornite, boulangerite and chilenite, how "erythrocalcite" is spelled and what specific gravity is assigned to epididymite; for errors, made in these in one of the standard reference works, are usually copied faithfully from one compilation to the next. In the present work three out of five of these errors have been avoided, indicating that more than the average amount of attention has been given to getting the data correct.

The minerals are arranged in these tables, for the most part, in the order of increasing value of some coordinate. Allowance is made for differences in choice of orientation by including the values for several of the orientations possible in each system. No consideration is given, however, to difference in choice of unit forms, so the tables will be most useful to those workers who possess the happy faculty of guessing correctly which forms of a crystal to be identified have been selected as the units by the authors.

EDGAR T. WHERRY

Colloid Symposium Monograph. Papers presented at the Fifth National Symposium on Colloid Chemistry, University of Michigan, June, 1927. Edited by Harry Boyer Weiser, Professor of Chemistry, The Rice Institute. The Chemical Catalog Company, Inc., 419 Fourth Avenue, New York, 1928. 394 pp. Illustrated. 16 × 23.5 cm. Price $6.50.

The continued prodigious increase in the extent and variety of our scientific knowledge is, of course, gratifying. To the student of science, however, who is attempting to gain or to maintain a grasp of his subject, this increase is somewhat disconcerting and disheartening. It would be utterly so, were it not that new generalizations and correlations are also being constantly made which, at one stroke, bring whole groups of facts within his comprehension.

Colloid chemistry represents such a generalizing and correlating development in chemistry. It strikes across the whole domain of organic and inorganic chemistry, illuminating many otherwise inexplicable phenomena.

This function of colloid chemistry is particularly apparent in the collection of twenty-four papers read at the Fifth National Symposium on Colloid Chemistry held at the University of Michigan and published in this Monograph. About half of the papers deal with general problems of colloidal chemistry; the others cover applications of colloidal chemistry to the most varied subjects: for instance, to the mechanism by which the kidneys operate, to the coagulation of gelatin, the winter hardiness of insects, the manufacture of photographic film, the eccentricities of molding sand and the nature of Portland cement. It is a useful collection.

One cannot, however, but wonder why this collection is called a monograph.

ARTHUR B. LAMB

Mechanochemistry and the Colloid Mill, Including the Practical Applications of Fine Dispersion. By PIERCE M. TRAVIS, President, Travis Colloid Research Co., Inc. The Chemical Catalog Company, Inc., 419 Fourth Avenue, New York, 1928. 191 pp. 17 figs. 16 X 23.5 cm. Price $4.00.

As stated by the author, the book was written in an attempt to help eliminate the guess method in operations that involve the dispersion or deflocculation of substances by mechanical means. The name "Mechanochemistry" was chosen because the subject matter includes a discussion of the principles that underlie such processes, as well as a description of the Colloid Mill and its functions.

The first thirteen chapters are devoted to the usual facts and theories involved in a discussion of the colloidal state of matter, and technical applications are frequently referred to. So much ground is covered in these chapters that the discussion is often necessarily limited; nevertheless, the author's very clear and concise style has permitted the inclusion of a vast amount of valuable information. For the accomplishment of the author's purpose, Chapter XII on the theory of emulsions is worthy of special mention.

While the early chapters, dealing largely with the theoretical side of the question, will be found of very great value to those engaged in technical practice, they are to be highly recommended to the beginner in the study of colloid chemistry.

Chapter XIV is an excellent presentation of the construction and functions of the Colloid Mill. The particular advantages or limitations of the various types for specific purposes are clearly pointed out.

Chapter XV deals with methods and standard practices that may be employed in the testing of colloidal systems. Both the student and the technical chemist will find this chapter very helpful.

ELLWOOD B. SPEAR

Über Konstitution und Zusammenhänge in der Sesquiterpenreihe. (The Constitution and Relationships of the Sesquiterpenes:) BY DR. L. RUZICKA, Professor at the University of Utrecht. Fortschritte der Chemie, Physik und Physikalischen Chemie, Band 19, Heft 5, Serie A. Gebrüder Borntraeger, W 35 Schoneberger ufer 12 a, Berlin, Germany, 1928. iii + 57 pp. 16.5 X 25.5 cm. Price, M 4.80.

In view of the fact that the number of sesquiterpenes discovered in various ethereal oils has increased during the past eight or ten years to over 400, such a résumé as this is timely. No attempt is made to cover the general chemistry of the substances in this field. The author has taken up in particular the reactions leading to a knowledge of the structure of the carbon skeleton of these compounds, the correlation of the various sesquiterpenes, the relationship between the various individuals and the synthesis of a few of the most important ones.

An introductory chapter mentions in brief the work which was accomplished before 1921. The rest of the article comprises, for the most part, a condensation of the author's brilliant researches which have been completed during the past six or seven years. The value for constitutional work of the dehydrogenation method with sulfur has been stressed. A classification and tabulation of the various important groups of sesquiterpenes is included.

For one who may be interested in obtaining a fundamental knowledge of sesquiterpenes from the standpoint of structure, this pamphlet will be invaluable.

ROGER ADAMS

Die Chemie der Zellulose und ihrer Begleiter. (The Chemistry of Cellulose and its Associated Compounds.) By KURT HESS, Member of the Kaiser Wilhelm Institute of Chemistry. Akademische Verlagsgesellschaft m.b.H., Markgrafenstrasse 4, Leipzig C 1, Germany, 1928. xxi + 836 pp. 157 figs. 16 X 23.5 cm. Price, unbound, M 57; bound, **M 59.**

The long expected *magnum* opus from the pen of Professor Hess has finally appeared and will rank for some time to come as the outstanding monograph on the chemistry of cellulose. After a brief introduction and a chapter on the development of the cell wall, the author plunges into a comprehensive review of compounds associated with cellulose, their isolation and analysis, and reactions which throw some light on their possible constitution. Not a little of this long chapter is devoted to lignin and rounds out Fuchs' excellent monograph on lignin by including the very recent and important investigations of Freudenberg, Hagglund, and Herzog.

Subsequently we find a good review of the isolation and purification oi cellulose and its solution and reprecipitation. Here, as we might expect, the cuprammonium solutions are discussed at length, since their polarimetric study first led Hess to the hypothesis that the ultimate cellulose molecule is [$C_6H_{10}O_5$], an hypothesis which he still maintains. Substitution products of cellulose also receive particular attention since Hess' laboratory has systematically studied cellulose esters and ethers, obtaining them in microcrystalline form and determining their molecular weights in various solvents. One of the longest sections in the book is devoted to the degradation of cellulose and here again the work of Hess' laboratory is brought to the fore. An interesting section deals with cellulose acetolysis in which, according to Friese and Hess, cellobiosan acetate is the exclusive product in the earlier stages of the reaction. The final section of Hess' portion of the work is devoted to problems of constitution, in which the author points out experimental methods for determining the possible size of the cellulose molecule. He ends in expressing the hope that researches on the synthesis of glucosans will be forthcoming in the near future.

Professor Hess has been fortunate in his choice of collaborators. Dr. J. R. Katz of the University of Amsterdam has added a thorough and scholarly presentation of the micellar theory and the swelling of cellulose, which is very welcome. A chapter presented historically, on the anisotropy of cellulose, is followed by another which Dr. Katz entitles "Is Cellulose a Crystalline Body?' and which includes detailed x-ray studies on natural fibers and on cellulose derivatives, and a useful supplement on the technique used in this type of work. Subsequently Dr. Katz critically and cautiously discusses various estimates of the size and arrangement of crystallites in cellulose fibers. The final and perhaps the most stimulating part of Dr. Katz' section of the book is devoted to the mechanism of swelling of cellulose, and merits a careful reading by all investigators in the field of cellulose chemistry.

In the very last portion of Dr. Hess' book we find a satisfactory chapter by Dr. R. Haller on the behavior of cotton and artificial cellulose fibers toward dyes.

Some cellulose chemists may take issue with Dr. Hess on certain of his hypotheses and feel that the experimental data presented in their support are quite inadequate. However, these very hypotheses are driving Hess' more cautious colleagues into new and untried fields of investigation, and for this alone he deserves their unstinted praise. He has given them an interesting reference book, the importance of which is beyond question.

LOUIS E. WISE

Fundamentals of Dairy Science. BY ASSOCIATES OF LORE A. ROGERS IN THE RESEARCH LABORATORIES OF THE BUREAU OF DAIRY INDUSTRY, United States Department of Agriculture. American Chemical Society Monograph Series. The Chemical Catalog Company, Inc., 419 Fourth Avenue, New York, 1928. 543 pp. 31 figs. 15.5 × 23.5 cm. Price, $5.50.

This book, it can be safely stated, is the most notable contribution that has been made to the literature of dairy science. It is unique in purpose and plan. It represents the successful accomplishment of a very difficult task. It is eminently satisfactory in filling "a need experienced by advanced students and research workers in the field of dairy science" and in presenting "basic data, fundamental observations and unbiased discussions of researches that contribute to the present status of the dairy industry." It cannot fail in its hope "to stimulate research along lines now lagging, thereby correcting somewhat the lack of balance in our knowledge of the scientific basis of the dairy industry."

In the discussion of milk and milk products, the book, comprising 542 pages, is divided into 4 parts and 15 chapters—(1) the constituents (5 chapters), (2) the physical chemistry (4 chapters), (3) the microbiology (4 chapters) and (4) the nutritional value and the physiology of milk secretion (2 chapters).

Twenty-eight present and former associates of Dr. Rogers contributed to the book. In five chapters there was one writer for each, while in the others the work was divided, two to six writers contributing to each chapter.

A superficial examination without knowing the purposed scope of the book as stated in the preface might lead one to think that some subjects were very inadequately treated as, for example, the composition of milk and milk products, but the book is intended only for those who are already familiar with the elementary facts of dairy science.

When one reads studiously, the impression gains that the editorial committee has shown excellent judgment in compositing the contributions of the different writers for the purpose of unifying the general scheme of the book. To avoid producing an encyclopedia, much restraint must have been exercised by the contributors.

Those interested in dairy chemistry will find a stimulating presentation in the first and second parts, especially the chapters discussing "Acid-Base and Oxidation-Reduction Equilibria of Milk" and "Physical Equilibria of Milk." It is a gratification to find in the chapter on "Metabolism and Growth of Bacteria" more than usual attention given to the chemical reactions taking place in different fermentations.

The reviewer of a book of such exceptional value hesitates to offer any criticism. However, it is his duty to call attention to the erroneous statement on page 211, "The free paracasein in cheddar cheese is soluble in a warm 5 per cent. salt solution, while the paracasein lactate produced by the acid in cottage cheese is insoluble in similar solutions," making reference to Bulletin 261, N. Y. (Geneva) Agr. Exp. Sta., 1905. Later work at the same station annihilated the existence of supposed casein and paracasein lactate (Tech. B. No. 3, 1906), while the substance soluble in warm, dilute solution of sodium chloride was shown in 1012 (Tech. B. No. 26) to be not free paracasein but a compound of paracasein with a minimum amount of calcium.

While the references to literature number over 1300, there are some statements of fundamental facts which are not recognized by proper references.

The book accomplishes an important purpose in revealing how much we do not yet know in the different fields of dairy science. The reviewer, in expressing his own personal gratitude to those who have made possible the preparation of this valuable book, represents the attitude of mind of every one who will have occasion to use it. The dedication of the book to Dr. Rogers in recognition of his twenty-five years of service in his present position is an honor well deserved.

L. L. VAN SLYKE

The Journal of the
American Chemical Society

VOL. 50 OCTOBER, 1928 No. 10

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

THE EFFECT OF THE POSITION OF SUBSTITUTION ON THE IONIZATION CONSTANTS OF SOME ORGANIC ACIDS

BY D. A. MACINNES

RECEIVED MARCH 14, 1928 PUBLISHED OCTOBER 6, 1928

Since the early work of Ostwald[1] a number of attempts have been made to obtain a definite relation between the ionization constant of a substituted fatty acid and the position, α, β, y, ... of substitution in the carbon chain. Wegscheider,[2] for instance, has given a table of factors by which the constant of an unsubstituted acid may be multiplied to obtain the corresponding constant of a substituted acid. With chlorine substitution, for example, these factors are $\alpha = 90$, $\beta = 6.2$, $\gamma = 2.0$, $\delta = 1.3$. Such factors are, however, admittedly approximate and are entirely empirical. The subject has also been discussed in various papers by Fliirscheim, Michael, Walker, Nelson and Falk, Derick, Simms, and Hixon and Johns.

The following simple relation, which has apparently been overlooked by the writers on the subject, holds for a large number of substituted acids. Briefly, if the logarithm of the ionization constant of each acid is plotted against $1/d$ in which $d = 1$ for the α position, 2 for the β position, etc., remarkably straight lines are obtained for a number of series of substituted acids. For instance, in Fig. 1, the data for the chlorine and hydroxyl substituted acids are plotted as described. The points under consideration are those marked a, β, y and δ corresponding to the equivalent substituted acids: the other points will be discussed later. In this plot the data have been chosen for the longest chain acid for which measurements are available. These straight lines mean, of course, that the data fit an equation of the type

$$\log K_s = C + S\frac{1}{d} \qquad (1)$$

in which K_s is the ionization constant of the substituted acid and C and S are constants. A similar plot, with a slightly greater value for the slope S, is obtained if the data are used for the acids having the substituent

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[1] Ostwald, *Z. physik. Chem.*, **3,** 170, **241,** 369 (1889).

[2] Wegscheider, *Monatsh.*, **23,** 287 (1902).

always on the last carbon atom of the chain. Such a series is, for instance, chloro-acetic acid, β-chloropropionic acid, γ-chlorobutyric acid, etc. The agreement is even better in this case than with the long chain series. It appears unlikely that the relation can be accidental. It must have a definite physical origin.

In this connection it is important to recall that if the mutual electric potentials of two charged spheres carrying charges of like sign are plotted as abscissas against the reciprocals of the distances between their centers a straight line is obtained. Thus a system consisting of two like-charged spheres will gain in mutual potential energy, E, by being brought near to each other, according to the relation

$$E = C' \frac{1}{d}$$

the energy E and the constant C' depending on the two charges and the dielectric constant of the space d separating them. It seems, therefore, that it may be more than an analogy that the free energy of ionization, R T log K, is connected with the distance, d, between the carboxyl group and, for instance, a combined chlorine atom by the same function as the energy of a system of two electrical charges is affected by the distance between them.

At an infinite distance, however, the expression for the electrical energy becomes zero, whereas the ionization constant of a long chain acid with the substituent at infinity would have, from Equation 1, an ionization constant

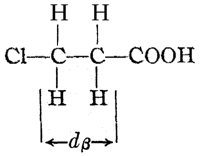
$$\log K_{\infty} = C$$

This is assuming, of course, that the tendencies observed in the change of ionization constants for the first members of the chain would continue without modification for very long chains, which may not be the case.

It might be expected, at first sight, that $\log K_{\infty}$ should be the ionization constant of such an unsubstituted long chain acid. The ionization constant of such an acid is nearly independent of the length of the chain, and varies irregularly between the narrow range 1.4×10^{-5} and 1.6×10^{-5}. The constant C, however, leads to a value of $\log K_{\infty}$ about 65% lower than this for chlorine substitution and about 43% lower for hydroxyl substitution. Though these constants are of the same order of magnitude as the ionization constant of the unsubstituted acid, it is evident that the latter does not fit into the equation or as a point in the plot.

On further consideration, however, it becomes clear that the unsubstituted acid is by no means a member of the series of substituted acids. The attachment of a chlorine or hydroxyl group to the chain can only take place by means of a vigorous chemical reaction or series of reactions, involving the removal of a hydrogen atom and its replacement by another atom or group. That this is attended by a lowering of the total energy of the molecule is shown by the fact that the heat of combustion of the substituted substance is lower than that of the unsubstituted material. It does not seem unreasonable to suppose, therefore, that the primary effect of the halogen or hydroxyl substitution into the molecule is a *lowering* of its free energy of ionization. The second effect is an increase of the ionization constant produced by bringing the negative substituent near to the carboxyl group. According to this point of view $C = \log K_\infty$ is the ionization constant of a hypothetical acid in which the chemical change of substitution has taken place, but in which the substituent is still at a long (theoretically infinite) distance from the carboxyl group. The term $S(1/d)$ is, accordingly, a measure of the potential energy involved in bringing the two negative groups near to each other. In any case, and whatever may prove to be the final interpretation of the physical meaning of the constant C, the effect of change of position of a substituent can, strictly, only be studied with isomeric compounds. Otherwise the results of changes of position of atoms or groups will be confused with the results of chemical reactions.

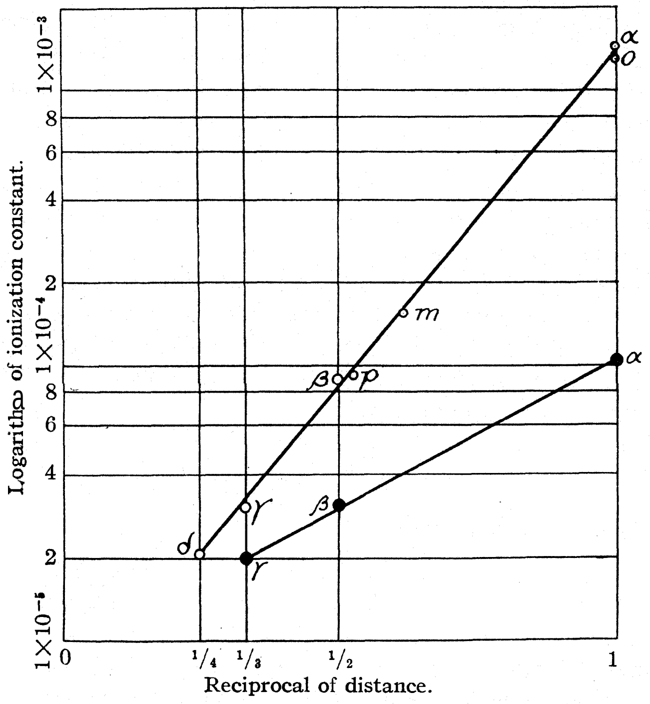
It is of interest to speculate as to the significance of the distance d in terms of atomic dimensions. It is my opinion that it refers to the distance between the polar bond joining the carboxyl to the carbon chain and the polar bond joining the other substituent to the chain, as, for instance, with β-chloropropionic acid



$$\mathrm{Cl{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}COOH}$$

The movement of a valence electron from a carbon atom to the outer shell of electrons of, for instance, a chlorine atom, probably takes place at such a bond. If the charges involved were situated in the center of the carboxyl carbon and chlorine atoms the series involving d would be $1/(1 + x)$, $1/(2 + x)$, $1/(3 + x)$ (x being the distance between the charges when the two groups are in contact) instead of 1, $^1/_2$, $^1/_3$, . . . as in Fig. 1. Using the available data on the sizes of atoms I have attempted to give values to x, without success. The best agreement with the data is obtained when $x = 0$. The length, d, appears therefore to be the distance between the polar bond joining the carboxyl group to the chain and the polar bond connecting the substituent to the chain, although, if the polar bond is a simple electric dipole, with a constant separation of the charges, the observed relations would not be expected.

Since the simple relation given in Equation 1 applies to the chlorine substituted aliphatic acids, it is important to discover whether the relation also applies to the aromatic series. In this connection it is important to note that o-chlorobenzoic acid and a-chlorobutyric acid have very nearly the same ionization constant. The two values are, respectively, 1.3×10^{-3} and 1.4×10^{-3}. It therefore seems reasonable to suppose that, as a close approximation, the polar bonds of the carboxyl group and of the chlorine atom are the same distance apart in the two molecules. Due to the angular relations imposed on the bonds by the ring structure, this can be nearly true for a flat ring, even though the substituent is on the second carbon atom from the carboxyl group in the ortho acid and on the first carbon atom in the a-substituted acid. With the "puckered" ring structure to be discussed below the bonds can approach still nearer each other. However, if we take the ratios of the o-, m- and p-distances as 1,2 and 3, respectively, we obtain a decided curvature on a plot similar to Fig. 1. More nearly straight lines, which are shown in Fig. 2, are obtained for the chlorine and methyl substituted benzoic acids, if the ratios of the distances across a regular hexagon, through the intervening space for the meta and para position, are used. With a regular hexagon, the ratios for the o-, m- and p-positions become $1 : \sqrt{3} : 2$. Though the plots in Fig. 2 are nearly straight lines, there is, nevertheless, a distinct bend upward in both.



○ = Cl substitution; ● = OH substitution.

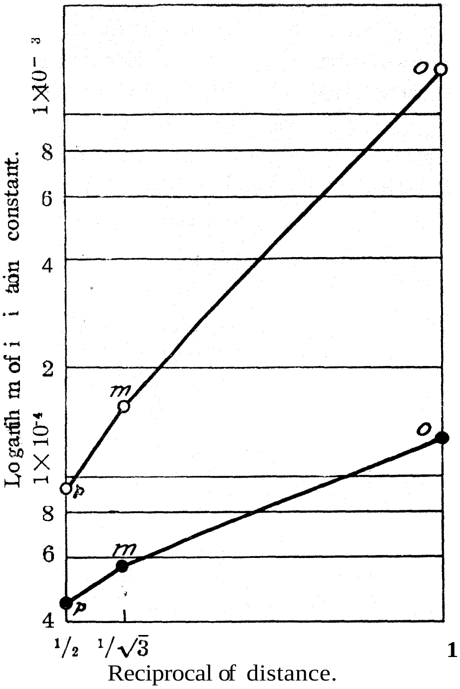
Fig. 1.—Chlorine and hydroxyl substituted acids.

A more probable structure for benzene seems to be, however, a "puckered" ring, that is to say, one in which the carbon atoms, and therefore the bonds to the hydrogen or other radicals, are in two parallel planes each containing three carbon atoms.[3] According to this conception the polar bonds would be at the corners of two equilateral triangles which are at a distance, we will call y, apart. The spacial arrangement is shown in Fig. 3. Considering the radius of a circle in which the triangles can be inscribed as unity the ratios of the *o*-, *m*- and *p*-distances are readily seen, in such a model, to be

$$d_o : d_m : d_p = \sqrt{1 + y^2} \ : \ \sqrt{3} \ : \ \sqrt{4 + y^2}$$

By assuming successive values for the distance y, a value 0.36 was found at which the curves in Fig. 2 become straight lines. This empirical procedure would be of little interest except that, dividing these newly computed ratios by $\sqrt{1 + y^2}$ (so that the ortho distance now equals unity) *the points for the three chlorobenzoic acids fall on the line containing the points for the long chain aliphatic chloro substituted acids.* The resulting points are marked o, *m* and *p* on Fig. 1. The equation

$$\log (K \times 10^5) = -0.30 + 2.44\,(1/d)$$



○ = ClC_6H_4COOH; ■ = $CH_3C_6H_4COOH$.

Fig. 2.

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[3] Attempts to explain the structure of benzene by positions of electrons led to the arrangement described. See, for instance, Huggins, THIS JOURNAL, 44, **1607** (1922), and 45, **264** **(1923)**; Lewis, "Valence and the Structure of Atoms and Molecules," Chemical Catalog Company, New York, 1923, p. 92; Morse, *Proc. Nat. Acad. Sci.*, **13**, 789 **(1927)**. Nendricks and Bilicke, THIS JOURNAL, 48, 3007 (1926), and Dickinson and Bilicke, *ibid.*, 50, **764** (1928), have arrived, by analysis of x-ray measurements, at a structure for benzene hexabromide having the bromine atoms in two parallel planes each containing three atoms, as in Fig. 3. Victor Henri, *Compt. rend.*, **174**, **809** **(1922)**; *J. Phys. Radium*, **3**, **181–214** (1922), has arrived at the same conclusion as a result of his extensive measurements on absorption spectra. On the other hand, the workers in the field of electric moments of molecules favor a flat molecule for benzene (Smyth and Morgan, THIS JOURNAL, 49, **1030** (1927), and Williams, *ibid.*, 50, **2350** (1928)), although the evidence seems inconclusive.

therefore, holds for both series of acids provided the distances d are computed as just described for the benzene substituted series. It is not impossible that the data are insufficiently accurate to decide between the two structures for the benzene ring, and the computations do not preclude the possibility of other structures. However, it is of interest to note that the data for these ionization constants at present in the literature favor the structure in which the carbon atoms are in two planes, provided, of course, that the underlying assumptions of this paper are accepted.

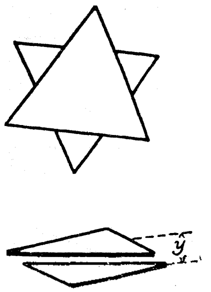

Fig. 3.

Most of the relatively few substituted benzoic acids that have been measured in the o-, m- and *p*-forms show at least fair agreement with the relations observed for the chlorine and methyl substituted acids. An exception, if the present data can be trusted, is the nitrobenzoic series. The hydroxyl acids agree reasonably well with the relation, but there is apparently no connection between the aromatic and aliphatic acids as is found for the chlorine series.

Turning our attention to the bromine and iodine substituted compounds, it has been found that the ortho and meta acids have, very closely, the same ionization constants as the corresponding chlorine compounds. This is shown in Fig. 4 in which the solid line, it will be observed, has the same ordinates and abscissas as in Fig. 1. (The data for the para-iodo and para-bromo acids have not yet been obtained.) With the aliphatic bromine and iodine compounds there seems to be a secondary effect producing systematic deviations from this line. Except for the a-substituted iodo acids, this effect is relatively small, and the solid line is the best that can be drawn through the points. A perceptible effect of the kind may possibly be seen in the slight deviations of the aliphatic chlorine compounds and it increases with the weight or complexity of the halogen atom. This effect may be due to the same cause that produces the other well-known systematic changes in carbon chains.

In these computations it has been assumed that the aliphatic carbon chains are straight, or, at least, that the distance d increases by regular increments as the substituent is moved out on the chain. This would be expected to be the case if the groups at each end strongly repel each other. If, however, a basic group such as NH_2 is substituted in the chain, this group and the carboxyl group can apparently attract each other, producing distorted molecules. Thus a basic group far out on a carbon chain may, by bending, get very near the carboxyl group, resulting in a lowering of the ionization constant and possibly inner salt formation. The ionization constants of amino substituted fatty acids are in fact found to be very small. On the other hand, the effects of substitution by basic groups in benzoic acid follow closely what would be expected from an undeformable benzene ring. The experimental data are particularly uncertain in this field and they are difficult to interpret since the acids are amphoteric and the ionization "constants" change rapidly with dilution. However, plots of the average "constants," as given by Scudder,[4] for amino- and N-methylaminobenzoic acids, give straight lines within the large experimental error when plotted as described above. It is found that the basic groups yield acids which increase with the distance of the substituted group from the carboxyl group. The CH_3NH-group, being probably more strongly basic than the NH_2-group, gives a weaker ortho acid and the effect of removal to the meta and para positions is greater than is the case with the amino group. Both of these effects would be expected from the theory as outlined above.

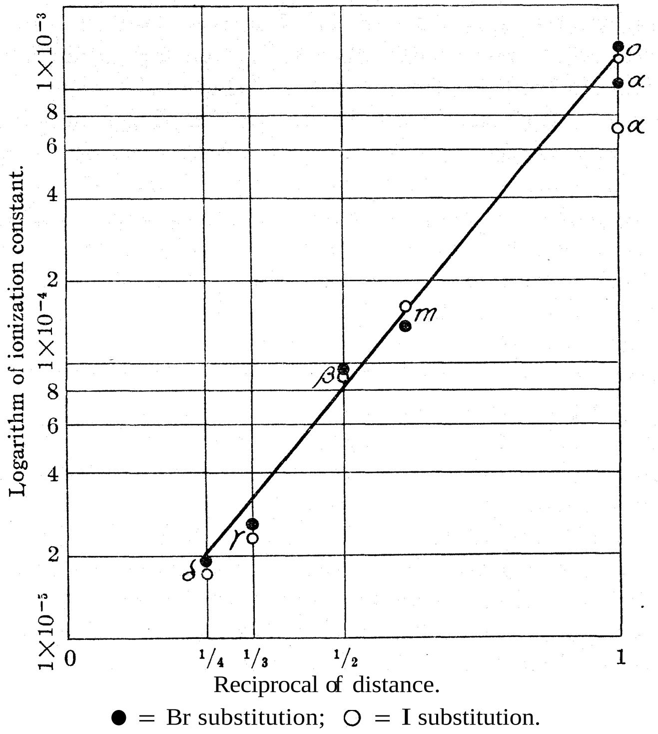

Fig. 4.—Bromine and iodine substituted acids.

It is an interesting fact that the aliphatic and aromatic data fall on the same line when the structure of the aliphatic molecule is such that a straight carbon chain is to be expected. The necessary condition is a strong electronegative group on each end of the chain. With com-

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[4] Scudder, "Conductivity and Ionization Constants of Organic Acids," D. Van Nostrand Co., New York, 1914.

pounds containing a carboxyl and a basic group there is no relation yet evident between the behavior of the aliphatic and aromatic series. The data for the latter fit Equation 1 at least roughly, as has just been stated. The aliphatic compounds, however, have very small ionization constants, which would be expected if bending and a consequent close approach of the positive and negative groups should occur. This appears to be evidence that the benzene ring is a stable system, and that the aliphatic chains are comparatively flexible.

Through the kindness of Dr. E. W. Washburn and Dr. James Kendall I have had access, before publication, to the recomputations of ionization constants made by the latter for the International Critical Tables. In these recomputations the best value for the limiting conductance of the hydrogen ion was used, and the data were otherwise, as far as possible, brought to the same standards for necessary fundamental constants. The plots in this paper were prepared from these recomputed constants which, as a matter of fact, differ but little, on the scale of precision which concerns us here, from those found in the last edition of Landolt and Bornstein. The constants used are all at 25°.

No attempt has been made in this paper to recompute the constants to allow for interionic attraction and ionic activities, as the author has done in a previous paper.[5] In the first place, sufficiently accurate data are not available for the recomputation for any except the few acids dealt with in that paper. Also such computations have shown that the value of a constant found by the older method of computation, for more dilute solutions, is not very different, due to a compensation of two factors, from a corresponding value computed on the newer basis. The latter, however, holds over a far wider range of concentrations even for relatively strong acids. The small difference between the two methods of computation may be illustrated by the constants for o-chlorobenzoic acid. The older method gives 1.28 X 10^{-3} as a limiting value and the newer 1.23 X 10^{-3}, the difference hardly appearing on a plot of the scale of Pig. 1. Provision is, however, already being made to redetermine the conductances of solutions of the chlorine substituted acids in order to obtain constants based on the more modern conceptions.

Brief mention may be made of some of the conclusions reached by others in this field. Derick[6] has proposed a "rule of thirds," which may be stated as follows. If K_u and K,, K_β, K_γ are the ionization constants of the unsubstituted acid and the *a*-, *β*- and y-substituted acids, respectively, Derick finds that

$$\frac{(\log K_u)}{(\log K_\alpha)} - 1 : \frac{(\log K_u)}{(\log K_\beta)} - 1 : \frac{(\log K_u)}{(\log K_\gamma)} - 1 : \ldots. = 1 : \frac{1}{3} : \frac{1}{9} \ldots$$

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[5] MacInnes, THIS JOURNAL, 48, 2068 (1926).

[6] Derick, *ibid.*, 33, 1152, 1167, 1181 (1911); 34, 74 (1912).

approximately, for several series of substituents. It is difficult to find a physical basis for this observation, especially as the chemical effect of substitution and the effect of shifting the substituent are both included, as has been shown above, when the formula contains K_u. Hixon and Johns[7] have, in an interesting paper, shown that the logarithms of the ionization constants for a large series of substituents can be plotted on smooth curves and expressed as empirical equations, as functions of an arbitrary "electron combining capacity," and also that the effect of the distance along the chain at which substitution takes place can be dealt with according to empirical formulas of the same form.

Summary

The ionization constants K_s of chlorine and hydroxyl substituted aliphatic acids follow the formula

$$\log K_s = C + S\frac{1}{d}$$

in which C and S are constants and $d = 1$ for the a-position, *2* for the β-position, etc. Theoretically this equation would follow if, in the first place, the substituting and carboxyl groups repel each other according to the inverse square of the distance between their polar bonds, and, secondly, the free energy of ionization is increased in proportion to the mutual potential energy of the two groups.

The ionization of the chlorine substituted benzoic acids follows the same formula accurately if the ortho distance is equal to the a-distance and a slightly "puckered ring" structure for the benzene nucleus is assumed.

The constants for bromine and iodine substituted aliphatic acids show small systematic deviations from the equation, although the corresponding aromatic compounds agree with it closely.

NEW YORK, N. Y.

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[7] Hixon and Johns, THIS JOURNAL, 49, 1786 (1927).

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

PHOTOCHEMICAL OZONIZATION AND ITS RELATION TO THE POLYMERIZATION OF OXYGEN

BY OLIVER R. WULF[1]

RECEIVED MARCH 14, 1928 PUBLISHED OCTOBER 6, 1928

It is a familiar fact that ozone is formed photochemically by irradiating oxygen gas with ultraviolet light. However, the assumption has always been made that this results from the absorption of radiation by the molecule O_2. The researches on photochemical ozonization, combined with related ones on the absorption of light by oxygen, afford evidence that the latter is not always the case, and that, rather, depending on the wave length used, the absorption may be due to another molecule, a polymer of O_2.

Most of our knowledge of this photochemical reaction has been gained through the quantitative researches of Warburg,[2] who studied ozonization at the wave lengths 2070 Å. and 2530 Å. in oxygen gas at high pressures, and measured the photochemical efficiency of ozonization for each of them. At wave length 2070 Å. he found conditions which nearly satisfied the photochemical equivalence equation, approximately two molecules of ozone being formed per quantum absorbed. This was not the case at 2530 Å. He concluded that the quantum corresponding to the former wave length was sufficient to dissociate the molecule 02, and that this process was in reality the primary photochemical act.

The above wave lengths, however, lie to the red of the familiar ultraviolet absorption of oxygen at room temperature and ordinary pressures. The author has recently discussed the absorption of the O_2 molecule in relation to that occurring at 2530 Å. and 2070 Å. in oxygen at high pressure.[3] It does not appear that either of the two known electronic levels in the O_2 molecule can account for the absorption at 2530 Å. nor for the major part of that at 2070 Å. The absorption of oxygen gas at these wave lengths resulting in ozonization is thus evidence for the existence of another molecular species than O_2 in oxygen gas.

A second point directly related to the above is evidence in this same direction. It was originally assumed by Warburg that, in those cases where unit quantum efficiency is found in endothermic photochemical processes, the primary act is the dissociation of the absorbing molecule. The results of recent experiments have borne out Warburg's point of view.[4]

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[1] National Research Fellow in Chemistry.

[2] Warburg, *Berl. Ber.*, **1911**, 746; **1912**, 216; **1914**, 872; *Z. Elektrochem.*, 26, 54 (1920); 27,133 (1921).

[3] Wulf, *Proc. Nat. Acad. Sci.*, **14**, 609 (1928).

[4] This does not mean necessarily that the longest wave length yielding unit quantum efficiency is a measure of the energy of dissociation of the molecule. In general it may be considerably greater, as discussed for instance in ref. **3.**

Where it has been possible to test this experimentally, it appears to be true, and stoichiometrical considerations make it plausible. Thus we know today that the primary act in the photochemical dissociation of hydrogen bromide and of hydrogen iodide is indeed dissociation of the molecule,[5] and these are classical illustrations, as a result of Warburg's researches,[6] of reactions in which the conditions of the photochemical equivalence equation are apparently met. Yet so far as we now know, neither of the two wave lengths used by Warburg are sufficient to dissociate the molecule O_2, the most probable value for its dissociation energy being 7 volts,[7] corresponding to a quantum of wave length 1751 Å. Here, then, is further indication that there exists in oxygen gas a molecular species other than O_2, which is actually absorbing the light, and for which in the absorption of wave length 2070 Å. the primary act is dissociation of the molecule.[8]

Professor G. N. Lewis[9] has given evidence that there is polymerization in oxygen and from the data on the magnetic susceptibility of oxygen at low temperatures has computed a value for the change in heat content accompanying this polymerization. He concludes that at the temperature of liquid air, or at room temperature and a pressure of several hundred atmospheres, a considerable fraction of the oxygen is in the form of the molecule O_4.

A series of researches on the absorption of light in gaseous oxygen at high pressures and in liquid oxygen bear out this point of view. These have been enumerated, and discussed in part, by the author in the articles mentioned under references 3 and 8. New absorption enters whose character and behavior with changing pressure indicate that it is not due to the molecule O_2. It increases in intensity more nearly as the square of the pressure, rather than directly as the pressure. Its character and position afford evidence that in the region of 2400 Å. the molecule O_4 is undergoing dissociation by the absorption of light into the components O_3 and O. Calculation of the energy of this dissociation supports the point of view; and at the same time a plausible explanation is afforded of the

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[5] Coehn and Stuckardt, *Z. physik. Chem.*, 91, 722 (1916); Bonhoffer and Steiner, *ibid.*, 122, 287 (1926); Tingey and Gerke, THIS JOURNAL, 48, 1838 (1926); Bernard Lewis, *J. Phys. Chem.*, 32, 270 (1928); Bonhoffer and Parkas, *Z. physik. Chem.*, 132, 235 (1928).

[6] Warburg, *Bert. Ber.*, 1916,314; 1918,300.

[7] Hogness and Lunn, *Phys. Rev.*, 27, 732 (1926); Birge and Sponer, *ibid*, 28, 259 (1926).

[8] The author has recently discussed, *Proc. Nat. Acad. Sci.*, 14, 614 (1928), the estimations of the heat of dissociation of oxygen that have been made from Warburg's data on photochemical ozonization. See Born and Gerlach, *Z physik.*, 5, 433 (1921), and Warburg, *Z. Elektrochem.*, 26, 58 (1920).

[9] Lewis, THIS JOURNAL, 46, 2027 (1924).

results of Warburg's quantum efficiency measurements. The wave length 2530 Å., which is to the red of this limit, would not be expected to give conditions approximating the equivalence equation, as has been discussed above, and indeed Warburg found that it did not, while λ 2070 Å., which is well to the short wave length side of this limit, did give conditions approximating the equivalence equation.

Thus there is evidence that the molecule O_4 is the absorbing molecule in photochemical ozonization at wave lengths 2530 Å. and 2070 Å., and that in the region of 2400 Å. a continuous absorption begins and stretches to shorter wave lengths, representing the dissociation of O_4 molecule into O_3 molecule and oxygen atom.

The behavior of this absorption with changing pressure is further evidence that it is due to the molecule O_4, and affords the possibility of making a quantitative estimate of the degree of polymerization. It is evident that the existence of the equilibrium between O_4 and O_2 gives at once a qualitative explanation of the tendency for this absorption to increase more rapidly than as the first power of the pressure. For low total pressures there would be predicted an increase proportional to the square of the pressure, as was recorded by early investigators. Liveing and Dewar suggested two possible explanations: (1) the existence of the molecule O_4 in equilibrium with O_2; and (2) an alteration of the O_2 spectrum by the influence at high pressures of neighboring molecules on those absorbing. Quantitative absorption measurements made by Warburg will now be considered.

For the two wave lengths 2070 Å. and 2530 Å., Warburg[10] measured the absorption over a range of pressures, in the case of the first wave length extending from 27.5 kg./cm.^{2} to 392.5 kg./cm.^{2}, and both for 95% oxygen and for air. Wave length 2530 Å. lies in the discontinuous spectrum,[3] that is, in the midst of the band progression that precedes the continuous spectrum. The change of the absorption of this wave length with pressure might be complicated by the pressure broadening of the band spectrum. Wave length 2070 Å., however, lies in the continuous spectrum, and the assumption that the absorption due to it is proportional to the number of absorbing molecules will probably be approximately true even to fairly high pressures. Warburg found that the absorption increased more rapidly than the pressure, but somewhat more slowly than the square of the pressure. He believed that there was sufficient evidence against polymerization as a possible explanation; at least this appears to be the case from a previous paper[11] in which he considered this absorption in liquid oxygen. Nernst had pointed out, for instance, that oxygen obeyed Trouton's rule and that this was evidence against the

[10] Warburg, *Berl. Ber.*, 1915, **230.**

[11] Warburg, *Verhandl. deut. physik. Ges.*, *17*, 194 (1915).

opinion[12] that liquid oxygen was appreciably polymerized.[13] Warburg felt rather that this failure of oxygen to obey Beer's law showed that the molecular absorption was influenced by neighboring molecules, an effect which Ångstrom[14] had ascribed to the action of collisions. Warburg treated his results entirely from this point of view.[15]

In view of the considerable amount of evidence pointing to the existence of the polymer O_4, it is our purpose to apply the idea of the polymerization to Warburg's results. Before passing to the calculation of the equilibrium constant, however, it must be mentioned that, as had been noticed by earlier observers, Warburg also found there was a considerable difference between the absorption of the oxygen in compressed air and that in compressed oxygen, the former being approximately two-fold greater than that in 95% oxygen for the same partial pressure. It seems probable, however,

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[12] See, for example, Hunter, **J.** *Phys. Chem.*, 10, **330** (1906); Dolezalek, *Z. angew. Chem.*, 222,2460 (1909); *Z. physik.* Chem., *71*, 191 (1910).

[13] The argument with regard to Trouton's rule would apply, however, only if the degree of polymerization in the liquid state were considerable and if the change in heat content accompanying depolymerization were large. At the normal boiling point oxygen appears to be about one-quarter polymerized, and Lewis (ref. 9) finds the change in heat content accompanying depolymerization to be 128 calories. The molal heat of vaporization of oxygen at the normal boiling point is 1632 cal. Dana, *Proc.* ***Amer.*** *Acad.*, **60**, 241 (1925).

[14] K. Angstrom, *Arkiv. Mat. Astron.* ***Fysik***, *Bd. 4* (1908).

[15] **A** brief discussion regarding this type of explanation seems necessary. According to it, the molecule acquires the ability to absorb through the influence of impacts by other molecules, this dying away with time after each impact. Thus this absorption depends not only on the number of molecules of this kind present, but also upon the number of times they are struck per unit of time. There is some similarity between such an explanation and the idea of polymerization. It would seem, however, that the new absorption, as it decays with time, might reasonably be expected to change not only in intensity but also in character, reverting toward that of the unstruck molecule. This new absorption in oxygen, while somewhat diffuse, as would be expected of any absorption at high pressures, bears the characteristics of clear-cut molecular absorption. It would seem more in keeping with present ideas to attribute it to some definite molecular species having a definite electronic configuration of its own, and in this way polymerization seems a more acceptable explanation. In long paths of oxygen the new spectrum appears at relatively low pressures and its general form is preserved even into the liquid state. That this absorption is some of the known absorption of O_2 in a displaced or distorted form appears not to be the case. The character of this spectrum has been discussed by the author under reference **3.** There is also a little evidence against the collisional point of view in the observation of Liveing and Dewar that this new absorption of oxygen appeared if anything to be slightly weakened in passing from normal temperature to 100°. The number of impacts per unit of time increases ***as*** the square root of the temperature, and thus, barring other complications, this would lead to ***a*** slight increase in the absorption from the point of view of Warburg's treatment. On the basis of the second suggestion of Liveing and Dewar, which depended on the average proximity of the molecules, no change would be expected, while from the point of view of polymerization one would predict a slight decrease in the O_4 concentration and hence in the absorption.

that the equilibrium $O_4 \rightleftarrows 2O_2$ may be considerably different in a solvent. At the highest pressure used by Warburg the concentration of nitrogen is less only by a factor of six than that of the solvent in water solution. That there is a difference in the amount of O_4 in pure oxygen and in air containing oxygen at the same partial pressure is not out of accord with the idea of polymerization.

Using Warburg's absorption data, the author had calculated the equilibrium constant in terms of partial pressures.[16] However, the assumption upon which the entire calculation rests is that the absorption is proportional to the number of O_4 molecules present. The absorption being thus employed as a measure of concentration (which is not proportional to partial pressure at these high pressures), it is evidently consistent to use units of concentration in the calculation and to express the equilibrium constant as

$$K_\rho = \frac{\rho_2^2}{\rho_4} = \frac{(\rho - \rho_4)^2}{\rho_4} = \frac{16c_2^2}{c_4}$$

where ρ_2, ρ_4 and p are the densities of O_2, O_4 and of the mixture, respectively in grams per cc., and the c's indicate concentrations in moles per cc. In the region where ρ_4 is small compared to ρ_2, one may write as a close approximation

$$\rho_4 = \frac{\rho^2}{K_\rho + 2\rho}$$

but above this, where the degree of association is appreciable, the expression is

$$\rho_4 = \frac{1}{2}\left(K_\rho + 2\rho - \sqrt{K_\rho^2 + 4\rho K_\rho}\right)$$

The absorption observations at the lower pressures are at higher concentrations than the pressure would indicate on the basis of perfect gas behavior, while just the reverse is true concerning the observations at the highest pressure, these being at a lower concentration than the pressure would indicate. Both these facts tend to raise the value of the constant compared with that calculated in terms of partial pressures and as will be seen make a very considerable difference in the final value.

For wave length 2070 Å. Warburg gives at seven different pressures the value of $z = \log_{10} J_0/J$ for 95% oxygen, where J_0 and J are the initial intensity and the intensity after passing through a length d of the gas. Assuming that Beer's law holds for the absorbing molecular species, O_4,

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[16] Wulf, Yroc. *Nat. Acad. Sci.*, **14**, 356 (1928). Over this range of pressures oxygen shows considerable deviation from the perfect gas law, the pv product passing through a minimum in the vicinity of 150 atmospheres and at 400 atmospheres being appreciably greater than its value at one atmosphere. The calculation was looked upon, however, as an approximate estimation. The result $K_\rho = 531$ atm. or, in other units, $K_\rho = 0.35$ g./cc., appeared not unreasonable, even though this indicated a rather surprisingly large degree of polymerization, considering that assumptions had been made which could be only approximately true.

we may write

$$z = \log_{10}\frac{J_0}{J} = d\cdot\mu_4\cdot c_4\cdot\log_{10} e = \beta\cdot p_4$$

where μ_4 is the molal absorption coefficient of the molecule O_4 for this wave length, and c_4 is the number of moles of O_4 per unit volume. It is evident that values of z for two values of p will afford a determination of K_p and the proportionality factor β.

In the following table the first and fifth columns are taken directly from Warburg's paper. The third and fourth columns give the corresponding pv product and density of the gas mixture which the author has obtained from the available data on the pressure–volume relations in oxygen at 20°.[17] The last column contains the values corresponding to the absorption of pure oxygen.[18] These are plotted in the figure against the corresponding densities of the gas mixture.

TABLE I

RESULTS

Pressure Kg/cm.²	Pressure Atm.	pv pa = 1 at 0° and 1 atm.	Density, g./cc.	z 95% O_2	z 100% O_2
27.5	26.6	1.056	0.0360	0.144	0.154
47.5	46.0	1.043	.0630	.382	.409
67.5	65.3	1.031	.0905	.736	.788
97	93.8	1.017	.132	1.30	1.39
195	188.6	1.014	.266	4.69	5.02
293.5	284.0	1.053	.385	9.84	10.53
392.6	380.0	1.127	.482	13.9	14.87

The curve inserted in the figure corresponds to the equation

$$z = \frac{\beta}{2}\left(K_p + 2p - \sqrt{K_p^2 + 4pK_p}\right)$$

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[17] Below 100 atm. there are recent data: above this the earlier measurements of Amagat have been used. The nearest temperature at which the latter measurements were made is 15.65°; but those also made by Amagat at 0 and 99 5° showed that above 100 atm. a linear interpolation would be quite justifiable and the values for pv at 100 atm. and above were so determined. These two sets of data do not meet exactly. The discrepancy is not great, however, and in the plotting of the 20" pv–p curve up to 500 atm. a smooth joining of the data has been made. The difference in the value of pv at 100 atm. as given by the two sources of data is only about 1%.

[18] Warburg deduced a formula to convert the absorption of 95% oxygen to the case of pure oxygen. This resulted in a uniform 7% increase at any pressure. Since in treating this work from the viewpoint of the polymerization we apply an equation of different form to Warburg's results than that which he used, it is evidently the experimentally observed absorption which we must consider rather than the equation which Warburg finally arrived at as expressing best his results on the basis of the theory mentioned in footnote 15. But it is advisable to apply the correction to the observed values, since the absorption for pure oxygen will be greater than for 95% oxygen at the same total pressure, and by an amount which is at least approximately given by the 7% correction.

with the values of $K_p = 1.2$ g./cc. and $\beta = \mathbf{133}$ cc./g. The percentage deviations of the observed from the calculated values about cancel one another. It should be noted that there is, however, a tendency for the values of z at low values of p to lie above the computed ones, while at high values of p the reverse is true. The cause of this is not evident. It may be due to deviations from the fundamental assumption of the proportionality between the absorption and the number of molecules of O_4 per unit volume. It may also be due to the fact that a small amount of absorption due to the molecule O_2 is also present at this wave length. If the curve were lowered somewhat in the vicinity of $c = 0.1$, holding the value at $c = 0.4$ as it is, for instance, this would result in an increase in the value of K_p. The reduction of the observations from 95% oxygen to pure oxygen by the factor 1.07 does not greatly affect the result.

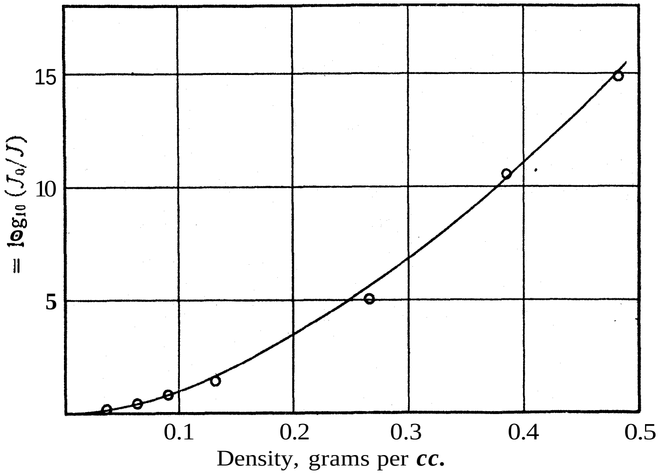

Fig. 1.

The value of the equilibrium constant obtained by Professor Lewis from the magnetic susceptibility measurements of Perrier and Onnes is $K_p = 4$ g./cc. Thus the value obtained in the present work is a little more than three-fold smaller, but the author feels that the agreement is satisfactory considering that assumptions which could only be approximately true have entered into this treatment of the absorption data. It may be that only the order of magnitude of the present result is significant.

The molal absorption coefficient of the molecule O_4 for this wave length may also be estimated. Warburg's values of z given in the table were for a thickness of gas of 1.72 cm. From the above

$$\mu_4 = \frac{\beta\cdot\rho_4}{d\cdot c_4\cdot\log_{10} e} = \frac{\beta\cdot M_4}{d\cdot\log_{10} e} = \frac{133 \times 64}{1.72 \times 0.434} = 1.1 \times 10^4 \text{ cm.}^2 \text{ per } mole$$

It might be suggested that the extent of polymerization indicated above, although small, should make itself evident in the observed pressure–volume relations. A moment's reflection shows that in the absence of any knowledge of the independent behavior of O_2 and O_4, no quantitative conclusions can be drawn. It may be pointed out, however, that the *pv* value for oxygen falls markedly below that for nitrogen, and at high pressures by an amount that is of the order to be expected if the difference is due in a considerable degree to the decrease in the number of molecules. Furthermore, the constant b of the van der Waals equation is smaller for oxygen than for nitrogen, which is suggestive in view of a tendency for this quantity to increase with increasing molecular weight, within a series of molecules built of the same number of atoms. It is not meant to imply that the molecule O_2 should behave at high pressure just as the molecule N_2, but the difference might not be expected to be great and the observed difference is in the direction to be accounted for by the polymerization. It is true that the ratio of pa for nitrogen and oxygen varies very little from 500 atm. to 3000 atm. Yet at these pressures the concentration is no longer even approximately proportional to the pressure and the increase in the total gas concentration will be small, the composition of the mixture changing only slowly in the direction of being richer in O_4. But again, the molecular size determined from viscosity measurements also gives a value for oxygen smaller than for nitrogen, and it is not evident that this should be affected by the polymerization. The paramagnetism of oxygen is undoubtedly also a factor in conditioning its behavior. There appears, at least, to be nothing in the pressure–volume relations inconsistent with the idea of polymerization, while the latter affords a plausible explanation of some points. The present work rests upon the facts of photochemical ozonization in connection with the new absorption of oxygen, which appears in the liquid and in the gas at high pressures and which shows so striking a departure from Beer's law.

This work had its origin in discussion with Professor T. R. Wogness of this Laboratory, and the author gladly acknowledges his indebtedness to him for valuable suggestions.

Summary

The characteristics of photochemical ozonization at wave lengths 2070 Å. and 2530 Å. afford important evidence for the existence of a polymer of the molecule O_2 in oxygen gas.

Related experiments on the absorption of light by oxygen gas at high pressures and in liquid oxygen support this, and indicate that this polymer is the molecule O_4.

Qualitatively, the change of the absorption with the pressure agrees with the idea that the absorption is due to the molecule O_4. Quantita-

tively the data afforded by the absorption measurements of Warburg lead to a value of the equilibrium constant $K_p = 1.2$ g./cc. Probably this is significant only in order of magnitude owing to the approximations entering into the treatment of the data.

BERKELEY, CALIFORNIA

Benzoyl peroxyde

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WASHINGTON]

THE INFLUENCE OF ACIDS AND BASES ON THE INHIBITORY EFFECT OF GELATIN UPON THE CATALYTIC DECOMPOSITION OF HYDROGEN PEROXIDE BY COLLOIDAL PLATINUM

BY H. V. TARTAR AND N. K. SCHAFFER

RECEIVED MARCH 15, 1928 PUBLISHED OCTOBER 6, 1928

Introduction

Roth Groh[1] and Iredale[2] have stated that the inhibitory effect of protective colloids upon the catalytic decomposition of hydrogen peroxide by colloidal platinum is approximately proportional to their protective properties as measured by Zsigmondy's "gold number." Tartar and Lorah[3] and later Reinders,[4] using proteins as protective colloids, investigated the influence of different degrees of acidity and alkalinity on the "gold number" and concluded that the variation of the protective action was in accordance with the known amphoteric character of the proteins.

The work presented herein is a study of the influence of different degrees of acidity and alkalinity on the inhibitory effect of gelatin upon the catalytic decomposition of hydrogen peroxide by colloidal platinum. It was undertaken in order to determine whether or not under these ,conditions the variation of the inhibitory effect is similar to that of the protective effect, as shown by Zsigmondy's "gold number."

Experimental Part

***(a)* Preparation of Materials.**—The colloidal platinum was prepared by Bredig's arc method using a direct current, 110 volts and 8 amperes. The platinum was dispersed in a solution of 0.001 M potassium hydroxide as a peptizer. After standing for a few weeks in clean Pyrex flasks to permit the larger platinum particles to settle, the sol was carefully decanted and made uniform by mixing. The concentration then determined was 12.5 mg. of platinum per liter.

The gelatin ("Silver Label" brand) was purified and made isoelectric according to the procedure recommended by Loeb[5] and dried *in vacuo* at 65–70'. The gelatin sol used was prepared by adding 0.05 g. of gelatin to 100 cc. of water and heating the mixture

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[1] Groh, *Z. physik Chem.*, *88*, **414 (1914).**

[2] Iredale, **J.** *Chem. Soc.*, 119, **109 (1921);** *ibid.*, 121, **1636 (1922).**

[3] Tartar and Lorah, **J.** *Phys. Chem.*, 29, *792* **(1925)**

[4] Reinders, *Chem. Weekblad,* 22, **481 (1925).**

[5] Loeb, "Proteins and Theory of Colloidal Behavior," McGraw-Hill Book Co., New York City, 1922, p. **35.**

at 50° for four hours to permit the sol to come to "equilibrium."[6] The sol was then diluted to 250 cc. and allowed to cool slowly to 25°. Five cc. of this sol in 100 cc. of the reaction mixture gave a concentration of 0.001% of gelatin. This concentration was used in all experiments. The gelatin sol was used a few hours after its preparation to eliminate any effects due to aging.

The hydrogen peroxide (Merck's) was purified by distillation under reduced pressure.

(b) Method of Procedure.—The reactions were run in uniform, calibrated, 100cc. volumetric flasks, kept in a thermostat at 25°. The desired quantity of platinum sol was pipetted into the fiask and the gelatin, acid, or base added; then the mixture was immediately diluted to 95 cc. and shaken. At this time the flask was placed in the thermostat and after exactly fifteen minutes, 5 cc. of the hydrogen peroxide solution was added, the time observed and the mixture shaken. The initial concentration of the hydrogen peroxide was determined in a separate flask containing none of the catalyst At subsequent intervals 5 cc. of the reaction mixture was pipetted into dilute sulfuric acid and titrated rapidly with potassium permanganate, 0.03 N.

It was found expedient to express the results in terms of the time required for half of the peroxide used to decompose, the half period, since the velocity constant is inversely constant proportional to the time for 50% decomposition.

Although the order of the reaction is uncertain, reaction constants using the unimolecular formula, $K = 1/t \log_{10} (a/(a - x))$, were calculated for a few typical acid and alkali runs with and without gelatin, to afford some idea of the progress of the reactions. The data are given in Table I. With

TABLE I

TYPICAL ACID AND ALKALI RUNS WITH AND WITHOUT GELATIN AND THE CALCULATED REACTION CONSTANTS

t = time in minutes. $a-x$ = re. of potassium permanganate

Sulfuric Acid at PH of 3.3

Without gelatin			With gelatin		
t	$a-x$	K	t	$a-x$	K
0.0	12.40	....	0.0	12.40	...
2.5	9.42	0.047	9.0	9.67	0.0119
5.5	7.01	.045	16.0	8.05	.0117
8.0	5.41	.045	22.5	6.85	.0116
11.0	4.02	.044	28.0	5.91	.0115
			31.0	5.50	.0114

Sodium Hydroxide

Without gelatin, PH = 8 4			With gelatin, PH = 11.85		
t	$a-x$	K	t	$a-x$	K
0.0	4.05	....	0.0	3.89	...
39	3.05	0.0031	4.0	3.19	0.021
65	2.45	.0034	6.5	2.74	.023
81	2.13	.0035	11.0	2.15	.023
85	2.05	.0035	12.5	2.01	.023
90	1.90	.0037	14.0	1.78	.024
			15.5	1.66	.024

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[6] Elliott and Sheppard, *J. Ind.* and Eng. *Chem.*, 13,699 (1921).

sulfuric acid without gelatin the value for K fell rapidly, showing that the colloidal platinum quickly became less active as a catalyst. At this same acid concentration in the presence of gelatin, however, the value for K decreased very much more slowly, indicating a stabilizing action of the gelatin. With the alkalies, K increased both in the presence and absence of gelatin.

The hydrogen-ion concentration was determined electrometrically. Very little difficulty was experienced from the presence of the gelatin and the colloidal platinum.

Results and Discussion

(a) Reproducibility.—In general, under carefully controlled conditions the reproducibility of the experimental results was excellent with alkalies, but only fair with acids. It was better with than without gelatin. Preliminary experiments showed that the period during which the platinum sol remained diluted and the time that the acid or alkali was in contact with the platinum, before the addition of hydrogen peroxide, had to be controlled. Immediate dilution of the platinum sol and addition of hydrogen peroxide gave extremely poor results. Bredig and Muller von Berneck[7] have reported like findings in their studies of the catalysis of the decomposition of hydrogen peroxide. It was found that the method given above gave the best results with acids; however, the half period even in this method had to be shortened (by increasing the concentrations of platinum and hydrogen peroxide) to give results of quantitative significance. The smaller the time of the catalysis, the less the time for the action of foreign influences.

Reproducibility of results with acids below a PH of 3.5 equaled that with alkalies; however, from a PH of 3.5 to 8,[8] deviations of 15% or more occasionally occurred. Similar discrepancies have also been noted by Bredig and Ikeda,[9] who in studying the effect of various substances on the hydrogen peroxide catalysis with platinum, report that, "between parallel runs sometimes there occur errors of more than 20 per cent. in the velocity constants, which by no means are accounted for by errors of manipulation; but are explained by very slow changes in the condition of the platinum sol, due to its extremely great sensitiveness toward traces of certain poisons, which cannot be excluded from the air of a large chemical laboratory."

(b) Experiments **with** Acids.—The results are given in Table II and presented graphically in Fig. 1 for acetic, sulfuric and phosphoric acids, respectively. In all these runs, 50 cc. of the platinum sol was used, the concentration in 100 cc. of the reaction mixture being 6.25 mg. of platinum

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[7] Bredig and von Berneck, Z. *physik. Chem.*, **31**, 286 (1899).

[8] Since the platinum sol contained sodium hydroxide, it was possible to add acids and yet the sol react alkaline.

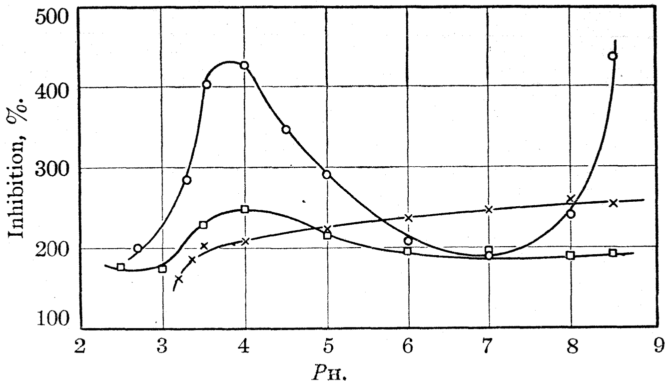
[9] Bredig and Ikeda, Z. *physik. Chem.*, **37**, 3 (1901).

per liter. The initial concentration of the hydrogen peroxide was 0.076 *N*. The per cent. of inhibition at any *Pa* was calculated by subtracting the half period without gelatin from that with gelatin, dividing the result by the half period without gelatin and multiplying by 100.

TABLE II

VARIATION OF THE INHIBITORY EFFECT OF GELATIN WITH CHANGE OF PH WITH DIFFERENT ACIDS

PH	Half period, without gelatin, *T* minutes	Half period, with gelatin, T_G minutes	Inhibition, $\frac{T_G-T}{T}100$, %
	Acetic Acid		
3.20	10.5	27.7	164
3.35	10.6	30.5	188
3.50	10.7	32.5	204
4.00	10.9	33.5	207
5.00	11.1	36.0	224
6.00	11.3	38.0	236
7.00	11.5	40.0	248
8.00	11.7	42.0	259
8.50	11.9	43.0	254
	Sulfuric Acid		
2.70	6.2	18.6	200
3.30	6.8	26.2	285
3.55	7.5	37.6	402
4.00	9.5	50.0	427
4.50	11.4	51.0	347
5.00	13.0	51.0	292
6.00	17.0	51.0	209
7.00	18.0	51.0	191
8.00	15.0	51.0	240
8.50	9.5	51.0	437
	Phosphoric Acid		
2.50	7.8	21.5	176
3.00	8.0	22.0	175
3.50	8.5	28.0	229
4.00	9.5	33.0	247
5.00	11.5	36.5	217
6.00	13.5	40.0	196
7.00	14.5	43.0	197
8.00	16.0	46.5	191
8.50	16.5	48.5	194



○, sulfuric acid. □, phosphoric acid; ×, acetic acid.

Fig. 1.—Influence of acids on the inhibitory effect of gelatin upon the catalytic decomposition of hydrogen peroxide.

Inspection of the curves for the acids shows that in all cases the inhibition increases rapidly to a PH of 3.5 to 4, but beyond this PH it constantly increases with acetic acid, decreases with phosphoric acid and first decreases then increases with sulfuric acid. However, the noteworthy conclusion to be drawn from these results is that the inhibitory effect in the acid range is not completely comparable to the protective effect, for if it were, we should expect the inhibitory effect to increase not at a PH of **3.5** but at 4.7, the isoelectric point of gelatin, as was the case of the "gold number."[3] Apparently the acids affect not only the gelatin but also the catalysis. The different shapes of the curves are perhaps attributable to the specific effects of the acid anions.

(c) Experiments **with** Alkalies.—The experiments with alkalies convincingly disclose a dissimilarity between inhibition and protection. The data are presented in Table III and Fig. 2 for potassium hydroxide, barium hydroxide and sodium hydroxide, respectively. Reinders[4] has shown that the protective effect of gelatin from a PH of 5.5 to 11 is large and constant, whereas it is here shown that the inhibitory effect in the alkaline range is small, variable and even becomes accelerative at certain concentrations. The smallest recorded inhibition in the acid range is even greater than the largest inhibition in the alkaline range. Groh[1] reported less efficient protective action of gelatin in 0.1 N sodium hydroxide than in neutral solution. Rocasolano,[10] studying inhibition, found an increase of catalytic power beyond a certain concentration of sodium protalbinate, which he attributed to its alkaline reaction.

TABLE III

VARIATION IN THE INHIBITORY EFFECT OF GELATIN WITH CHANGE OF PH WITH DIFFERENT ALKALIES

PH	Half period, without gelatin, T, minutes	Half period, with gelatin, T_G, minutes	Inhibition, $\frac{T_G - T}{T}$ 100, %
	Potassium Hydroxide		
8.7	160.0	116.0	−27.5
9.0	95.0	95.0	0.0
9.5	52.0	70.0	34.0
10.0	35.0	51.0	50.0
10.5	23.0	35.5	52.1
11.0	16.0	22.0	37.5
11.5	11.0	13.3	20.9
12.0	8.4	10.3	22.6
12.5	8.1	9.6	18.5
	Barium Hydroxide		
8.7	773.0	106.0	−38.7
9.0	86.0	86.0	0.0
9.2	71.0	77.0	8.5
9.5	56.0	66.0	17.9
10.0	38.0	48.0	26.3
10.5	26.5	33.5	26.3
11.0	17.5	21.5	22.8
11.5	11.0	12.5	13.6
11.9	8.0	8.0	0.0
12.1	7.0	6.2	−11.4
	Sodium Hydroxide		
8.1	176.0	90.0	−48.8
8.5	76.0	40.0	−47.4
9.0	50.0	26.0	−48.0
9.5	34.0	18.0	−47.0
10.0	23.0	14.0	−39.1
10.5	15.0	10.7	−28.7
11.1	10.0	10.0	0.0
11.5	8.0	11.0	37.5
12.0	8.2	16.0	95.1
12.3	10.0	24.0	140.0

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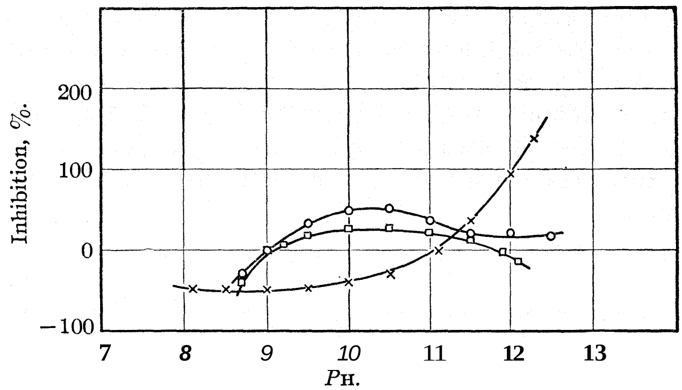
[10] Rocasolano, *Compt.* rend., **173,** 41 (1921).

The potassium hydroxide and barium hydroxide curves are very similar, indicating that the hydroxyl ion is the dominant factor in the catalysis. The hydroxyl ion apparently promotes the catalysis by its peptizing action on the platinum and also by directly decomposing the hydrogen peroxide." Since in alkaline solution the reaction is markedly accelerated, a smaller quantity of platinum sol had to be used. With potassium hydroxide and barium hydroxide, 10 cc. of the platinum sol was used, giving a concentration of 1.25 mg. of platinum per liter. The initial concentration of the hydrogen peroxide was 0.075 N. In the runs with sodium hydroxide only 5 cc. of the platinum sol was used, a concentration of 0.625 mg. of platinum per liter. The initial concentration of the hydrogen peroxide was 0.0077 N and titrated with 0.001 N potassium permanganate. The divergencies between the potassum hydroxide and barium hydroxide curves on the one hand and the sodium hydroxide on the other are undoubtedly chiefly due to the different proportions of the materials used. Thus from Fig. 2 barium hydroxide at a *PH* of 9.5 and potassium hydroxide at a PH of 9.6 give per cent. inhibitions of 17.9 and 37.5, respectively, whereas using the concentrations of hydrogen peroxide and platinum as in the sodium hydroxide runs and keeping the *PH* the same, the per cent. inhibitions were found to be —7.9 and —20.9, respectively.



○, potassium hydroxide; □, barium hydroxide; X, sodium hydroxide.

Pig. 2.—Influence of bases on the inhibitory effect of gelatin upon the catalytic decomposition of hydrogen peroxide.

In conclusion the writers wish to point out that the catalysis of hydrogen peroxide by colloidal platinum will be markedly influenced by the extent and character of the platinum surface. Zsigmondy[12] specifies very fully how the gold sol must be prepared for the determination of the "gold

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[11] Lemoine, *Compt.* rend., **161,** 47 (1915).

[12] Zsigmondy, *Z. anal.* Chem., **40,** 687 (1901).

number." In any use of the catalysis by platinum of the decomposition of hydrogen peroxide for the measurement of protective action, there should be a careful standardization of the method.

Summary

1. A study has been made of the influence of different concentrations of acid and alkalies on the inhibitory effect of gelatin upon the catalytic decomposition of hydrogen peroxide by colloidal platinum.

2. In the acid range the variation of the inhibition is evidently a function of the specific effect of the acid anion as well as of the hydrogen-ion concentration.

3. In the alkaline range the variation of the inhibition depends chiefly upon the hydroxyl ion concentration.

4. At any P_H the inhibition depends upon the concentration of the hydrogen peroxide and platinum used.

5. The results indicate that not only the gelatin but also the catalysis itself is influenced by the acids and alkalies; therefore the variation of the inhibitive effect is not similar to the protective effect as shown by the "gold number."

SEATTLE, WASHINGTON

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE PENNSYLVANIA STATE COLLEGE]

THE EQUILIBRIUM BETWEEN HYDROGEN-CARBON MONOXIDE AND METHANE-CARBON DIOXIDE IN THE CORONA DISCHARGE

BY GERALD L. WENDT AND GREGG M. EVANS

RECEIVED MAY 2, 1928 PUBLISHED OCTOBER 6, 1928

Introduction

The subject of chemical reaction in the electrical discharge has long been of interest. Andrews and Tait,[1] Brodie,[2] Thenard,[3] and Berthelot[4] seem to have been the earliest workers. Since then a large number of investigators[5] have studied various reactions, and many others have worked on

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[1] Andrews and Tait, *J. Chem. Soc.*, **13**, **344** (1861).

[2] Brodie, *Phil. Mag.*, [4] **44**, **470** (**1872**).

[3] Thenard, *Compt. rend.*, **75**, **118** (**1872**).

[4] Berthelot, *ibid.*, **82**, **1357** (**1876**); *Bull. soc. chim.*, [2] *26*, **101** (1876).

[5] Anderegg, THIS JOURNAL, **39**, **2581** (**1917**); **47**, **2429** (**1925**); *Trans. Am. Electrochem. Soc.*, *44*, **203** (**1923**); *Proc. Indiana Acad. Sci.*, **1921**, **p. 157**; **(b)** Briner, Meiner and Rothen, *Helv. Chim. Acta*, **9**, **409** (**1926**); *(c)* Collie, *J. Chem. Soc.*, **79**, **1149** (**1901**); (d) Comanducci, *Rend. accad. sci. Napoli*, **15**, **15** (1909); (e) Crespi and Lunt, *J. Chem. Soc.*, **127**, **2051** (**1925**); (f) Crocker, *Phys. Rev.*, **8**, **344** (**1916**); **(g)** Dem'yanov and Pryanishnikov, *J. Russ. Phys.-Chem. Soc.*, **58**, **462** (**1926**); (h) Elliott, Joshi and Lunt, *Trans. Faraday Soc.*, **23**, **57** (**1927**); (i) Elliott, *ibid.*, **23**, 60 (**1927**); **(j) Grubb,** *Thesis.*

the electrical considerations. In general two types of apparatus have been used: the ozonizer, with the discharge taking place between two concentric cylinders, and the type here used, with the discharge between a central wire and a concentric cylinder. Although both of these have been called by the name of corona, the name having been applied as early as 1872 by Reynolds[6] to the phenomenon on the balls of a static machine, the wire-in-cylinder type corresponds more closely to the corona of the electrical engineer,[7] and will be so called in this paper.

Since the gases are important commercially, and since from at least one side the reaction has been studied catalytically, it seemed worth while to study the effect of the corona discharge upon the reaction, $2H_2 + 2CO = CO_2 + CH_4$. This reaction has accordingly been investigated with emphasis upon the gaseous phase, and this has been found to reach a constant composition from both sides of the reaction. The method of constant pressure has been used to avoid any influence of pressure changes upon the course of the reaction. Since the gas volume continues to contract even after this constant composition is reached, it is evident that some other reaction accompanies or follows the one given, and probably goes to completion.

The Experiments

Gases Used.—Carbon monoxide was generated from sodium formate and concentrated sulfuric acid, stored over saturated brine containing sodium hydroxide, analyzed and transferred as soon as possible to the gas holder. Hydrogen and carbon dioxide were taken from tanks, the former being led over hot copper for removal of oxygen. Natural gas[8] was used for methane. This contained about 0.4% of carbon dioxide and 3.4% of ethane.

Hydrogen and carbon monoxide, or methane and carbon dioxide, whichever pair was being used, were mixed in as nearly equal proportions as possible by means of approximate calibrations on a gas holder of the type suggested by Burrell, Seibert and Jones,[9] but constructed entirely of glass, mercury being used as the confining liquid.

Univ. of Chicago, 1921; (k) Jackson and Northal-Laurie, J. *Chem. Soc.*, 89, 1190 (1906); (l) Joshi, *Trans. Faraday Soc*, 23, 227 (1927); (m) Rideal and Kunz, *J. Phys. Chem.*, *24,* 379 (1920); (n) Lob, *Z. Electrochem.*, 12, 282 (1906); (o) Losanitsch and Jovitschitsch, *Ber.*, 30, 135 (1897); (p) Lunt, *Proc. Roy. Soc. London*, **108A,** 172 (1925); (q) Lunt and Ramavenkatasubbier Venkateswaran, J. *Chem. Soc.*, *1927,* 857; (r) Montemartini, *Gazz. chim. ital.*, II, 52, 96 (1922); (s) Newsome, THIS JOURNAL, 48,2035 (1926); (t) Ott, *Ber.*, 58, 772 (1925); (u) Sacks, *Ann. Phys.*, 47, 886 (1915); (v) Wendt and Farnsworth, THIS JOURNAL, 47,2494 (1925); (w) Wendt and Snyder, *ibid.*. 50, 1288 (1928).

[6] Osborne Reynolds, *Chem. News*, 25, 113 (1872).

[7] Peek, "Dielectric Phenomena in High Voltage Engineering," McGraw-Hill Book Co., New York, 1920; Whitehead, "Dielectric Phenomena," D. Van Nostrand Co., New York, 1927.

[8] We are indebted to Mr. Walter F. Booth, of the Little Rock Gas and Fuel Co.. Little Rock, Arkansas, for the gift of several cylinders of natural gas unusually high in methane content and practically free from non-hydrocarbons.

[9] Burrell, Seibert and Jones, U. S. Bur. *Mines Bull.*, No. 197, p. 61.

The mixture was analyzed after standing for several hours and the calculated amount of gas added to correct the composition of the mixture to equality in the two constituents. After standing overnight a check analysis was made to determine the final composition of the mixture. Preparing gas mixtures of equal parts was difficult and it was impractical to make corrections to within 1% of the exact amounts. Special efforts were made to exclude oxygen from the mixture because of pronounced effects on the reaction caused by even small quantities of this gas. The mixture was drawn off from this holder with a gas buret, dried over concentrated sulfuric acid in a Hempel gas buret and loaded into the corona tube.

The Corona Tube.—The corona tube is shown in Fig. 1. It was constructed of Pyrex glass, the foundation being a twenty-inch, sealed-in Liebig condenser. To the ends of the inner tube were sealed as shown the 3-way stopcocks for manometer, vacuum and loading connections, and to the lower end the large cylinder D. In this latter was inserted a piston made from a rubber stopper and a jointed rifle cleaning rod, by means of which the volume of the apparatus could be varied. The total length of the main tube was 103.5 cm. The length of the short top segment was 6.5 cm., and its volume 16.7 cc. The length of the tube within the condenser jacket, to which the discharge was confined, was 51 cm. and its diameter 1.15 cm. Its actual volume was **53.8** cc. The distance from the lower end of the jacket to the center of the stopcock B was 8.5 cm. The length of the large cylinder was **37.5** cm. and its internal diameter **2 cm.** The 85cc. calibration mark was slightly below the lower stopcock, and with the piston inserted at its lowest possible point the total volume was 175 cc. The reaction space was then approximately one-third of the total volume. This is small, but experiments showed that diffusion of bromine from the lower end of the tube was practically complete in five minutes; nor could any difference greater than the experimental error be found in the analysis of samples taken from the top of the tube immediately after cessation of the discharge, and the next sample from lower down in the tube. The volume of the tube could be varied from about 83 cc. to the maximum by movement of the piston. The 2mm. capillary connecting the stopcock **A** with the main tube was 4 cm. long and that for C, 8 cm. The manometers were both of 2mm. capillary. The amount of dead space was therefore negligible. The high potential electrode consisted of a platinum wire 0.51 mm. in diameter (B. and S. gage 24), centered in the inner tube and

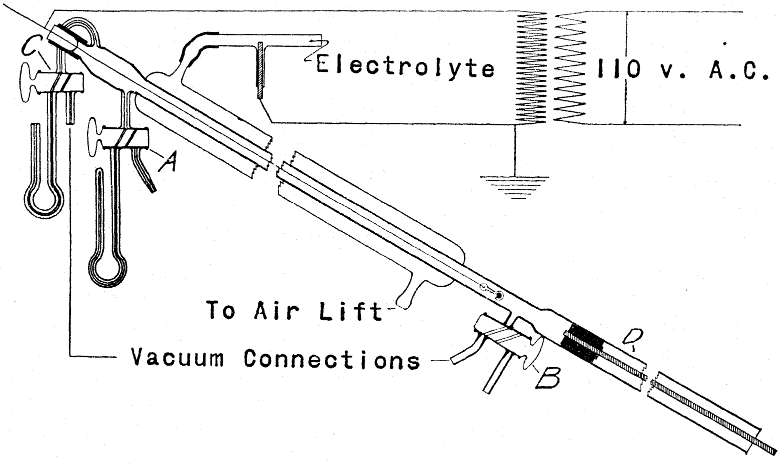


Fig. 1.

fastened at its lower end to a heavy platinum wire hook, which in turn engaged a glass cross bar in the tube about two centimeters above the lower stopcock. At the upper end it was sealed through the lower end of a short cylinder of glass tubing of the same size as the corona tube, a flexible connection for the purpose of centering and putting tension upon the wire being obtained by means of a piece of heavy rubber tubing, wired and shellacked. A cord from the top of the wire was led over a pulley to a weight. A dilute solution of acid was circulated by means of an air lift through the outer jacket and a reservoir set above the tube and served both as the grounded electrode and a cooling medium. A thermometer for measuring the temperature of the electrolyte was inserted at the lower opening of the condenser jacket.

Electrical Equipment.—The power was taken from the 110-volt, 60-cycle lighting circuit, through a Thordarsen transformer with a secondary rating of 20,000 volts. The line voltage was subject to fluctuations of at times as much as 10%, so that it was impossible, even with careful watching of the meters, to keep the input absolutely constant. The primary amperage, the voltage drop across the transformer and the secondary milliamperage were measured by means of appropriate Weston instruments. The secondary voltage was obtained by means of a 10,000 volt Braun electrostatic voltmeter with a series condenser, the effect of the condenser being obtained by means of low voltage measurements with and without the condenser inserted. These measurements are believed to be accurate to within 5%.

Manipulation.—Each time before using the reaction tube was cleaned with boiling dichromate-sulfuric acid cleaning solution, washed with distilled water until the washings no longer tested acid to methyl orange, and dried by means of air which had been run through two wash bottles of concentrated sulfuric acid and a tube filled with glass wool to remove acid spray. To make a run the piston was lubricated with a small amount of paraffin stopcock grease (which did not measurably absorb the gases used) and inserted in the cylinder D to its upper end. The mercury in the open manometer was drawn to the stopcock at C and the stopcock was turned to connect with the vacuum. The open end of B was cbnnected by means of a rubber tube with a leveling bottle of mercury, the mercury raised just to the stopcock and held by turning the cock. The stopcock at A was connected with the vacuum manometer and evacuation begun. A pressure as low as twenty millimeters was ordinarily easily obtainable with the water pump used. The tube was then shut off from the vacuum line and held under vacuum to test for leaks. The gas buret containing the dried mixture was next connected with the opening at A and the gas allowed to enter the tube. The buret was then disconnected and the end of the capillary capped. This evacuation and filling were twice repeated, evacuating once from C and once from B, so as to sweep out as completely as possible all air in the side tubes. After the last filling a second buret-full was drawn in by pulling the piston carefully down to the calibration mark for the desired initial volume. This was ordinarily 160 cc. The stopcock C was then connected with the open manometer, the gases were brought down to atmospheric pressure by momentarily opening A, and the power was turned on. During the run the pressure was kept constant by changing the volume as required by means of the piston. At the end of the run the analytical buret was connected with A and the sample forced out by means of the piston, or by running in the mercury at B, first sweeping out the capillary at A. To get samples of the tube washings a few cubic centimeters of the solvent were drawn in at A and run up and down in the tube by means of the mercury, finally being ejected into a container.

As a milliameter was available only toward the latter part of the work, the runs were made unless otherwise stated with a constant primary current of two amperes. This gave a primary voltage drop of 87 to 88 volts, corresponding to fifteen kilovolts in the secondary circuit, as calibrated. The secondary current increased during an experiment from 6 4 to somewhat over 7.0 milliamperes, depending upon the length of the run.

Analytical Methods.—The Hempel type of gas analysis apparatus was used, as any of the Orsat types suitable for complete analysis were found insufficiently portable for use in this connection. A calibrated 50cc. buret was employed, made from an Exax titration buret, with mercury as the confining liquid. Carbon dioxide was absorbed in potassium hydroxide, oxygen in alkaline pyrogallol, carbon monoxide in ammoniacal cuprous chloride, and hydrogen and methane were determined by combustion over mercury. In the preliminary analyses of the carbon dioxide and methane mixtures the ethane could be determined separately, but in the final analyses both ethane and methane show under methane. In the preliminary analyses of the hydrogen and carbon monoxide mixtures carbon monoxide was more conveniently determined by combustion. No unsaturated compounds beyond the error of the analytical methods could be found, so that after the first ten or fifteen experiments this determination was omitted. The formaldehyde titrations were made with potassium iodide, 0.01 N dichromate and 0.01 *N* thiosulfate solutions.

The Results

The Equilibrium.—The initial expansion due to the "corona pressure," as recorded by former investigators in this field, was evident on closing the switch. This was followed by a slower expansion caused in part by temperature increase. An expansion would be expected when carbon dioxide and methane were used for the starting gases. Actually this lasted for only about twenty-five minutes and a correction for the temperature increase taking place during that time showed that the actual corrected maximum came after fifteen minutes. From then on the gas contracted. When starting with hydrogen and carbon monoxide, and correcting for temperature, an almost linear contraction began at once.

The analyses of a series of runs are shown in Table I and plotted in Fig. 2, No exact analysis of the starting mixture is shown because the runs were made from several mixtures differing slightly in composition. All contained, however, from 48 to 49% of each of the gases used. It will be seen that the same percentage composition of the resulting gas mixture is obtaiaed from both' sides of the reaction. Averaging the results from runs of 180 minutes and longer gives this composition as 13.3% carbon dioxide, 37.1% carbon monoxide 8.7% methane, and 37.6% hydrogen.

Since contraction continued even after attainment of this constant composition, the record of the actual volumes throughout the reaction is also important. In Table II are shown the volumes as actually recorded in the longest run in each part of Table I, and for each gas the number of

TABLE I

PERCENTAGE COMPOSITION UP THE GASES DURING THE REACTION

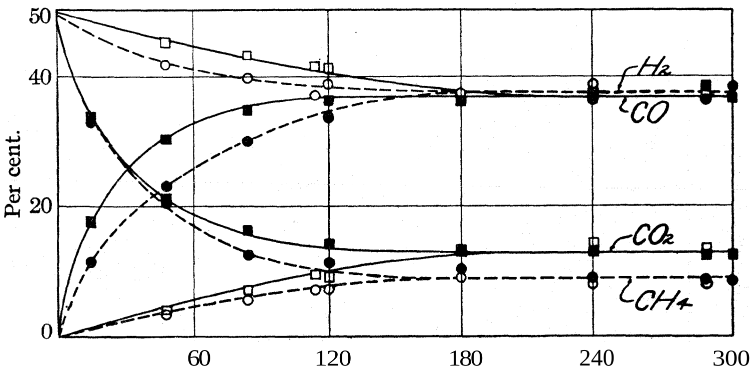
Starting with equal amounts of carbon dioxide and methane

	Minutes							
	15	48	84	120	180	240	289	300
CO_2	33.6	21.2	16.4	14.3	13 1	13.0	12.4	12.4
O_2	0.2	0.4	0.2	0.3	0.3	0.2	0.3	0.2
CO	176	30.4	34.8	36.2	36.1	37.0	38.6	36.7
CH_4	32 9	20.5	12 6	11.6	10.3	9.0	8.7	8.4
H_2	116	23.0	30.0	337	36.7	36.4	36.5	38.5
N_2 (diff.)	4.1	4.5	5.0	3 9	3 5	4.4	3 5	3.8

Starting with equal amounts of hydrogen and carbon monoxide

	Minutes						
	48	84	112	120	180	240	289
CO_2	4.1	7.4	9.5	8.9	13.4	14.5	13.7
O_2	0.0	0.2	0.2	0.2	0.2	0.0	0.0
CO	45.3	43.4	41.5	41.3	36.6	36.7	37.1
CH_4	3.7	5.8	7.3	7.6	9.0	7.9	8.0
H_2	41.8	39.9	37.2	38.8	37.1	38.8	38.8
N_2 **(diff.)**	5.1	3.3	4.3	3.2	3.7	2.1	2.4

cubic centimeters which may be assumed to have been present at the times stated, judged by the analyses of the individual runs stopped at those points. These amounts are plotted in Fig. 3. It will be seen that the amounts of the gases being formed in the reaction reach a maximum and then decrease, the slope of the line finally being the same as-that of the same constituent when starting from the opposite side of the reaction. Due to difference in starting volume and to the initial increase in volume from the carbon dioxide and methane side, they would not be expected to reach the same actual amount. It is evident then, that some other reaction takes place simultaneously with the one we are discussing and causes



□, ○—from CO and H_2; ■, ●—from CO_2 and CH_4.

Fig 2.—Percentage composition of gases during reaction.

TABLE II

GAS VOLUMES DURING THE REACTION—CUBIC CENTIMETERS AT STANDARD CONDITIONS

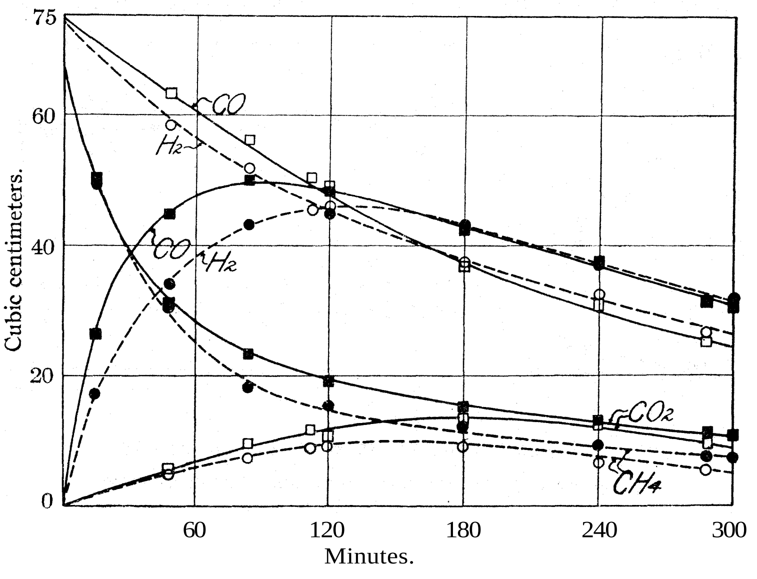
Starting with carbon dioxide and methane

	Minutes								
	0	15	48	84	120	180	240	289	300
Total vol.	140	149	148	143	133	118	101	86.4	83
CO_2	68.3	50.0	31.4	23.5	19.0	15.4	13.1	10.7	10.3
CO	...	26.2	45.0	48.8	48.1	42.4	37.4	31.7	30.4
CH_4	68.0	49.0	30.3	18.0	15.4	12.1	9.1	7.5	7.0
H_2	...	17.3	34.1	43.0	44.8	43.3	36.8	31.6	32.0

Starting with hydrogen and carbon monoxide

	Minutes							
	0	48	84	112	120	180	240	289
Total vol.	152	140	130	122	119	101	84	69
CO_2	...	5.7	9.6	11.6	10.6	13.5	12.2	9.5
CO	75.7	63.5	56.4	50.6	49.2	37.0	30.8	25.6
CH_4	...	5.2	7.5	8.9	9.1	9.1	6.6	5.5
H_2	73.6	58.5	51.9	45.4	46.1	37.5	32.6	26.8

the contraction in volume. This was confirmed by the formation of a solid deposit. It is important that there is no further change in gas composition during this change in volume.



□, ○—from H_2 and CO; ■, ●—from CO_2 and CH_4.

Fig. 3.—Gas volumes during reaction.

The equation for the equilibrium constant for the reaction $2CO + 2H_2 = CO_2 + CH_4$ would be written $K_p = [CO_2]\,[CH_4]/[H_2]^2\,[CO]^2$. Inserting the average percentages given above, the actual value would be $K = (0.133 \times 0.087)/(0.1413 \times 0.1377)$. This gives for the experimental value of the equilibrium constant $K = 0.5946$. Using the equation for the free energy change in this reaction as given by D. F. Smith,[10] A F = --56,950 + 15.07.5 T ln T − 0.01078 T^2 + 0.00000031 T^3 − 30.34 T, and substituting the free energy values calculated therefrom for the temperatures 900 and 950° absolute in the Equation, $\Delta F = -RT \ln K$, we have, $K_{900} = 0.7686$ and $K_{950} = 0.20\%$. The equilibrium point for this reaction reached under the conditions of this investigation would therefore seem to correspond to an absolute temperature of between 900 and 950°. Lunt[5p] and Wendt and Farnsworth[5v] have previously found evidence of a high temperature effect in the corona discharge.

Other reactions are possible from the mixture of gases employed in these experiments, for instance, $3H_2 + CO = CH_4 + H_2O$. All such reactions, however, involve the formation of water. A number of experiments mere made in which a vessel containing phosphorus pentoxide was inserted in the reaction tube, being attached to the piston. In no case did this result in a change in the composition of the equilibrium gas mixture. If water had been a component of the equilibrium its removal in this manner should have had a marked effect on the equilibrium concentrations. The presence of even a small quantity of free oxygen, for instance, entirely altered all the concentrations. The fact that phosphorus pentoxide had no effect indicates that these reactions involving water need not be considered in this equilibrium.

The intensity of the electric discharge influences the rate at which equilibrium is obtained. In order to measure the effect of changes in the corona, runs were made with carbon dioxide and methane with the secondary milliamperage at 6.4, and at 4.0. The first was a two-hour run and the second was run until the volume contracted to that reached by the first. The volume loss in the first run for the last linear part of the time-volume curve was at the rate of 8 cc. per hour, and for the second run, 4.9 cc. per hour. The secondary voltage in the first run was 14,000 and in the second 9700. The reaction velocity seems more nearly proportional to the secondary current than to voltage or volt-amperes. There is, of course, an unknown amount of surface leakage involved but as the milliameter was in the grounded line this was reduced to a minimum. Neither of the analyses differed by more than the experimental error from that for the corresponding two-hour run shown in Table I.

To study the effect of the proportion of the total gas mixture which was actually in the discharge region upon the velocity of the reaction, a run was made with a starting volume of only 82 cc. of carbon dioxide and methane, and run to the maximum volume at fifteen minutes. The final volume was 92 cc., and the composition of the resulting gas mixture was as follows: CO_2, 25.3%; O_2, 0.1%; CO, 24.3%; CH_4, 26.3%; H_2, 19.8%;

[10] D F. Smith, *Ind. Eng Chem.*, **19,** 801 **(1927).**

N_2, 5.2%. This, when compared with the fifteen-minute run in Table I in which 160 cc. was used, shows that the rate of reaction is roughly proportional to the fraction of the total volume exposed to the discharge.

Non-Gaseous Products.—The continued reduction in volume indicated that other products besides the above gases were formed. In fact some of them were visible. In from five to ten minutes from the closing of the electrical circuit brown spots appeared on the central wire, which soon blackened, and by the end of three hours the wire was entirely covered. Location of the original spots seemed to coincide with the position of the negative beads of the discharge. In runs of more than two hours' duration a brown deposit appeared on the inside of the glass tube itself. In preliminary work when aluminum carbide was used as the source of methane, so that hydrogen as well as methane and carbon dioxide were present in the starting mixture, there was evidence of drops of clear liquid on the walls of the glass tube; this was no longer obtained after the use of the natural gas began. Investigation of the brown deposit showed that the greater part of it was carbon suboxide, as it had the properties attributed to that substance by Brodie[2] and Crespi and Lunt[5e] as prepared under slightly different circumstances. In addition, however, the water solution from washing the tube gave a decisive though weak test for aldehyde with Schiff's solution, although the water which had stood in contact with the gaseous phase alone showed only a very faint trace. A slight roughening of the wire due to sputtering was visible after the removal of the deposit.

The Decrease in Volume after Equilibrium.—In order to study the continuous decrease in volume after the composition of the gases had reached equilibrium a number of possibilities were investigated. To determine whether the contraction continues indefinitely or comes to an end while reactive gases are still present, a mixture of methane and carbon dioxide was exposed to the action of the corona for a total of forty-five hours. The discharge was confined to a length of about two and a half centimeters of the upper end of the wire by emptying the jacket of electrolyte and using for a grounded electrode a strip of aluminum foil of the above width wrapped around the tube where the two upper stopcocks are attached. An air blast was used to cool the tube and sweep away ozone. During a run totaling forty-five hours with this small discharge, 170 cc. of gas contracted to less than 17 cc. The last part of the contraction was followed by allowing mercury to flow up into the region inside the condenser, as was done in taking samples for analysis. The stoppage of the reaction was necessitated only by the approach of this mercury, which was, of course, at high potential, to the outer aluminum electrode. The contraction had not up to that time shown any signs of stopping, and probably would have gone to completion had it been possible to continue the experiment. As deposition of solids took place only in the discharge region, such products were in this case thus left within the influence of the corona throughout the run. The deposit on the walls as well as on the wire was black, indicating considerable carbonization of the primary deposit. It was not possible to obtain a sufficiently large sample of gas for an accurate analysis, but it was possible to determine that all four gases of the equilibrium mixture were still present.

The effect of the corona on pure carbon monoxide and on pure methane was tested in order to determine whether either gas alone was responsible. Hydrogen alone could not be responsible, and Wendt and Farnsworth[5v] have investigated carbon dioxide alone and found no such effect. The contraction might have been due to the formation of carbon suboxide according to the equation $4CO = C_3O_2 + CO_2$. Crespi and Lunt[5e] studied this reaction in an ozonizer under constant volume conditions and found that contraction stopped after 225 minutes. Carbon suboxide was the principal solid product. We made a run with pure carbon monoxide and contraction in our case stopped after eight hours, when an original volume of 173 cc. had contracted to 133 cc. The analysis of the gas was as follows: CO_2, 10.7%; O_2, 0.1%; CO, 86.3%; CH_4, 0.0%; total absorbed, 97.1%. The deposit on the walls of the tube was similar in appearance and properties to the deposit formed on the glass during the regular reaction, but was lighter in color, indicating that while the deposit in the regular reaction was principally carbon suboxide, some carbonization had taken place. This reaction of carbon monoxide alone, therefore, could not account for the continued contraction, both because the deposit appeared to be different and because contraction did not continue indefinitely.

A run was made with methane alone in the tube, but in this case, also, equilibrium was reached, indicated by a stoppage of expansion when an original volume of 80 cc. had expanded to 88 cc. The composition of the final gas was as follows: CO_2, 0.0%; unsaturated compounds, 0.5%; O_2, 0.5%; CO, 0.8%; CH_4, 38.4%; H_2, 57.2%; total absorbed, 97.4%. The deposit on the tube in this case took the form of droplets of viscous liquid, probably polymerization products similar to those found by Lind and Glockler[11] in their experiments with ethane in electrical discharges. The action of methane alone thus fails to explain the large contraction taking place in the experiments with gas mixtures.

Since no single constituent accounts for the contraction, those reactions which give condensed products deserved further study. Two possible reactions which might cause a complete contraction without affecting the proportions of the four gases present at equilibrium are, $H_2 + CO = HCHO$, and $H_2 + CO = C + H_2O$. Schiff's solution, as mentioned above, showed the presence of aldehyde, but a titration with thiosulfate, potassium iodide and potassium dichromate of a solution of the deposit from a five-hour run

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[11] Lind and Glockler, Preprint No. 6, *Trans. Am. Electrochem. Soc.*, Sept. 22, 1927.

reduced only half a cubic centimeter of the 0.01 N dichromate, an amount hardly above the error of the method. Contardi[12] has shown that polymers of formaldehyde which would be insoluble in water are not stable in the electrical discharge. It is evident, then, that the influence of the formaldehyde reaction is small.

To study the possibility that the formation of carbon and water is involved, an attempt was made to produce the reaction $2C + 2H_2O = 2H_2 + 2CO = CO_2 + CH_4$, by depositing carbon on the wire from methane and running the discharge with the tube filled with steam. We were unable to keep the discharge region sufficiently hot to prevent condensation of the steam, even though boiling salt solution was used in the jacket; the vacuum so created caused air leakage through the melted stopcock grease and only a trace of methane was found.

The calculation of the carbon, hydrogen and oxygen balances in the remaining gaseous constituents during the course of the contraction gives an indication of the nature of the volume loss and the fate of the gaseous materials apparently lost. Table III shows a balance of the gaseous constituents at the beginning and end of the long runs in Table I. Inasmuch as these losses appear to be very close to the proportions in CH_2O, or C and H_2O, and the amount of formaldehyde formed has been found to be very small, carbon and water seem the most probable end products of the reaction under these conditions. Losanitsch and Jovitschitsch[50] state that their final product from hydrogen and carbon monoxide in the ozonizer at seventy volts was glycolaldehyde. Due to the higher voltage used in this investigation and the greater current density at the small diameter

TABLE III

CARBON, HYDROGEN AND OXYGEN BALANCE

FROM CARBON DIOXIDE AND METHANE

	C, g.	H, g.	O, g
Start of reaction			
68.3 cc. CO_2 = 0.1340 g.	0 0367	. .	0.0978
68.0 cc. CH_4 = .0486 g.	.0364	0 0121	. ..
Total	0.0731	0.0121	0.0978
End of reaction			
10.3 cc. CO_2 = 0.0202 g.	0.0055	.....	0.0147
30.4 cc. CO = .0380 g.	.0163	.....	.0217
7.0 cc. CH_4 = .0050 g.	.0038	0.0013	
32.0 cc. H_2 = .0029 g.	.....	.0029	.....
Total	0.0256	0.0042	0.0364
Losses	.0475	.0079	.0614
Atoms	.00396	.0079	.00384
Ratio	n	$2.0\,n$	$0.97\,n$

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[12] Contardi, *Gazz. chim. ital.*, 51, I, 109 (1921).

TABLE III (*Concluded*)

FROM HYDROGEN AND CARBON MONOXIDE

		C, g	H, g.	O, g.
	Start of reaction			
75.7 cc. CO	= 0.0947 g.	0 0406	. .	0.0541
73.6 cc. H_2	= .00657 g.	. .	0 00657	
Total		0.0406	0 00657	0.0541
	End of reaction			
9.5 cc. CO_2	= 0.0186 g.	0 0051		0.0136
25.6 cc. CO	= .0320 g.	0137		.0183
5.5 cc. CH_4	= .00393 g.	00295	00098	. . . . .
26.7 cc. H_2	= ,00238 g.		00238	
Total		0 02175	0 00336	0.0319
Losses		01885	.00321	.0222
Atoms		00157	00321	.00139
Ratio		*n*	2.2 *n*	0.9 *n*

wire electrode, different results might well be expected from those obtained in the ozonizer type apparatus at the low voltage. It is interesting to note, however, that in glycolaldehyde, as well as in formaldehyde and with carbon plus water, the ratio of carbon, hydrogen and oxygen is the same, namely, $C_nH_{2n}O_n$, and that this is the same as the ratio in either pair of starting gases, hydrogen and carbon monoxide, or methane and carbon dioxide. Hence the contraction and condensation do not change this ratio. The fact that the removal of water during the reaction by means of phosphorus pentoxide does not change the equilibrium concentrations indicates that water can take part only in this final reaction, whereby all gaseous constituents are removed in the form of carbon and water, a reaction which is under the experimental conditions apparently irreversible.

Summary

The reaction $2CO + 2H_2 = CO_2 + CH_4$ has been studied under the conditions existing in a corona discharge. The reaction reaches an equilibrium when approached from either side in which the composition is 13.3% carbon dioxide, 37.1% carbon monoxide, 8.7% methane, and 37.6% hydrogen. This equilibrium would under purely thermal conditions correspond to an absolute temperature of 900 to 950°. The gas volume continues to contract after the equilibrium is reached and the most probable end products are carbon and water according to the equation $CO + H_2 = C + H_2O$.

STATE COLLEGE, PENNSYLVANIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY]

OXIDATION-REDUCTION POTENTIALS OF THE PENTACYANO-FERROATES

BY DAVID DAVIDSON[1]

RECEIVED MAY 7, 1928 PUBLISHED OCTOBER 6, 1928

Baudisch and his coworkers[2] have shown that sodium pentacyano-aquo-ferroate[3] (I) and sodium pentacyano-ammine-ferroate[4] (II) may act as catalysts in the oxidation of pyrimidines, purines and hydantoins by means of oxygen or air. The present paper deals with the oxidation-reduction potentials of mixtures of the ferrous and ferric forms of these salts as well as of sodium pentacyano-nitrito-ferroate[3] (III) as compared with the ferrocyanide (IV) electrode.

Previous investigators[5] have found that the potential of the ferrocyanide electrode depends on the concentration of potassium ions. For a given solution of potassium chloride, however, the potential of the electrode followed the equation

$$\text{E.m.f.} = E_0' - RT/F \ln C_o/C_i$$

C_o and C_i were the total concentrations of the ferrous and ferric salt, respectively. $C_o + C_i$ was small compared with [KCl].

$$\left[\begin{array}{ccc} \mathrm{CN} & & \mathrm{H_2O} \\ & \mathrm{II} & \\ \mathrm{CN} & \mathrm{Fe} & \mathrm{CN} \\ \mathrm{CN} & & \mathrm{CN} \end{array}\right] \mathrm{Na_3} \qquad \left[\begin{array}{ccc} \mathrm{CN} & & \mathrm{NH_3} \\ & \mathrm{II} & \\ \mathrm{CN} & \mathrm{Fe} & \mathrm{CN} \\ \mathrm{CN} & & \mathrm{CN} \end{array}\right] \mathrm{Na_3}$$

I II

$$\left[\begin{array}{ccc} \mathrm{CN} & & \mathrm{NO_2} \\ & \mathrm{II} & \\ \mathrm{CN} & \mathrm{Fe} & \mathrm{CN} \\ \mathrm{CN} & & \mathrm{CN} \end{array}\right] \mathrm{Na_4} \qquad \left[\begin{array}{ccc} \mathrm{CN} & & \mathrm{CN} \\ & \mathrm{II} & \\ \mathrm{CN} & \mathrm{Fe} & \mathrm{CN} \\ \mathrm{CN} & & \mathrm{CN} \end{array}\right] \mathrm{K_4}$$

III IV

Similar results have been obtained with the molybdo- and tungstocyanides.[6] The preliminary study was therefore limited to solutions of the iron salts in normal potassium chloride.

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[1] Rockefeller Institute Fellow.

[2] (a) Pfaltz and Baudisch, THIS JOURNAL, 45, 2972 (1923); (b) Pfaltz, *ibid.*, 45, 2980 (1923); (c) Baudisch and Bass, *ibid.*, 46, 184 (1924); (d) Baudisch and Davidson, J. *Biol. Chem.*, 71,501 (1927); (e) 75,247 (1927).

[3] Hofmann, ***Ann.***, 312, 1 (1900).

[4] Manchot, *Ber.*, 45,369 (1912).

[5] (a) Lewis and Sargent, THIS JOURNAL, 31, 357 (1909); (b) *ibid.*, 31, 363 (1909); (c) Muller, *Z physik. Chem.*, *88*, 46 (1914); (d) Schoch and Felsing, THIS JOURNAL, 38, 1928 (1916); (e) Linhart, *ibid.*, 39, 615 (1917); (f) Butler and Davies, J. *Chem. Soc.*, 125, 1101 (1924).

[6] (a) Collenberg, Z. *physik. Chem.*, 109, 353 (1924); (b) Collenberg and Guthe, *Z. anorg. allgem. Chem.*, 136,252 (1924).

Apparatus and Methods

The electrode vessel consisted of a glass cup of 75 cc. capacity, fitted with a rubber stopper which bore a dropping funnel, nitrogen inlet, gold plated platinum electrode, salt bridge containing *N* KCl, 5 cc. buret (when employed) and a mechanical stirrer equipped with mercury seal and driven by an air turbine. The second leg of the salt bridge was placed in a beaker containing *N* KCl, into which a normal calomel electrode dipped. Weighed quantities of the salts were placed in the cup, the stopper was affixed and the air rinsed out with nitrogen. Fifty cc. of N KCl was placed in the dropping funnel. By properly regulating the nitrogen pressure and opening the cock of the dropping funnel, the potassium chloride solution could be de-aerated just before use. Finally the solution was allowed to run into the cup, stirring was begun and readings were taken at intervals. The potentiometer used was a Leeds and Northrop Student Type with a needle galvanometer. The measurements were carried out at room temperature (21°).

The solutions studied were prepared by dissolving a total of 0.2 millimole of the two salts in 50 cc. of N KCl. Usually three ratios of ferrous to ferric salt were measured: (a) 0.15 ferrous + 0.05 ferric (3:1); (b) 0.10 ferrous + 0.10 ferric (1:1); (c) 0.05 ferrous + 0.15 ferric (1:3).

Potassium Ferrocyanide

The apparatus and method were checked by measuring the ferrocyanide electrode. The potentials given in Table I remained constant during the twenty minutes they were observed.

TABLE I

POTENTIALS OF THE FERROCYANIDE ELECTRODE

Soln.	*N* KCl cc.	Ferrous, millimole	Ferric, millimole	E m f.	E m.f. $- E_0'$ Pound	Calcd.
(a)	50	0.15	0.05	0 171	−0.029	−0.028
(b)	50	.10	.10	.198	..	..
(c)	50	.05	.15	.225	.027	.028

The value of 0.198 volt is practically identical with that obtained by Butler and Davies,[5f] the difference in temperature being allowed for.

Sodium **Pentacyano-Ammine-Ferroate**

Solutions containing ferrous and ferric "ammine" salt gave potentials which varied with time as shown in Fig. 1. Moreover, at no time was the difference between the potentials of solutions (b) and (a) or of (b) and (c) equal to the value of 0.028 volt calculated from the electrochemical equation given above. It was constantly greater. Thus, for example, ten minutes after the solutions were prepared, (b) − (a) = 0.040 volt and (c) − (b) = 0.041 volt. Since this anomalous behavior of the electrode could be attributed to the hydrolysis of the "ammine" salts[3]

$$Na_3Fe(CN)_5{\cdot}NH_3 + H_2O \rightleftharpoons Na_3Fe(CN)_5{\cdot}H_2O + NH_3$$
$$Na_2Fe(CN)_5{\cdot}NH_3 + H_2O \rightleftharpoons Na_2Fe(CN)_5{\cdot}H_2O + NH_3$$

a second series of measurements was made in which the solvent contained 0.5 cc. of concentrated ammonia, the total volume and normality in potassium chloride being maintained by using the proper quantities of *N* and 2*N* potassium chloride.

As is seen from Fig. 2, this had the effect of stabilizing the potentials except in solution (c), in which case, apparently, reduction of the ferric salt by the added ammonia caused a gradual fall in the potential, which fall became uniform after five minutes. The extrapolation indicated in the figure yielded a value which harmonized with those of (a) and (b) which are given in Table II.

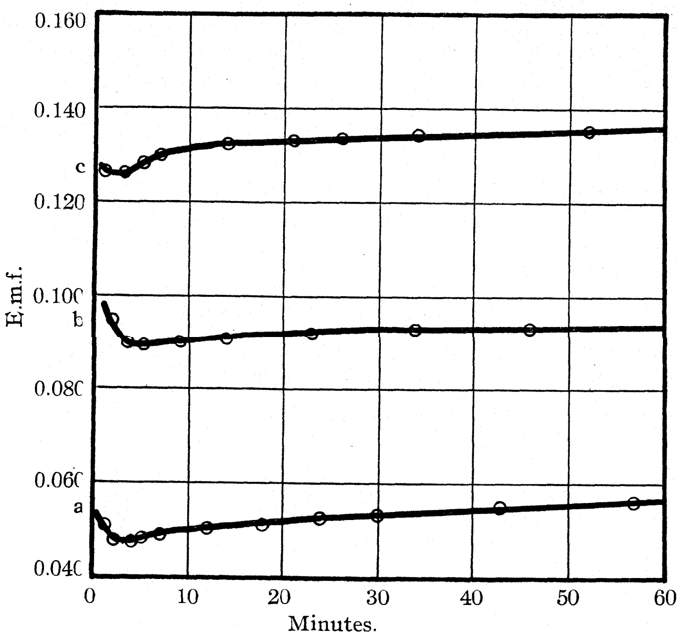

Fig. 1.—Variation of the pentacyano-ammine-ferroate electrode with time. [Ferrous]/[ferric] = a, 3; b, 1; c, $^1/_3$.

TABLE II

POTENTIALS OF THE PENTACYANO-AMMINE-FERROATE ELECTRODE

Soln.	*N* KCl, cc.	2*N* KCl, cc.	Concd NH$_3$, cc.	Ferrous, milli-mole	Ferric, milli-mole	E.m f.	E m.f. − E'_0 Found	Calcd.
(a)	49	0.5	0.5	0.15	0.05	0.064	−0.028	−0.028
(b)	49	.5	.5	.10	.10	.092	..	..
(c)	49	.5	.5	.05	.15	.120	.028	.028

An independent series of measurements was made to determine the effect of ammonia concentration. Fig. 3 and Table III reproduce the results obtained with solvents containing 0.5, 1.0 and 2.0 *cc.* of concentrated ammonia, respectively.

TABLE III

EFFECT OF AMMONIA CONCENTRATION ON THE POTENTIALS OF THE PENTACYANO-AMMINE-FERROATE ELECTRODE

Soln	N KCl, cc.	2N KCl, cc.	Concd. NH$_3$, cc	Ferrous, milli-mole	Ferric, milli-mole	E m f.	E.m.f. − E_0' Found	Calcd.
(a)	49	0.5	0.5	0.15	0.05	0.063	−0.029	−0.028
(b)	49	.5	.5	.10	.10	.092	..	..
(c)	49	.5	.5	.05	.15	.119[a]	.027	.028
(a')	48	1.0	1.0	.15	.05	.063	−.029	−.028
(b')	48	1.0	1.0	.10	.10	.092	..	..
(c')	48	1.0	1.0	.05	.15	.119[a]	.027	.028
(a'')	46	2.0	2.0	.15	.05	.063	−.029	−.028
(b'')	46	2.0	2.0	.10	.10	.092[a]	..	..
(c'')	46	2.0	2.0	.05	.15	?	?	.028

[a] Extrapolated.

As Fig. 3 indicates, the results with different concentrations of ammonia were practically identical as long as the disturbance caused by the oxidation of the ammonia did not occur. Of the (b) solutions, that containing 2.0 cc. of ammonia, (b''), displayed a falling potential. The readily extrapolated value, however, agreed with those obtained in the other (b) solutions. In the (c) solutions the potentials fell increasingly rapidly so that extrapolation was hardly feasible in the last case, (c''). Nevertheless, it is evident that within the limits of ammonia concentrations employed the potential of the electrode is independent of the ammonia concentration,

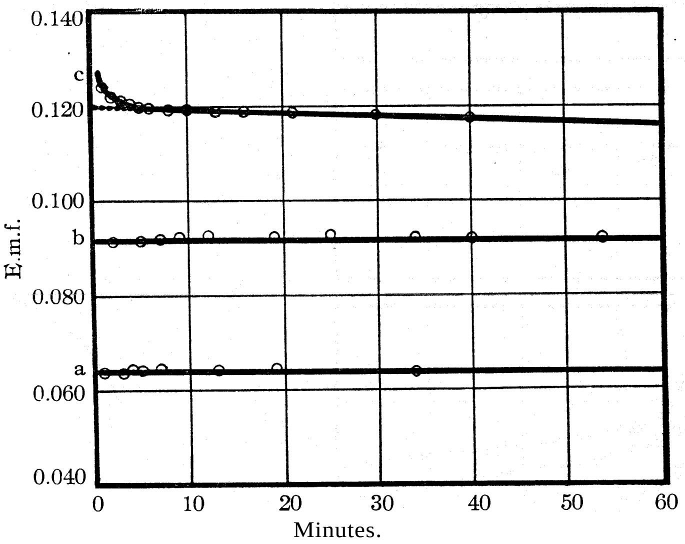

Fig. 2.—Stabilizing effect of ammonia on the pentacyano-ammine-ferroate electrode.

although with increasing ammonia concentration the solutions become increasingly unstable.

Sodium Pentacyano-Aquo-Ferroate

Application of the method described above to sodium pentacyano-aquo-ferroate gave the following results.

TABLE IV

POTENTIALS OF THE PENTACYANO-AQUO-FERROATE ELECTRODE

Soln.	*N* KCl, cc	Ferrous. millimole	Ferric, millimole	E.m.f.	E.m.f $-E_0'$ Found	E.m.f $-E_0'$ Calcd
(a)	50	0 15	0.05	0.100	−0.069	−0.028
(b)	50	.10	.10	.169	..	..
(c)	50	.05	.15	.294	.125	.028

The color of the solutions indicated, however, that compound formation was occurring between the ferrous and ferric salts, since the deep blue color of the ferric salt was only apparent in (c), while solutions (a) and (b) were only slightly darker than solutions of the ferrous salt alone. That compound formation actually occurs was demonstrated by titrating the ferrous salt with a solution of the ferric compound.

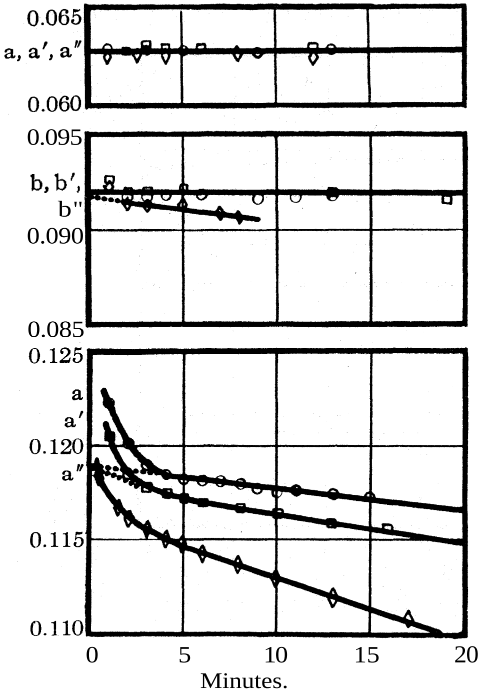

Fig. 3.—Effect of [NH_3] on the pentacyano-ammine-ferroate electrode. a, b, c contain 0.5 cc. of concd. NH_3 in 50 cc. of solution; a′, b′, c′, 1.0 cc.; a″, b″, c″, 2.0 cc.

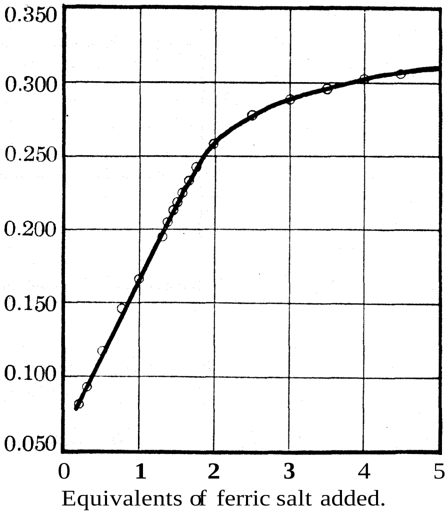

Fig. 4.—Titration of $Na_3Fe(CN)_5\cdot H_2O$ with $Na_2Fe(CN)_5\cdot H_2O$.

A quantity of the ferric salt (approximately 0.25 millimole) was weighed into a 5cc. volumetric flask, while a weight of ferrous salt equivalent to one-fifth of the ferric salt (approximately 0.05 millimole) was weighed into the cup. Fifty cc. of *N* KCl was introduced into the cup in the usual way. The ferric salt was made up to **3** cc. with *N* KCl, the solution introduced into the buret and the titration begun. Fig. 4 is a plot of this titration. More information is obtained from a plot of e.m.f. against log C_o/Ci (Fig. 5). This curve shows an inflection point at e.m.f. = 0.219

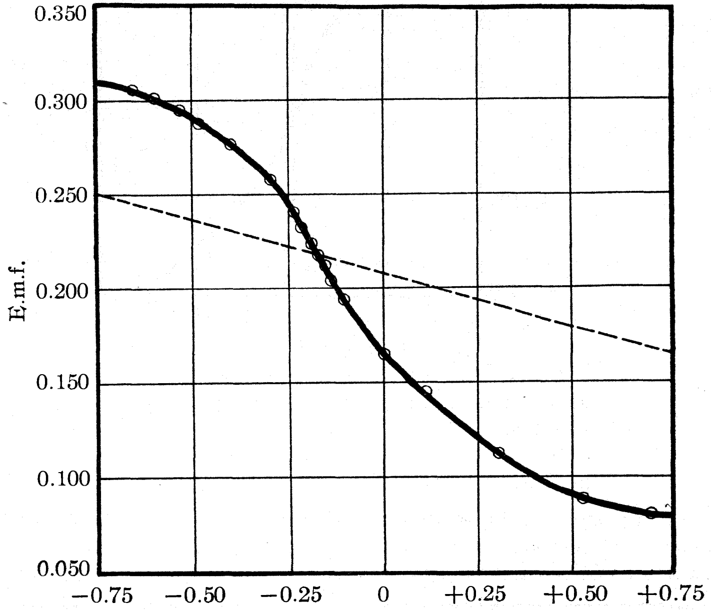

Fig. 5.—Titration of $Na_3Fe(CN)_5 \cdot H_2O$ with $Na_2Fe(CN)_5 \cdot H_2O$. The dotted line is the curve of e.m.f. = $E'_0 - 0.058 \log([\text{ferrous}]/[\text{ferric}])$.

and log C_o/Ci = −0.176. This point corresponds to the composition of the compound.[7] Hence, the ratio of ferrous to ferric salt in the com-

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[7] This becomes more evident by considering the simpler case of a system in which the reductant, *red.*, and the oxidant, *ox.*, form a compound, *red.ox.* A solution of the "pure" compound will contain *red.ox.*, as well as the two components, *red.* and *ox.* arising from its dissociation.

Let [*red.*] = concentration of uncombined reductant
[*ox.*] = concentration of uncombined oxidant
[*Red.*] = concentration of total reductant
[*Ox.*] = concentration of total oxidant
concentration = activity.

If one adds an excess of *red.* to a solution of the compound its dissociation is depressed; that is to say, a small proportion of this excess combines with a large proportion of the free *ox.* present. In other words. [*red.*] is slightly less than the sum of that originally present and that added, while [*ox.*] has been greatly decreased. Therefore, [*red.*]/[*ox.*] > [*Red.*]/[*Ox.*], and the e m f.-log [*Red.*]/[*Ox.*] curve lies below the normal curve;

that is, below that of Equation 1. Moreover, since equal increments in log *Red.* cause diminishing decrements in log *[ox.]*, (d log *[red.]*/*[ox.]*)/(d log *[Red.]*/*[Ox.]*) diminishes as log *[Red.]*/*[Ox.]* increases. Similar reasoning applies to additions of excess of *ox.* Hence, the resulting curve, Fig. 6, has an inflection point at log *[Red.]*/*[Ox.]* corresponding to the compound. This point also lies on the straight line which normally obtains in the absence of compound formation. In general, for a compound *m·red.·n·ox.*, the inflection point will occur at log *[Red.]*/*[Ox.]* = log *m*/*n*. Fig. 7 represents the curves calculated for a titration, during which, of course, the quantity of the compound varies widely.

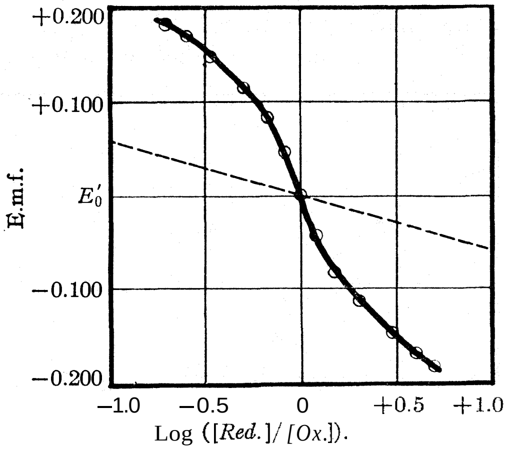

Fig. 6.—Calculated curve for the effect of excess of *red.* or *ox.* on the potential of *red.ox.*, whose dissociation constant = 0.011. [*red.ox.*] = 1. The dotted line is the curve of e.m.f. = E_0' − 0.058 log ([*Red.*]/[*Ox.*]).

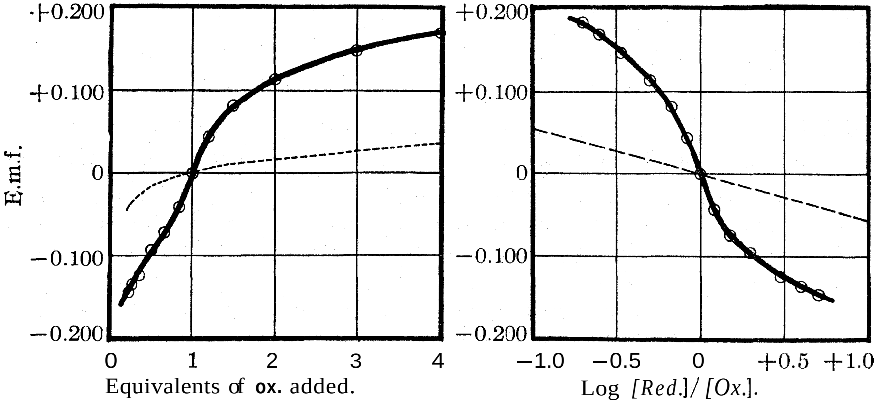

Fig. 7.—Calculated titration curves of one mole of *red.* in one liter of solution titrated with *ox.* Ox. and *red*, form a compound, *red.ox*, whose dissociation constant is 0.011. The volume of the solution is not appreciably altered during the titration. The dotted curves represent the equation e.m.f. = E_0' − 0.058 log ([*Red.*]/[*Ox*]).

plex is antilog $-0.176 = 0.67$, or 2:3, and the formula of the compound[8] is $2Na_3Fe(CN)_5H_2O \cdot 3Na_2Fe(CN)_5H_2O$. The value of E'_0 is obtained from the coordinates of the inflection point since this is the only point at which the ratio of uncombined ferrous salt to uncombined ferric salt is equal to the ratio of the total ferrous salt to the total ferric salt. Thus

$$0.219 = E'_0 - (0.058)(-0.176); \quad E'_0 = 0.209 \text{ volt}$$

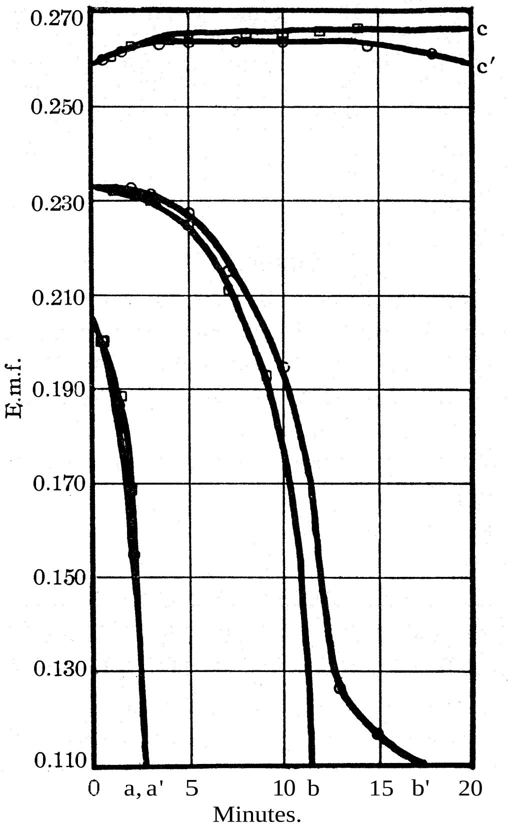

Fig. 8.—Variation of the pentacyano-nitrito-ferroate electrode with time. a', b', c' contain added nitrite.

Sodium Pentacyano-Nitrito-Ferroate

Solutions of this system gave potentials which varied rapidly with time (Pig. 8), parallel with a change in color from red (the color of the ferric salt) to yellow. Addition of 1 cc. or more of N $NaNO_2$ made little difference in the behavior of the electrode. Nevertheless, if the curves (except

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[8] Complex formation between the iron cyanides has also been noted by Briggs, *J. Chem. Soc.*, 117, 1026 (1915).

the (c) curves, which were constant for several minutes) are extrapolated to zero time, values are obtained which differ from each other in agreement with Equation 1.

TABLE V

POTENTIALS OF THE PENTACYANO-NITRITO-FERROATE ELECTRODE

Soln.	N KCl, cc.	N $NaNO_2$, cc.	Ferrous, millimole	Ferric, millimole	E m f.	E m f. $- E'_0$ Found	Calcd.
(a)	50	0	0.15	0.05	0.207[a]	−0.026	−0.028
(b)	50	0	.10	.10	.233[a]	..	..
(c)	50	0	.05	.15	.266	.033	.028
(a′)	50	1	.15	.05	.208[a]	−.027	−.028
(b′)	50	1	.10	.10	.235[a]	..	..
(c′)	50	1	.05	.15	.264	.029	.028
(b″)	50	10	.10	.10	.232[a]	..	..

Mean $E'_0 = 0.234$

[a] Extrapolated.

Summary

Under comparable conditions, the oxidation-reduction potentials of the following complex iron cyanides against the normal calomel electrode were: $K_4Fe(CN)_6$–$K_3Fe(CN)_6$, 0.198 volt; $Na_3Fe(CN)_5{\cdot}NH_3$–$Na_2Fe(CN)_5{\cdot}NH_3$, 0.092 volt; $Na_3Fe(CN)_5{\cdot}H_2O$–$Na_2Fe(CN)_5{\cdot}H_2O$, 0.209 volt; $Na_4Fe(CN)_5NO_2$–$Na_3Fe(CN)_5NO_2$, 0.234 volt.

Indication was obtained of the formation of the compound, $2Na_3Fe(CN)_5{\cdot}H_2O{\cdot}3Na_2Fe(CN)_5{\cdot}H_2O$.

STANFORD UNIVERSITY, CALIFORNIA

[CONTRIBUTION FROM THE MAYO CLINIC]

THE USE OF GELATIN OLEATE MIXTURES FOR THE DEMONSTRATION OF SMALL AMOUNTS OF CALCIUM[1]

BY SAMUEL AMBERG,[2] JOHN LANDSBURY[3] AND FRANCES SAWYER[4]

RECEIVED MAY 21, 1928 PUBLISHED OCTOBER 6, 1928

In a study of the penetrability of gelatin by dyes added to blood serum, Bennhold[5] found that it was impossible to use oxalated plasma because the calcium in the gelatin formed a precipitate of calcium oxalate which interfered with the experiments. Although this difficulty can be overcome by the use of ash-free or isoelectric gelatin,[6] it seemed probable that the formation of a stabilized ring reaction might furnish a method for the

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[1] Read before the American Society of Biological Chemists, Ann Arbor, Michigan, April 12 to 14, 1928.

[2] Section on Pediatrics, The Mayo Clinic.

[3] Fellow in Medicine, The Mayo Foundation.

[4] Fellow in Chemistry, The Mayo Foundation.

[5] H. Bennhold, "Ueber die Adsorptionsfahigkeit der Serumkolloide tubulär Nierenkranker gegenuber Farbstoffen," Z. ges. *exptl. Med.*, 49, 71–94 (1928).

[6] Obtained from the Eastman Kodak Company.

detection of minute amounts of calcium or other alkaline earths. It was also decided that results of interest might be obtained by a study of the effect produced by the addition of oxalate, oleate and other anions to a gelatin solution in contact with a solution of the alkaline earths.

Technique

Solutions of ash-free gelatin were so prepared that the final concentration was 5%. These solutions contained substances such as ammonium oxalate, sodium oleate, potassium oleate, sodium fluoride and sodium citrate. Freshly prepared tubes are preferable.

To insure as nearly as possible uniform conditions of temperature the tubes were kept in an ice chest at about 40°. They were read usually after standing from one to four hours, and again on the next day. The tubes, which were 9 mm. in inner diameter, were charged with about **3** cc. of gelatin mixture. The solutions were prepared roughly and the figures are approximate. The solutions to be tested were always added in the amount of 1 cc. The reactions which occurred may be characterized as stabilized ring reactions.

The gelatin in these experiments, as in others in which alkali was added, was dissolved in water, with enough space left in the tube for additions. When dissolved, 20 cc. of 0.01 N solution of oleate for each 100 cc. was added, followed immediately by 12.5 cc. of 0.1 N sodium hydroxide or potassium hydroxide. Then sufficient alkali was added to bring the reaction to a hydrogen-ion concentration of about P_H 7.4, using phenol red as the indicator. The alkalinity varied from about P_H 7.2 to 7.8, but was always greater than P_H 7. In later experiments potassium oleate[7] replaced the sodium oleate. The potassium oleate has the advantage of greater clearness, although both salts behaved similarly.

The water used for, the solutions was redistilled in an all-glass apparatus and only ash-free filter paper was used. Tubes with distilled water were used as controls, in none of which was there a reaction. Such controls are necessary for the detection of faint reactions. Reactions which could readily be distinguished from those of the controls were accepted as positive.

The solutions tested were lithium sulfate, sodium chloride, sodium sulfate, sodium nitrate, potassium chloride, potassium iodide, potassium sulfate, magnesium sulfate, strontium chloride, barium acetate, calcium hydroxide, calcium sulfate, calcium acetate, calcium oxalate, sodium hydroxide and potassium hydroxide. These solutions, with the exception of the hydroxides, were brought to a hydrogen-ion concentration of P_H 7.4 to *7.6.*

Slight or negative reactions were obtained with the sodium, potassium

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[7] Obtained from Kahlbaum.

and lithium salts in solutions stronger than 0.02 N, with reference to the metal; with 0.002 *N* solutions reactions were not obtained. Sodium and potassium hydroxide in concentrations of 0.02 *N* or greater produced some reaction.

The reactions of magnesium solutions were similar to those of the sodium solutions. With concentrations of $M/400$ the reactions were always positive, whereas with concentrations of $M/4000$ they became questionable or negative. Strontium chloride reacted definitely at a concentration of $M/4000$ and questionably at $M/40,000$, whereas barium acetate always reacted at a concentration of $M/80,000$, perhaps even more regularly than the calcium solutions. At a concentration of $M/160,000$ the reaction was questionable or absent.

The calcium compounds, as a rule, also reacted in concentrations of $M/80,000$; occasionally a reaction was questionable or negative. With concentrations of $M/160,000$ a questionable reaction was occasionally seen. Solutions made by exposing freshly precipitated and thoroughly washed calcium oxalate to redistilled water and then brought to a hydrogen-ion concentration of about P_H 7.4 also reacted promptly.

When calcium solutions were added to a watery solution of oleate of the same strength and reaction as in the gelatin tubes, in concentrations lower than $M/4000$, the tubes containing calcium could not be distinguished from the controls. A stratification of the solution could not be produced, as would be expected.

Solutions of gelatin containing 0.001 N potassium oleate gave the same results as the usual concentration of 0.002 *N* but with a concentration lower than 0.001 *N* the potassium oleate solutions did not react with the lower concentrations of the calcium solutions.

When ammonium oxalate, sodium fluoride or sodium citrate was added to the gelatin in place of the oleates, it required a greater concentration of calcium solutions to obtain reactions, and in these reactions the precipitate showed peculiar differences in distribution.

Summary and Conclusions

1. Gelatin may be used under certain conditions to obtain ring reactions when a stratification of solutions cannot be accomplished. This method can be amplified.
2. Sodium or potassium oleate mixtures can be used for the detection of small amounts of calcium, the limit being approximately 0.0005 mg. of calcium in 1 cc.
3. The reaction is not specific for calcium.

ROCHESTER, MINNESOTA

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

THE ACTIVITY COEFFICIENTS OF SODIUM AND POTASSIUM HYDROXIDES IN THEIR CORRESPONDING CHLORIDE SOLUTIONS AT HIGH CONSTANT TOTAL MOLALITY

BY HERBERT S. HARNED AND JOHN MCARTHUR HARRIS, JR.

RECEIVED JUNE 15, 1928 PUBLISHED OCTOBER 6, 1928

The logarithm of the activity coefficient of hydrochloric acid' in solutions of an alkali halide at constant total molality has been found to vary linearly with the acid concentration. Thus, if γ is the activity coefficient, and m the molal concentration of the acid

$$\log \gamma = \alpha m + \log \gamma_0 \qquad (1)$$

γ_0 is the activity coefficient of the acid at zero acid concentration in the salt solution of a given total molality and α is a constant.

In an extraordinarily careful study, Güntelberg[1] has shown that at 0.1 M total concentration this law is valid for the activity coefficient of the acid in lithium, sodium, potassium and cesium chloride solutions to within 0.04%. Harned[2] has shown that at 1 M and 3 M total molalities the above expression is valid to within ±0.2% for sodium and potassium chloride–hydrochloric acid mixtures. Results more recently obtained indicate that this law is valid for hydrochloric acid–sodium chloride mixtures at 6 M total molality.

The object of this investigation was to find whether equation (1) is also valid for the activity coefficients of all univalent alkaline hydroxides in their corresponding chloride solutions.

The thermodynamic properties of the alkali metal hydroxides differ from those of the corresponding chlorides. For example, sodium chloride has a higher activity coefficient than potassium chloride but the opposite is true of the corresponding hydroxides. As previously pointed out,[3] the hydroxides occupy a somewhat anomalous position in comparison with other strong electrolytes. If, therefore, deviations from the law expressed by Equation 1 are to be found, it is to be expected that they will be observed in the cases of the hydroxide–salt mixtures and will be more pronounced for sodium hydroxide–chloride than for potassium hydroxide–chloride mixtures. These latter mixtures have already been investigated at constant hydroxide–varying salt concentrations. From the few results obtained at constant total molality, indications were obtained that there was but little if any departure from the linear relation-

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[1] Guntelberg, *Z. physik. Chem.*, 123,199 (1926).

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

[3] (a) Harned, *ibid.*, 47,676 (1925); (b) *Z. physik. Chem.*, 117, 1 (1925); (c) Harned and Swindells, THIS JOURNAL, 48, 126 (1926).

ship. Since these previous studies did not constitute an exhaustive test, the electromotive forces of cells of the type

$$H_2 \mid MOH(m_1), MCl(m_2) \mid M_xHg \mid MOH(m_0) \mid H_2 \qquad (2)$$

in which $(m_1 + m_2)$ was kept constant, were measured.

Experimental Results

The experimental technique as well as the methods of preparation of the amalgams, solutions and electrodes was with minor alterations the same as that developed by Knobel,[4] Harned[5] and Åkerlöf,[6] and will require no further discussion. The electromotive forces are given in Table I. All measurements were made at 25°.

TABLE I

THE ELECTROMOTIVE FORCES OF THE CELLS $H_2 \mid MOH(m_1), MCl(m_2) \mid M_xHg \mid MOH(m_0) \mid H_2$ AND THE ACTIVITY COEFFICIENTS OF THE HYDROXIDES IN THE SALT SOLUTIONS

m_1	m_2	E	E, (mean)	γ	$\gamma_{calcd.}$	A
(a) MOH = KOH; MCl = KCl; M = K; $m_1 + m_2$ = 3.5; m_0 = 0.1080						
3 5	0	0 20412, 0.20423	0.2042	1 273	1.273	0.00
3	0.5	.19511, 0.19487	.1950	1.151	1.171	88
2 5	1	,18597,0 18627	.1861	1.061	1 076	72
2	1 5	.17654, 0 17618	.1764	0.981	0 990	58
1.5	2	.1648, 0.1639	1644	896	910	80
1	2.5	,14970,0.14976	,1497	.826	837	68
0.5	3	1280, 0.1284	.1282	770	.770	.00
(b) MOH = NaOH; MCl = NaCl; M = Na; $m_1 + m_2$ = 5; m_0 = 0.1080						
0.5	4 5	0 1397, 0.1384, 0.1374	0.1385	0 766	0 766	0 00
1	4	,1587,01584	,15855	800	.801	.06
1 5	3 5	.1703, 0 1697	.1700	817	.838	1.30
2	3	17953, 0 17944	.1795	.851	876	1.49
2 5	2.5	.18757, 0.18754	1876	.889	916	1.54
3	2	19425	19425	.926	957	1.69
3 5	1 5	20028	2003	.964	1 001	1 94
4	1	2070, 0 2072	2071	1 029	1.047	0 89
4 5	0 5	.21372	.2137	1.104	(1 094)	(−0.46)
5	.0	.21851, 0.21821	.2184	1.144	1.144	.00
(c) MOH = NaOH; MCl-NaCl; M = Na; $m_1 + m_2$ = 3; m_0 = 0.1060						
0 5	2 5	-0 11901, 0 11915	0.1191	0666	0.667	0 08
1	2	.13853, 0.13831	.1384	.687	.692	.37
1 5	1 5	,15037, 0 15032	,1503	.707	.718	.79
1	2	.15975, 0 15954	15965	.7335	.745	.76
2 5	0.5	16728, 0 16751	.1674	.763	.773	.67
3	0	17433, 0.17434	.1743	802	.802	.00

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[4] Knobel, THIS JOURNAL, **45,** 70 (1923)

[5] **Harned,** *ibid.,* 47, 676 (1925).

[6] **Åkerlöf,** *ibid., 48,* 1160 (1926).

Calculation of the Activity Coefficients

The activity coefficients of the hydroxides in the salt solutions were calculated according to the equation

$$E = 0\ 05915 \log \frac{\gamma_{M(s)}\gamma_{OH(s)}\, a_{H_2O(m_0)}\, (m_1 + m_2)\, m_1}{\gamma_{M(m_0)}\gamma_{OH(m_0)}\, a_{H_2O(s)}\, m_0^2} \tag{3}$$

where the subscripts (s) and (m_0) refer to the salt solutions and to the reference solutions, respectively. In all of the subsequent discussion, we let

$$\gamma = \sqrt{\frac{\gamma_{M(s)}\gamma_{OH(s)}}{a_{H_2O(s)}}} \text{ and } \gamma_0 = \sqrt{\frac{\gamma_{M(m_0)}\gamma_{OH(m_0)}}{a_{H_2O(m_0)}}}$$

and Equation 3 becomes

$$E = 0.1183 \log \frac{\gamma \sqrt{(m_1 + m_2)m_1}}{\gamma_0\, m_0} \tag{4}$$

The values employed for γ_0 were taken from the data of Harned and Åkerlöf.[7] Thus, for potassium hydroxide, $\gamma_{0\ 108}$ was taken to be 0.776, and in the case of sodium hydroxide, $\gamma_{0\cdot 106}$ and $\gamma_{0\cdot 108}$, were taken to equal 0.758 and 0.757, respectively. The final values computed in this manner are given in Table I.

Discussion of the Results

Figure 1 contains the plot of log γ_{KOH} against m_{KOH} in the solutions of 3.5 total molality. The upper plot is a straight line drawn through the points at 0.5 M and 3.5 M potassium hydroxide concentrations, and the lower curve is drawn through all the points. A slight curvature is noticeable although it should be remarked that if we had drawn the straight line through the 0.5 M and 3 M points, all points except that at 3.5 M hydroxide would have fallen on it with an error of about ±0.2 mv. In this case, however, the 3.5 M point would have been over a millivolt off the curve. We regard the results, therefore, as indicating a very small curvature. On the other hand, a pronounced curvature is observable in the case of sodium hydroxide–sodium

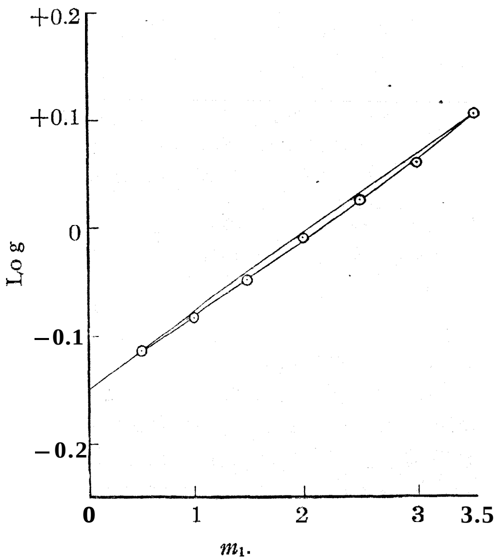

Fig. 1.—Log γ–m_1 of potassium hydroxide–chloride mixtures.

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

chloride mixtures at a total concentration of 3, and a very pronounced deviation from the straight line is apparent at a total molality of 5. This is shown by the graphs in Fig. 2. It should be noted that we have plotted $\sqrt{\gamma_M\gamma_{OH}/a_{H_2O}}$, not $\sqrt{\gamma_M\gamma_{OH}}$, owing to our lack of knowledge of the activity of water in these mixtures. The small change in a_{H_2O} in passing from the pure hydroxide to the pure salt solution would be expected to be approximately linear, and in any case would not be responsible for the pronounced curvatures. The points at 0.01 M and 0.1 M sodium hydroxide concentrations at a total concentration of three were obtained from the data of Harned.[3b]

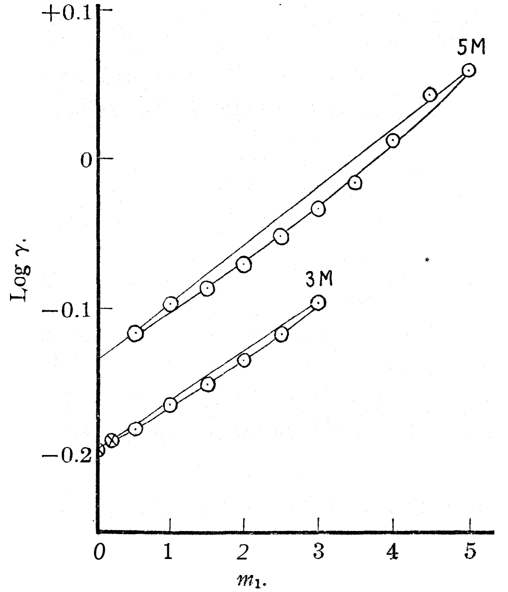

Fig. 2.—Log γ–m_1 plots of sodium hydroxide–chloride mixtures

The extent of the deviations from the straight lines shown in the figures is made apparent by the last two columns in Table I. The calculated values of γ were obtained from the equations for the straight lines, namely

$$\begin{aligned}
&\text{(a)}\quad \text{KOH–KCl } (3.5\ M);\ \log \gamma = 0.0728m - 0.150\\
&\text{(b)}\quad \text{NaOH–NaCl } (5\ M);\ \log \gamma = 0.0387m - 0.135 \qquad \text{(1a)}\\
&\text{(c)}\quad \text{NaOH–NaCl } (3\ M);\ \log \gamma = 0.0320m - 0.192
\end{aligned}$$

The differences between the calculated and observed values have been computed by the equation

$$\Delta = 118.3 \log \frac{\gamma_{\text{calcd.}}}{\gamma_{\text{obs.}}} \qquad (5)$$

and are, therefore, in millivolts.

These results leave little doubt that in the case of these solutions at these high concentrations there is a definite departure from the linear relationship. The maximum deviation is 0.88 mv. in the potassium hydroxide series. This corresponds to a 1.76% difference between the observed and calculated activity coefficients. The same maximum difference is obtained in the case of the sodium hydroxide–chloride mixtures at 3 *M* total molality. The 5 *M* total sodium hydroxide–chloride series indicates a maximum difference of 1.95 mv., which corresponds to a 3.9% difference between the calculated and observed activity coefficients.

Summary

1. Measurements at 25° of the cells

$$H_2 \mid KOH(m_1), KCl(m_2) \mid K_xHg \mid KOH(m\ ) \mid H_2$$

in which $(m_1 + m_2)$ was kept at a constant molality of 3.5 have been made.

2. Similar measurements of the cells

$$H_2 \mid NaOH(m_1), NaCl(m_2) \mid Na_xHg \mid NaOH(m_0) \mid H_2$$

at total molalities of 3 and 5 have been presented.

3. From these data the activity coefficients of the hydroxides in the chloride solutions have been computed.

4. The linear relationship given by Equation 1 does not hold for the activity coefficients of the hydroxides in these mixtures. The differences between the observed and calculated activity coefficients were not very large. The maximum difference which occurred with the 5 M sodium hydroxide-chloride mixtures was 3.9%.

PHILADELPHIA, PENNSYLVANIA

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

THE CATALYTIC OXIDATION OF CARBON MONOXIDE.
IV. THE PORE VOLUME OF THE CATALYSTS MANGANESE DIOXIDE, COPPER OXIDE AND MIXTURES OF THESE OXIDES

BY HAL D. DRAPER

RECEIVED JUNE 22, 1928 PUBLISHED OCTOBER 6, 1928

In this paper are presented the results of experiments, completed in 1922, on the pore volume and related physical properties of the catalysts investigated and reported on in the first papers of this series.[1] Results of tests upon the catalytic efficiency of related series of catalysts, in which the composition varied between MnO_x (where x is less than 2) and CuO, showed that all the mixtures were more catalytically active than either of the pure components, whether the mixing was effected by thorough kneading of the moist hydrated oxides with subsequent drying,[1a] or by stirring together finely ground portions of the previously dried or ignited components.[1c] These results point to the conclusion that the component oxides retain their characteristic properties in the mixtures and that the "mixture effect" is due to a speeding up of the electronic rearrangement postulated in the mechanism for the catalytic reaction.[2]

As in the previous papers, the members of the three series reported on here (Almquist's Series 1, 2 and 3) will be referred to by the numbers from 1 to 6, in the order of decreasing manganese dioxide content. The compo-

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[1] (a) Almquist and Bray, THIS JOURNAL, 45, 2305 (1923); (b) Hoskins and Bray, *ibid.*, 48, 1454 (1926); (c) Bray and Doss, *ibid.*, 48, 2060 (1926).

[2] Ref. 1 b, pp. 1470–1473.

sitions of these catalysts with respect to CuO, MnO_x, H_2O, CO_2 and impurities are given in the first paper.

Definitions of Terms Used.—In the following, "true density" shall indicate that value of the density obtained by immersing the evacuated granules beneath gas-free water and determining the loss of weight sustained. This value will represent the actual density of the solid only if there is no expansion or contraction of the water in the pores of the granule and if all the pores are completely filled. Neither of these conditions is actually fulfilled in all probability.

"Granule density" will indicate the mass in grams of a granule having the volume of one cubic centimeter. This volume will consist of the volume of the solid plus the intra-granular volume (pore volume).

"Apparent granule density" or "apparent density" will indicate the value obtained by filling a vessel with granules, settling them by gentle tapping, and dividing the mass of the granules by the volume of the vessel.

The entire intra-granular free space will be called the "pore volume," which consists of "micro-capillaries," "macro-capillaries" and "cavities."

Part I of the paper will give the results of the determination of the total pore volume and the related properties of the granules; Part II will give the results from which a knowledge of the distribution of the pore volume between micro-capillaries, macro-capillaries and cavities can be obtained.

Part I

Experimental.—The true densities of the granules of Series 1 and 2, and the three samples prepared at Washington, were determined by the method of Hulett.[3]

From 4 to 8 g. of the granules was placed in a Pyrex tube constructed as shown in Fig. 1, which was then sealed off at A. Tube B was then sealed to a vacuum line and the granules were evacuated at about 200° for from three to seven hours. Eight tubes were sealed to a ring close enough together to be immersed in the same heating bath, thus insuring that all of the granules of a given series received uniform treatment. When the pressure had fallen to about 0.003 mm., the tubes were sealed off at C.

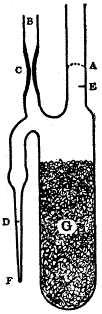

Fig. 1.

After cooling, each tube was cleaned, scratches were made at D and E and its weight reduced to *vacuo* was determined. Tube F was then inserted in tube H of the Pyrex "wash-bottle," Fig. 2, which contained distilled water, the two tubes being joined together by tight fitting rubber tubing. The water in the wash-bottle was then freed from dissolved gases by boiling under reduced pressure, and the gas-free water introduced into the granule tube by breaking the capillary at D.

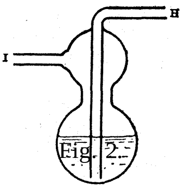

Fig. 2.

The density and pore volume of the granules was then determined as described by Cude and Hulett.[3]

Since it appeared from the results of Series 1 and *2* that a high degree of precision

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[3] Cude and Hulett, THIS JOURNAL, **42,391 (1920).**

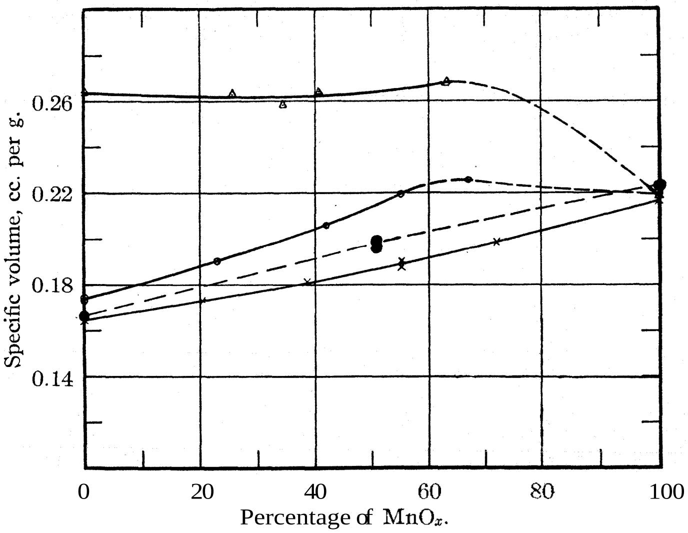
in the true density was not essential, a somewhat simpler method was used in this determination for Series 3.

Duplicate determinations made upon different specimens of the same sample gave a satisfactory check, as shown below.

Check Results on Two Specimens or Sample 5, Series 1 (Washed)

True density, g. per cc.	4 436	4 433
Specific volume, cc. per g.	0.2255	0.2256
Pore volume, cc. per g. of solid	0 49	0.50
Pore volume, cc. per cc. of solid	2.16	2.21
Granule density, g. per cc.	1 41	1.38

All the granules (Series 1 had to be washed free of soluble salts[4]) showed an initial "drift" in the density such as Hulett[3] and Harkins[5] found in experiments with charcoal, but of much smaller magnitude and of much shorter duration. None of these oxide granules required more than a



○ Series 1 (washed); X Series 2; △ Series 3, ● Washington samples.

Fig. 3.

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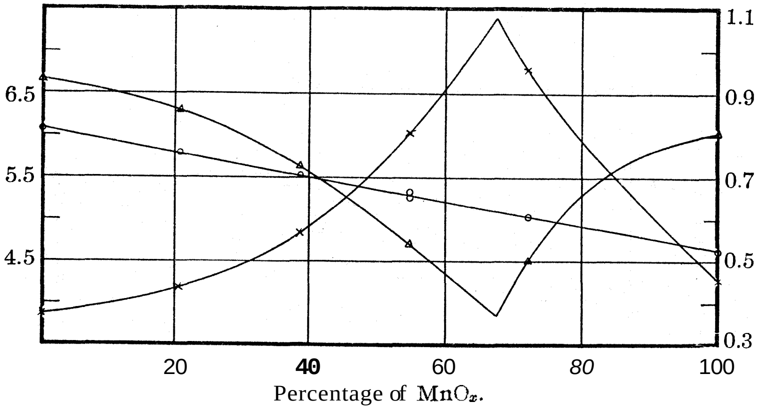
[4] Granules of Series 1 gave an unexpected result in showing a large drift almost exactly as described by Hulett and Harkins *but in the opposite direction.* Thus a 7g. specimen of Sample 6 changed from a density of 5.68 to 4.69 between Sept. 23 and Jan. 26, a change of 21%. From its mode of preparation, Sample 6 is presumably contaminated with sodium sulfate. The initial rapid decrease in density is due to the hydration of the salt to form the decahydrate. This then slowly goes into solution and diffuses out of the tube, causing the later slow decrease in density. A calculation based on this assumption indicated that 4.8% of sodium sulfate in the sample would account for the 21% change in density. Almquist[1a] found by analysis, 4.5% impurities, the nature of which he did not ascertain.

[5] Harkins and Ewing, This journal, 43, 1787 (1921).

few days before coming to a constant density, whereas with some of the charcoals several months elapsed before the "drift" disappeared. Hulett and Harkins attribute this drift to the slowness of penetration of the liquid into the micro-pores. Our results would indicate that the micro-pores of the oxide granules constitute a much smaller proportion of the total pore volume (a conclusion borne out by results described in Part II of this paper), or else that the oxides are more easily wetted by the water than is the charcoal.

Part of the results of these determinations are summarized in Table I and shown graphically in Fig. 3. It is believed that the determinations of true density in Series 1 and 2 are precise to a few hundredths of a per cent., but that the homogeneity of the samples is not greater than a few tenths of a per cent. The pore volume and apparent density are probably not precise to much better than 2%. The results given in the tables are expressed so that the last figure given is likely to be in error by not more than 3 or 4 units.



⊙ True density, g. per cc. (use left-hand ordinates). X Pore volume, cc. per g. of solid (use right-hand ordinates). △ Apparent granule density, g. per cc. (use right-hand ordinates).

Fig. 4.

Fig. 4 shows some of the properties of Series 2, which are typical of those obtained with Series 1 and 3. The sharp maxima and minima shown are probably not real, but some kind of maxima arid minima unquestionably exist in all three series between the composition of 50 and 70% MnO_x.

Discussion of Results.—One of the chief purposes of this investigation was to obtain an explanation of the "mixture effect" in the oxidation of carbon monoxide by gaseous oxygen as catalyzed by the oxide granules. As stated in the opening paragraphs of this paper, it was found that all of

TABLE I

CERTAIN PHYSICAL PROPERTIES OF POROUS GRANULES OF MANGANESE DIOXIDE, COPPER OXIDE AND MIXTURES OF THESE OXIDES

Sample	Tube no.	True density, g./cc.	Specific volume, cc./g.	Pore volume cc./g. of solid	Pore volume cc./cc. of solid	Granule density, g./cc.	Apparent density, g./cc.
			Series 1 (washed)				
1	17	4.553	0.2196	0.305	1.39	1.90	(0.81)[a]
2	21	4.436	,2255	.486	2.16	1.41	.76
	22	4.433	.2256	.499	2.21	1.38	
3	23	4.561	.2192	.860	3.89	0.93	.52
4	19	4.864	.2056	580	2.82	1.27	.68
5	18	5.260	.1901	.486	2.56	1.48	.85
6	13	5.741	.1742	.434	2.48	1.64	
	16	5.763	.1735	.434	2.50	1.65	.83
			Series 2				
1	33	4.612	,2168	.456	2.10	1.49	.81
2	32	5.038	.1986	.958	4.83	0.87	.50
3	35	5.309	,1883	.805	4.27	1 01	[b]
	31	5.254	.1903	.803	4.22	1 01	.54
4	30	5.511	.1814	.568	3.13	1.33	.73
5	29	5.789	.1727	.434	2.51	1.65	.86
6	28	6.083	.1644	.374	2.28	1.86	.93
			Series 3				
1		4.57	.261	.455	2.08	1.48	.72
2		3.72	.263	.633	2.69	1.01	.51
3		3.79	.258	.836	3.17	0.91	.49
4		3.87	,264	.702	2.72	1.01	.55
5		3.81	.269				.83[c]
6		3.83	.219				.94[c]
			Washington samples				
1	27	4.492	.2226				.42[c]
3	26	5.092	.1964	.628	3.19	1.21	[d]
	25	5.026	,1990	.631	3.17	1.21	.65
G	24	5.986	.1671	.727	4.35	1.13	.61

[a] All of the sample was used up in the various tests so that the apparent density could not be determined; assumed to be the same density as Sample 1, Series 2.

[b] Tube 35 was prepared at the same time as Tube 31, but had stood (sealed) for three months. No great change in the condition of the granules is produced by this treatment, judging from the satisfactory check.

[c] Samples were in the form of fine powders; the pore volume could not be determined by centrifuging.

[d] This sample had been put through the density determination before, and had been allowed to stand in water for four or five weeks. The slightly increased density probably means that the granules contained *a* small amount of soluble impurity which was dissolved out by this treatment. Some results obtained with this sample in **Part** II of this paper seem to indicate the presence of soluble impurities.

the mixtures were much **more** active catalysts than either of the pure components alone. One of the possibilities that needed investigation was whether the two oxides on mixing formed some definite compound. Since compound formation is generally accompanied by a departure from linearity in the specific volume–composition curve, we are now in a position to apply this criterion to the present case.

Compound Formation.—The granules of Series 2 and 3 were prepared with considerably greater care than those of Series 1, both in the washing of the component oxides free from soluble salts and in the mixing of the moist oxides before drying. Sample 1 (and probably 2) of Series 1 suffered a profound chemical and physical change when they were first wetted. In the case of Series 3, results of analysis'" indicate that the various samples lost carbon dioxide unequally upon drying. As for the Washington samples, the three bear no relation to one another in their origin, being taken from different batches of stock oxides. Series 2, therefore, is the only complete series tested, and we are confined to a consideration of results from this series alone in drawing conclusions as to the possibility of compound formation between the oxides.

An inspection of the specific volume–composition curve for Series 2 in Fig. 3 shows that the departure from linearity is very small, the maximum departure being about 2%. This result therefore indicates that there is probably no definite compound formed between the oxides. The work of Bray and Doss[1c] furnishes additional evidence against compound formation.

Correlation of Physical Properties of Granules and their Catalytic Activity.—In attempting to find a relationship between the physical properties thus far determined and the catalytic activity, results of Series 1 must be ruled out, since the determinations of catalytic activity were made with the unwashed granules, while the results given above were made upon granules which were washed free of soluble salts. The other granules, however, are comparable.

Since Almquist's results were obtained with 5.0 cc. of granules in each case, the properties of a *fixed volume* and not of a *fixed mass* of the granules must be considered. An inspection of the results calculated on this basis fails to reveal any marked break in any of the properties between the mixtures and the pure oxides corresponding to the great difference in catalytic activity. In the case of the mixtures, rough parallelism exists between catalytic activity and pore volume for Series 2, but the parallelism fails completely in Series 3 and the entire group of samples (Series 2, 8 and the Washington samples) considered as a whole.

It would appear, therefore, that the physical properties thus far discussed bear a very minor part in determining the catalytic activity of the granules.

An explanation of the marked maxima and minima in the properties other than the specific volume is found in the colloidal character of the pastes as discussed in Part II.

Part II

With the idea that compound formation could be detected by heat effects produced on mixing these oxides in a finely divided condition, samples of MnO_x and CuO were prepared for this purpose.

The MnO_x was prepared by the Fremy method, that is, by adding potassium permanganate to a concentrated solution of sulfuric acid and allowing the permanganic acid thus formed to decompose spontaneously. The copper oxide was prepared by adding a moderately dilute solution of copper sulfate to a solution of sodium hydroxide, the latter in slight excess; both solutions were at room temperature. Upon standing, the gelatinous, blue-green precipitate of hydrated copper oxide slowly changed to brownish black. (Incidentally, it is interesting to note that a sample prepared in the same way, but with an excess of copper sulfate, has been kept for several months with no apparent change in color.) Both precipitates were washed by decantation until no trace of sulfate could be detected in the washings. The precipitates were rendered semi-colloidal by this treatment; several weeks were required for the precipitates to settle out after being stirred up. This was especially marked in the case of the copper oxide, indicating either that the copper oxide particles were smaller than the MnO_x particles, or that they were less compact (average density less), or else they had adsorbed a greater number of ions per particle upon being peptized.

Quantities of these suspensions which contained about the same amount of solid were brought together in a calorimeter and stirred by hand for about five minutes. The sensitive thermometer showed only 0.001° rise in temperature, part of which was due to stirring. Later analysis showed in a total volume of 150 cc. 2.872 g. of solid consisting of 1.175 g. of copper oxide and 1.697 g. of MnO_x (by difference). The observed heat effect corresponds to only 10 calories per mole of one of the oxides. This result furnishes strong evidence against the formation of a definite compound between the two oxides.

However, it was noticed that the precipitate settled out much more rapidly after mixing, the supernatant liquid being clear after standing overnight, although, as mentioned before, several weeks were required for the settling of the pure oxide suspensions. This result indicated that the two colloidal oxides are of opposite sign—their properties and method of formation making it probable that the copper oxide is negatively, the MnO_x positively, charged due to the adsorption of hydroxyl and hydrogen ions, respectively.

The application of the above considerations has an extremely important bearing upon the whole theory of the formation of a porous granule. Almquist and Bray[6] give the following picture of the process. The terms in italics are inserted by Draper.

"The formation of the firm, porous granule may be thought of as follows. Each hydrated oxide is precipitated in the form of minute particles, the size *and configuration* of which are determined by the *nature of the substance* and the method of precipitation, *and also* by *the thoroughness of washing;*

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[6] Ref. 1 a, footnote, p. **2311.**

the more completely the soluble salts are removed, the finer the particles become through peptization of the precipitate. The filter cake, before it is dried, consists of particles surrounded by films of water which enable the relative positions of the particles to be easily changed, for example in a kneading process. In the preliminary drying as the water is slowly expelled, the particles are gradually drawn together, and in many places contact is sufficiently close to allow valence forces to come into play between the molecules of the different particles. The plastic material has now been transformed into a solid. Finally, as the water of hydration is gradually expelled, the body becomes porous."

Gelatinous and semi-gelatinous precipitates such as hydrated copper oxide, from the ease with which they may be peptized by washing, are thought to be composed of very small particles held together in a branching network, partly at least by the adsorbed substances on their surfaces. As such a precipitate is washed, the large flocks are progressively broken down into smaller and smaller particles, which must still be quite irregular in configuration until they approach the size of the ultimate particles which are of colloidal dimensions.

Now if a granule is formed from such a precipitate by the process given above, the pore volume (cc. per cc. of solid) will evidently be less the smaller and more regular the ultimate particles, that is, the more thoroughly the precipitate is washed. Comparison of the results for Sample 6 of Series 1 and 2 offers confirmation of this conclusion.

In the case of the pulverulent precipitates of MnO_x, the evidence given above indicates that the particles are considerably larger than the *ultimate* particles of copper oxide. As with most pulverulent precipitates, the particles are compact, rounded grains, which made a compact, dense granule. With particles which are nearly spherical, the pore volume might be expected to be nearly independent of their size,[7] but the proportion of macro-pores in the total pore volume will be less the smaller the particles.

The more irregular the particles of a given size, the larger the proportion of macro-pores might be expected to be.

From a comparison of the physical properties of the two oxides, one should expect the particles of the semi-gelatinous copper oxide in the thoroughly washed paste to be considerably smaller and considerably more irregular than the particles of the pulverulent MnO_x. Granules made from the pure copper oxide alone may therefore have a total pore volume which is greater or less than that of the granules made from the MnO_x, depending upon which of the two factors (size and irregularity)

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[7] It can be shown that the total free space in a given cube filled with close-packed spheres whose radius is small in comparison to the dimensions of the cube is independent of the radius of the spheres.

predominates. If the pore volume is approximately the same (as is the case in Series 2, Samples 1 and 6, Table I), we would predict that the proportion of cavities and macro-pores in the copper oxide granules would be greater, a prediction verified by results given later.

If our assumption as to the adsorption of ions of the opposite sign by the particles of the two oxides is correct, bringing the two pastes together will bring about peptization between the particles. This should have the effect of increasing both the size and the irregularity of the particles in the mixture. If the maximum effect is obtained in the case where the number of oppositely charged particles is the same, which appears logical since the peptization must take place particle by particle, the granule of maximum porosity should contain a large proportion of that oxide whose particles are the larger. Results given in Table I show that, from this standpoint also, the MnO_x particles are larger than those of copper oxide in Series 2. In Series 1, where the oxides were not so thoroughly washed, we find as predicted that there is less difference in the size of the oxide particles. In Series 3, the results indicate that the MnO_x particles are smaller; the copper oxide of this series was made from basic copper carbonate, which is much more pulverulent than the product made from the hydrated oxide.

It seemed desirable, in the light of the above considerations, to attempt to gain some idea as to the distribution of the pore volume between micro-capillaries, macro-capillaries and cavities in the various granules. A study of the adsorption curves for a vapor up to the saturation pressure should give us such information, since a relation can be developed connecting the vapor pressure and the curvature of the liquid surface in equilibrium with the vapor. For a liquid which wets the granules, the curvature of the liquid surface gives us a measure of the radius of the capillaries in which the liquid is condensed, and adsorption isotherms for the vapor will give the volume of all capillaries whose radius is equal to or less than that corresponding to each measured pressure. Since water had been used in determining the total pore volume, this liquid was used in determining the adsorption isotherms. A rather hasty run was made upon Sample 6 of Series 2 using ether instead of water. The isotherm had the same general shape as that for water, but the calculated value of the radius of the capillaries did not check closely for the smaller values, a result for which a number of explanations has been advanced[8,9,10,11] some assuming that the liquid in the capillaries is under relatively enormous positive or negative pressure; some that the "true adsorption"

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[8] Lamb and Coolidge, THIS JOURNAL, 42, 1146 (1920).

[9] Harkins and Ewing, *ibid.*, 43, 1787 (1921).

[10] Patrick and Grimm, ibid., 43, 2144 (1921).

[11] Bachmann, *Z. angew.* Chem., 79, 202 (1913).

may consist of single or multiple layers of the adsorbate, depending upon the nature of the adsorbent and the adsorbate.

Since capillary condensation is preceded by "true adsorption,"[12] the calculated values for the radii of the capillaries will differ for different adsorbates if the molecular dimensions of the latter are different. This difference may be relatively great in the event that one adsorbate forms a monomolecular and the other a multimolecular adsorbed film. It is not assumed, therefore, that the radii calculated below represent the actual dimensions of the pores; it is enough for our purpose to assume that the results obtained from the various granules, with water as adsorbate, are comparable.

To calculate the effect of curvature of the liquid surface upon the vapor pressure, the following well-known formula has been derived from the rise of a liquid in a capillary. A capillary of circular cross section, the walls of which are wet by the liquid, and whose radius is so small that the liquid surface is circular is assumed in the derivation.

$$r = \rho = \frac{2\gamma M}{DRT \ln p_0/p_1} = \frac{K}{\ln p_0/p_1} \tag{1}$$

K being a constant for constant temperature. In this formula ρ = the radius of curvature of the liquid surface, r = the radius of the capillary, D = the density of the liquid, p_0 = the vapor pressure of the liquid at a plane surface, p_1 = the vapor pressure of the liquid from the concave surface, M is the molecular weight of the vapor, R = the molecular gas constant, γ = the surface tension of the liquid and ln is the logarithm to the base e.

The volume of liquid condensed in a capillary of radius r and length l, closed at one end, and where $\rho > r$, is

$$\pi r^2 l - \pi \left[2/3\, \rho^3 - \rho^2 (\rho^2 - r^2)^{1/2} + 1/3\, (\rho^2 - r^2)^{3/2}\right] \tag{2}$$

Suppose that we have a system consisting of a network of capillaries threading a solid which is wet by water. If a volume, v, of water is absorbed at constant pressure, p, we know that the radius of curvature of the water surfaces in the capillaries has not changed during the absorption. If ρ is the radius of curvature of the water surface corresponding to the pressure p, the absorption is equivalent to that produced in circular cylindrical capillaries of radius ρ and total length L, where $\pi\rho^2 L = v$. The entire capillary volume of the solid can thus be represented by an aggregation of circular, cylindrical capillaries, at least as far as the volume and capillary properties are concerned. The actual shape of the pore will have a large effect upon the extent of surface exposed in the walls, but not upon the capillarity. The actual volume of water condensed in a porous body at any pressure of water vapor less than the saturation

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[12] *Bray and Draper, Proc. Nat. Acad. Sci.*, 12, 295 (1926).

pressure will depend largely upon the *average* length of capillaries having uniform cross section rather than the *total* length of pores having this cross section, as can be seen from Equation 2.

Consider a system composed of n_1 pores of uniform radius, r_1, and average length l_1, n_2 pores of uniform radius r_2 and average length l_2, ... n_k pores of uniform radius r_k and average length l_k. If water vapor is introduced at a pressure corresponding to a curved surface of radius ρ where $r_k < \rho < r_{k+1}$, the volume of water condensed when equilibrium is reached is evidently, from (2)

$$V = \pi\{n_1[l_1r_1^2 - 2/3\ \rho^3 + \rho^2\ (\rho^2 - r_1^2)^{1/2} - 1/3\ (\rho^2 - r_1^2)^{3/2}] + n_2[l_2r_2^2 - 2/3\ \rho^3 + \rho^2\ (\rho^2 - r_2^2)^{1/2} - 1/3\ (\rho^2 - r_2^2)^{3/2}] + \ldots\ldots + n_k[l_kr_k^2 - 2/3\ \rho^3 + \rho^2\ (\rho^2 - r_k^2)^{1/2} - 1/3\ (\rho^2 - r_k^2)^{3/2}]\} \qquad (3)$$

or

$$V = \pi \sum_{i\,=\,l}^{i\,=\,k} n_i[l_ir_i^2 - 2/3\ \rho^3 + \rho^2\ (\rho^2 - r_i^2)^{1/2} - 1/3\ (\rho^2 - r_i^2)^{3/2}] \qquad (4)$$

If, now, $p = r_{k+1}$, the volume condensed at equilibrium is the same as that given in (4) plus an additive term, $\alpha\pi[n_{k+1}\,l_{k+1}\,r_{k+1}^2 - {}^2/_3\,n_{k+1}\,r_{k+1}^3]$ (5), where α is the fraction of the capillaries of radius r_{k+1} which are filled.

Differentiating (4) with respect to ρ, we obtain

$$\frac{\mathrm{d}V}{\mathrm{d}\rho} = \pi\rho \sum_{i\,=\,1}^{i\,=\,k} n_i \left[\frac{\rho^2}{(\rho^2 - r_i^2)^{1/2}} + (\rho^2 - r_i^2)^{1/2} - 2\rho\right] \qquad (6)$$

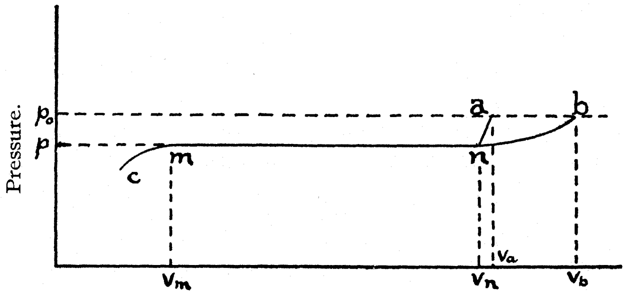
and since $\mathrm{d}V/\mathrm{d}p = (\mathrm{d}V/\mathrm{d}\rho)/(\mathrm{d}\rho/\mathrm{d}p)$, and from (1) $\mathrm{d}\rho/\mathrm{d}p = K/[p(ln\ p_0/p)^2]$

$$\frac{\mathrm{d}V}{\mathrm{d}p} = \frac{\pi K^2}{p(ln\ p_0/p)^4} \sum_{i\,=\,1}^{i\,=\,k} n_i \left\{\frac{K^2}{[K^2 - (r_i\ ln\ p_0/p)^2]^{1/2}} + [K^2 - (r_i\ ln\ p_0/p)^2]^{1/2} - 2K\right\} \qquad (7)$$

An inspection of (5) tells us that any considerable volume of water condensed at constant pressure may indicate either a very large number of short capillaries of uniform radius and length, $l > {}^2/_3\ r$, or else **a** relatively small number of long tube-like capillaries, or anything between these extremes. Equation 7 gives some important information about the adsorption curves, as follows: the slope of the pressure–volume curve is not dependent upon the average length of the capillaries; the contribution to the slope at any given point by capillaries of any given radius is directly proportional to the number of these capillaries present. This contribution is smaller the smaller the radius of the capillary; the slope of the curve is greater (other variables being constant) the larger p becomes. (Note that when V is plotted against p as the ordinate, $\mathrm{d}V/\mathrm{d}p = 0$ indicates a vertical tangent, and $\mathrm{d}V/\mathrm{d}p = \infty$ indicates a horizontal tangent.)

The actual condition of any porous body cannot be determined from the sorption curve alone, but in some cases we can obtain a valuable comparison between porous bodies by making use of the generalizations derived from the equations just developed.

In Fig. 5, cmna and cmnb represent theoretical sorption curves for such amounts of two porous granules A and B, that the same volume of water ($v_n - v_m$) is absorbed at the same pressure p, and in which the distribution of pores of various *radii less than that corresponding to the pressure* p (r_p) *is the same* (since the branches cm coincide in the two curves). Granules A and B thus have the same total volume of pores of radius r_p. Granule A differs from Granule B in having few *pores of radius greater than* r_p, the volume $v_a - v_n$ thus representing the water necessary to fill up the menisci of a relatively *small number of capillaries.* The much larger volume $v_b - v_n$ in the curve for Granule B indicates one of two conditions: (1) *a much larger number of* capillary menisci to be filled or (2) a smaller number of capillaries of uniform radius r_p, with funnel or trumpet shaped ends.



Volume of water absorbed, *cc.*

Fig. 5.

The following conclusion therefore seems justified: for a given volume of liquid condensed at constant pressure, p, the more abrupt the transition from the horizontal to the high pressure branch of the sorption curve, the fewer are the capillaries of radius r_p present in the granule and, therefore, the greater is the average length of these capillaries. For a granule whose sorption curve has a long, horizontal branch with a rather abrupt transition to the high pressure branch, we are justified in assuming that. there must be a rather small number of relatively long tube-like capillaries present.

Curves of type cmna were obtained by Lowry and Hulett[13] for sorption of water vapor by charcoal, in which we might expect to find a considerable number of tube-like pores.

Sorption curves were determined for Samples 1, 2, 3, 4 and 6 of Series 2 for water vapor up to saturation pressure at 25° (23.53 mm. of mercury at 45°), the results for better comparison being plotted for that weight of each sample which has a total pore volume of 1 cc. as determined in Part I. These results are shown in Fig. 6 and a typical run with calcula-

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[13] Lowry and Hulett, THIS JOURNAL, **42, 1403, Fig.** 6 **(1920).**

tions is given in Table II. It should be noted that the form of Equation 1 is such that values of p become rapidly less accurate as the value of p increases. Thus, an error of 0.005 cm. of mercury in the measurement of the pressure produces the following errors in the calculated values of p: at p = 1.00 cm. of Hg, p = 12.1 Å., dp = 0.07 Å., < 1% error; at p = 2.00 cm. of Hg, ρ = 60.0 Å., dp = 0.86 Å., 1.4% error; p = 2.35 cm. of Hg, p = 755 Å., dp = 116 Å., 15% error.

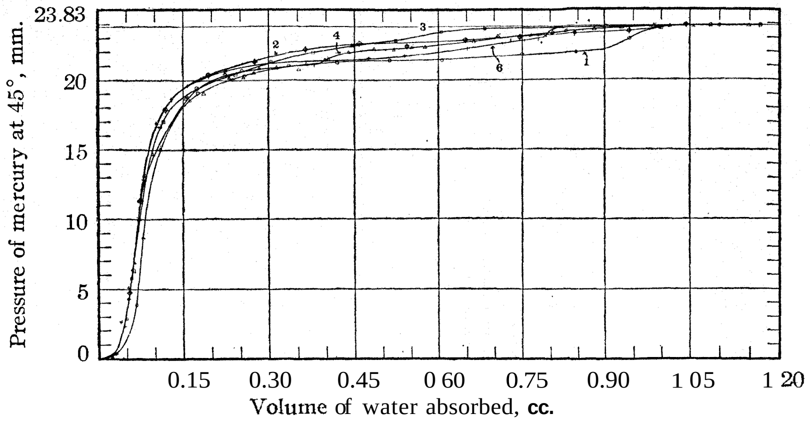

Fig. 6.

TABLE II

TYPICAL RUN ON DESORPTION CURVE FOR 0.5002 G. OF SAMPLE 2 WITH WATER VAPOR AT 25°

An excess (unmeasured) of water introduced into catalyst tube

Press. in main apparatus	Press in catalyst tube A	Weight of water in gas phase Main app.	Weight of water in gas phase Tube A	Total	Weight of water in gas phase initially	Weight of water desorbed	Total weight of water desorbed	Total weight of water in granules	Volume of water in 1.245 g. of granules	$1/\rho \times 10^{-6}$ cm.$^{-1}$	$\rho \times 10^8$ cm.
0.042	2.386	...	0.0021	0 0021	0.0021	0.0000	0.0000	0.4973	1.0408	..	..
2.373	2.348	0.0477	.0021	.0498	.0021	.0477	.0477	.4496	0.9410	0.14	710
2.335	2.338	.0470	.0021	.0491	.0021	.0470	.0947	.4026	.8426	.18	550
2.296	2.303	.0462	.0021	.0483	.0021	.0462	.1409	.3564	.7459	.33	310
2.335	2.293	.0470	.0021	.0491	.0021	.0470	.1879	.3094	.6476	.37	270
2.273	2.245	.0457	.0020	.0477	.0021	.0456	.2335	.2538	.5312	.57	175
2.275	2.261	.0458	.0020	.0478	.0020	.0458	.2793	.2180	.4562	.50	200
2.229	2.212	.0449	.0020	.0469	.0020	.0449	.3242	.1731	.3623	.71	140
2.080	2.128	.0419	,0019	.0438	0020	.0418	.3660	.1313	.2748	1.08	93
1.939	2.040	,0390	.0018	.0408	.0019	.0389	.4049	.0924	.1934	1.48	68
1.786	1.792	.0359	.0016	.0375	.0018	.0357	.4406	.0567	.1187	2.71	37
1.110	1.131	.0223	.0010	.0233	.0016	.0217	.4623	.0350	.0733	7.1	14
0479	0.486	.0096	,0004	.0100	.0010	.0090	.4713	.0260	.0544	15.1	6.6
1.173	...	.0236	...	.0236	.0004	.0232	.4945	.0028	.0059	..	..
0.141	...	.0028	...	.0028	.0000	.0028	.4973	.0000	.0000	..	..

The measurements recorded in the last two lines were taken when the tube was heated to 200°. In Column 10, the volume of liquid absorbed by 1.245 *g.* of the granules is calculated since 1.245 g. of these granules have a pore volume of 1.00 cc.

Experimental

The sorption curves were determined by means of the apparatus shown diagrammatically in Fig. 7. All of the glass parts were made of Pyrex glass. That part of the apparatus within the dotted lines was enclosed in an automatically controlled air thermostat, the temperature of the gas in the 2-liter bulb D being maintained at 45.00 ±0.02°. After assembling, the volume of the various parts of the apparatus was carefully determined, either by adding a known amount of air and measuring the pressure change produced or by adding distilled water from a buret. The volume of the catalyst bulb A and connecting tubes to a point a on manometer B was 97.9 cc., and that of D and connecting tubes between point a on manometer B and point b on manometer E was 2233 cc.

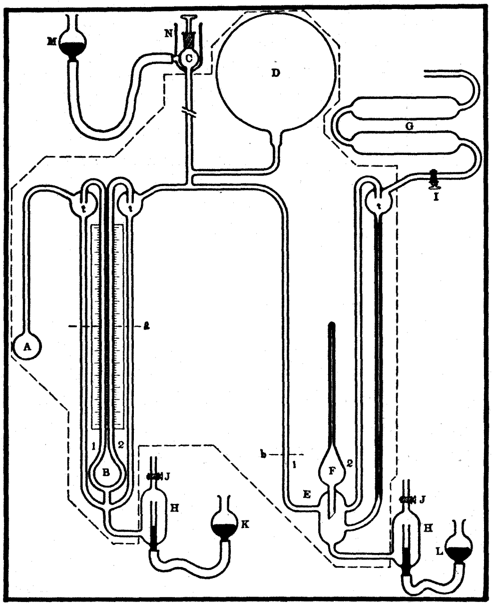

Fig. 7.

A 0.05 to 2.0 g. sample of the dried granules was placed in A, heated to 200° and evacuated through I for from three to seven hours. The small auxiliary thermostat (Fig. 8) was then adjusted to the catalyst tube and the temperature of the latter brought to 25.0 ± 0.1°, evacuation continuing until the pressure dropped to about 0.002 mm. as shown by McLeod gage F. The catalyst bulb was then cut off from the main apparatus, and the latter from the vacuum line by raising leveling bulbs K and L, respectively.

Gas-free water was then introduced into the apparatus by means of the device N, whose construction and operation have been described by Lamb and Coolidge,[8] the amount admitted being adjusted so that no vapor will condense. The amount of water present in the apparatus was then determined by measuring the pressure at manometer E, and applying the perfect gas laws. All pressures were measured by means of a cathetometer reading to 0.001 cm. Lowering K then admitted any desired amount of water into the catalyst bulb, the traps t serving to prevent any mercury from being thrown over into bulb A.

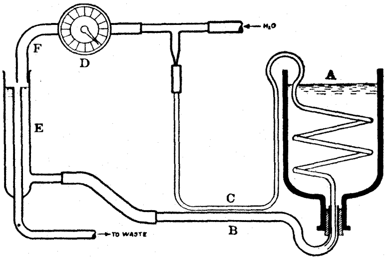

Fig. 8.

It was found simpler in practice, and the results were more reproducible when running desorption cycles. The majority of runs were made in this way. Experiments were made which demonstrated that the "zero point" could be checked to within 1% upon running an adsorption cycle, followed by a desorption cycle. It was also shown that the same curve was traced on both the adsorption and desorption cycles, no evidence of hysteresis appearing. The method of measuring the pressure probably involved the vaporization of a little of the sorbed water, so that final equilibrium may have been approached always from the same side, whether portions of water were being added or withdrawn.

The operation of the thermostat, Fig. 8, is almost self-evident from the diagram. A stream of water from the tap was passed through the tube marked "H_2O." Pinch clamp D (fitted with a dial and pointer) served to by-pass enough water through the small copper tube C to carry off just as much heat from A as entered by conduction from the air-bath.

Upon applying the principles developed from theoretical considerations to the individual curves, we arrive at the following conclusions.

Sample 1. Poorest catalyst.—A long, nearly horizontal portion of the curve with rather abrupt change near the saturation volume indicates the presence of long, tube-like pores in the granule. About 30% of the total volume sorbed is held in capillaries of radius 85 to 90 Å.; 80% is sorbed by capillaries less than 150 Å. in radius. This granule, as was predicted, is the finest grained of all those tested.

Sample 2. Most porous, second best *catalyst.*—Curve shows little evidence of either long, tube-like pores or large cavities. About 30% of the total volume is held in capillaries of 200 to 300 Å. radius.

Sample 3. Best catalyst.—No evidence of tube-like pores; a large number of rather large cavities. About 40% of the total volume is held in capillaries larger than 700 Å. in radius.

Sample 4.—The curve seems to give evidence of two sets of pores of nearly constant radius but rather short, one group having a radius of about 75 Å., and the other about 160 Å. This evidence is, however, rather doubtful.

Sample 6.—There is evidence, from the sharpness of the break in the curve, that there are relatively few capillaries of about 275 Å. radius and that a large number of large cavities exist in the granule. Twenty-five per cent. of the total volume is held in pores of radius greater than 300 Å. Nearly 30% of the volume is held in capillaries of radius between 75 and 110 Å. but there seems to be little evidence of tube-like pores in this range.

The generalizations that may be drawn connecting the porosity and the catalytic activity from the foregoing are:

1. The poorest catalysts are those which have the finest grained structures or, stated in another way, the poorest catalysts are those which sorb the greatest amount of water at relatively low pressures.

2. The best catalyst is one having high porosity (large total pore volume) with the smallest number of fine pores and the largest number of cavities.

3. For the mixtures, the slight difference in catalytic activity may be due to differences in the accessibility of the surface; the mixture *effect* still fails to find an explanation in the physical properties studied.

An additional result, for which it has been impossible to suggest an explanation that appears reasonable, may be pointed out at this point. In the region of "true adsorption" (vapor pressure less than half the saturation pressure) all the curves except that for Sample 1 coincide within the limits of error in the measurements. This would seem to indicate that the ratio of surface exposed to pore volume of the granules is the same for Samples 2 to 6, but is greater for Sample 1. Assuming cylindrical capillaries, their surface $S = 2\pi rl$, and their volume, $V = \pi r^2 l$, so that the ratio of surface to volume is $S/V = 2/r$, so that it would appear the material having the finest structure should have the greatest surface. Since Sample 1 has been shown by considerations enumerated above to have much the finest grained structure, it is to be expected that it should possess the largest adsorbent surface; the result that is hard to explain is that two granules which show such great differences in distribution of pore sizes as, say, Samples **3** and 6, should have the same surface.

In conclusion, I wish to express my gratitude for the help and encouragement given me by Professor W. C. Bray in the above investigation, and to my father for his assistance in making the sorption measurements.

Summary

It has been shown in the present investigation that: 1. The determination of the density of porous granules of certain oxides gave reproducible results by the immersion method of Hulett. No slow "drift" in the density of the granules similar to that encountered in determinations with charcoal was discovered. This indicates that there are few very small micro-capillaries in the former or else the resistance to filling of these pores is less. Adsorption curves prove the oxide granules to be much more coarse grained than the charcoal.

2. The porosity of the pure oxides is less than that of any of the mixtures made from them. This enhanced porosity is explained by colloidal phenomena.

3. There is no evidence of compound formation between the well washed oxides upon mixing.

4. An expression has been derived giving the volume of water sorbed by *a* porous body in terms of the radius of curvature of the water surface corresponding to the equilibrium pressure of the water vapor, the number and the radii and average length of the capillaries of the solid. The slope of the volume–vapor pressure curve depends upon the number and the radii of the capillaries present and the ratio of the saturation to the equilibrium pressure but not upon the average length of the capillaries. The sorption curves are shown to yield evidence as to the existence of long, tube-like capillaries in the granules in some cases.

5. Sorption curves have been determined for certain oxidation catalysts

in the form of porous granules. The poorest catalysts have the finest grained structure. No explanation for the "mixture effect" is discovered.

6. An apparent anomaly in the results has been pointed out. In the region of true adsorption, all the sorption curves except that for Sample 1 coincide, indicating nearly equal surface exposure per unit pore volume for all these granules, in spite of great difference in pore size.

FRESNO, CALIFORNIA

[CONTRIBUTION FROM THE PACIFIC EXPERIMENT STATION, U. S. BUREAU OF MINES, BERKELEY, CALIFORNIA]

THE HEAT CAPACITY AT LOW TEMPERATURES OF ZINC OXIDE AND OF CADMIUM OXIDE[1]

BY RUSSELL W. MILLAR[2]

RECEIVED JUNE 30, 1928 PUBLISHED OCTOBER 6, 1928

Research on the heat capacities of the oxides of metals previously reported by the author[3] has been continued. For the sake of a comparison of results with those of Parks and his co-workers,[4] the heat capacity of zinc oxide was redetermined.

Materials.—The zinc oxide used was the Sample 2 described by Maier, Parks and Anderson. It had been kept in an evacuated silica flask at 1100° for sixty hours. The product was microcrystalline and contained, according to them, less than 0.1% of impurities.

The cadmium oxide used was prepared by heating pure cadmium oxide in an open platinum dish at 1100° for three days. The product was finely crystalline and of much higher apparent densitv than the original powder.

The values of C_p, the heat capacity in calories per mole per degree, are presented in Tables I and II and in Fig. 1 opposite the corresponding temperatures in degrees Kelvin.

The entropy was calculated, as described previously, by extrapolation to the absolute zero by means of the sum of suitable functions of the form of Debye and of Einstein. For zinc oxide a Debye function with $\beta\nu$ = 295.5 and an Einstein function with $\beta\nu$ = 753 fitted the data with an accuracy of 0.5% to 250°K., although C_v and C_p begin to deviate at much lower temperatures. At higher temperatures the experimental values fall below those given by the theoretical functions. Using C_p and log T as coördinates, the curve was extrapolated to 37.58°K., where it joined the Debye curve at $C_v = 0.860$. Below this temperature the tables of Mieth-

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[1] Published by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.)

[2] Associate chemist.

[3] Millar, THIS JOURNAL, 50, 1875 (1928).

[4] (a) Parks and Kelley, *J. Phys. Chem.*, **30,** 47 (1926); (b) Maier, Parks and Anderson, THIS JOURNAL, 48, 2564 (1926).

TABLE I

THE MOLAL HEAT CAPACITY OF ZINC OXIDE

T, °K.	C_p cal./mole	T, °K.	C_p cal./mole	T, °K.	C_p cal./mole
89.7	3.794	142.9	5.895	225.0	8.318
95.8	4.080	81.8	3.488	228.4	8.443
102.5	4.375	84.2	3.561	231.8	8.413
109.0	4.649	167.0	6.818	277.3	9.267
116.6	4.941	174.7	7.059	282.5	9.400
120.1	5.078	183.2	7.309	284.8	9.432
124.2	5.237	189.7	7.548	286.9	9.527
128.7	5.450	196.8	7.697	289.1	9.480
131.2	5.576	204.7	7.996	295.3	9.505
134.9	5.650	210.8	8.052	297.9	9.641
139.2	5.796	220.1	8.220		

TABLE II

THE MOLAL HEAT CAPACITY OF CADMIUM OXIDE

T, °K.	C_p cal./mole	T, °K.	C_p cal./mole	T, °K.	C_p cal./mole
71.3	4.078	136.1	7.460	151.9	8.045
77.9	4.495	148.0	7.945	177.1	8.774
90.5	5.286	160.9	8.309	194.9	9.165
101.1	5.843	288.0	10.35	232.5	9.879
112.2	6.402	289.2	10.35	253.5	10.06
124.2	6.942	290.4	10.30		

ing[5] give the entropy as 0.308 cal. per mole. The area above this temperature represents 9.97 entropy units, so that for ZnO, $S°_{298} = 10.28$. The error is probably not over 0.05 unit.

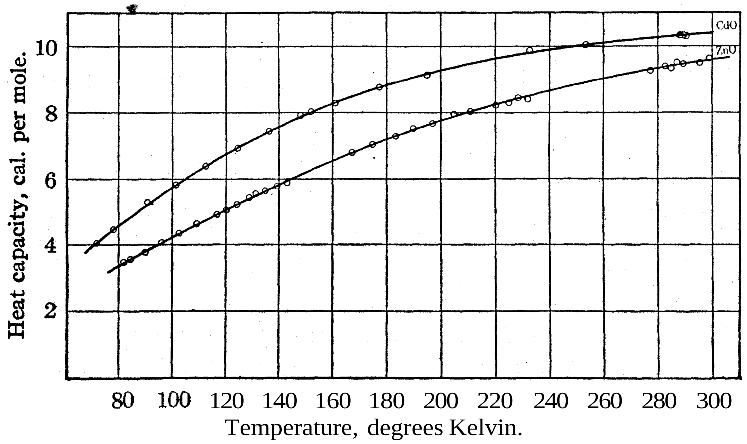

Fig. 1.—The molal heat capacities of cadmium oxide and zinc oxide.

A similar calculation for cadmium oxide, with $\beta\nu = 236$ and 478.5 for the Debye and Einstein functions, respectively, gives 0.36 entropy unit

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[5] Published in Nernst, "Die theoretischen und experimenteller Grundlagen des neuen Wärmesatzes," Wilhelm Knapp, Halle, 1918.

at 31.84°K. and, by graphical integration, 12.81 units between 31.84 and 298°K. Thus for CdO, $S°_{298} = 13.17$. The sum of these functions agrees with the data within 0.2% to 160°K., and exceeds the experimental values at higher temperatures. Obviously the theoretical values would exceed the values of C_v, if necessary data for their calculation existed, at still lower temperatures.

The values of the heat capacity of zinc oxide agree with those of Maier, Parks and Anderson within 0.2% at their lowest temperature, 88°K., but become appreciably lower at higher temperatures. At room temperature the deviation is 2%. Although widely different methods of calculation were employed, the entropy which they give, $S°_{298} = 10.4$, differs but little from the present value of 10.28.

No significance is to be attached to the agreement of various combinations of theoretical curves for heat capacity with the experimental values of this quantity, for all such mathematical treatments rest upon hypotheses not entirely true and, furthermore, are designed to give values of C_v and not C_p. However, extrapolations by means of these curves cannot be far from correct when the last measured value of the heat capacity is not more than 4 calories per mole, and they undoubtedly approach the absolute zero correctly.

After reviewing the direct determination of the heat of formation of zinc oxide and comparing the values obtained from the temperature coefficients of the equilibrium constant of the reaction $ZnO + CO = Zn + CO_2$ and of the e.m.f. of the cell $ZnO + Zn | Ba(OH)_2$ soln. $| H_2$, Maier, Parks and Anderson[4b] give 83,000 cal. as the best value. Roth and Chall[6] have recently obtained 82,905 cal. for dense zinc oxide and 82,825 for less dense material at 50°, while Parks, Hablutzel and Webster[7] give 83,240 cal. at 20°. We shall choose for $Zn_{(s)} + {}^1/_2 O_{2\,(g)} = ZnO_{(s)}$; $\Delta H = -83{,}000$.

Maier after a review (to be published soon) of the data, has chosen 62,000 as the probable value of the heat of formation of cadmium oxide.

For zinc and cadmium, Lewis, Gibson and Latimer[8] give $S°_{298} = 9.83$ and 11.80, respectively, and for O_2 we may use, as before, Millar's[3] value 49.2.

We have $Zn_{(s)} + {}^1/_2 O_{2(g)} = ZnO_{(s)}$, $\Delta H_{298} = -83{,}000$, $\Delta S°_{298} = -24.15$, $\Delta F°_{298} = -75{,}800$; and $Cd_{(s)} + {}^1/_2 O_{2(g)} = CdO_{(s)}$, $\Delta H_{298} = -62{,}000$, $\Delta S°_{298} = -23.23$, $\Delta F°_{298} = -54{,}200$.

Since the value of the free energy of zinc oxide which Maier, Parks and Anderson obtained from cells, –75,930, is doubtless much more nearly accurate than our knowledge of the heat of formation, it is more logical to calculate the latter from the entropy of formation. We obtain $\Delta H = -83{,}130$, a value probably accurate to within 100 calories.

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[6] Roth and Chall, *Z. Elektrochem.*, 34, 185 (1928).

[7] Parks, Hablutzel and Webster, This Journal, 49,2792 (1927).

[8] Lewis, Gibson and Latimer, *ibid.*, 44, 1008 (1922).

Summary

1. The heat capacities of zinc and cadmium oxide from 70 to 300° Kelvin have been determined.

2. The entropy of zinc oxide at 298°K. is 10.28 ± 0.05 cal./mole/degree, and of cadmium oxide is 13.17 ± 0.1 cal./mole/degree.

3. For zinc oxide we find from an accurate value of the free energy and the entropy of formation $\Delta H = -83{,}100 \pm 100$, and for cadmium oxide we find from the entropy of formation and a somewhat uncertain value of the heat of formation, $\Delta F^\circ_{298} = -54{,}200$.

[CONTRIBUTION NO. 582 FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

THE EQUILIBRIUM $2K_3Fe(CN)_6 + 2KI \rightleftharpoons 2K_4Fe(CN)_6 + I_2$ IN AQUEOUS POTASSIUM CHLORIDE SOLUTIONS

BY VICTOR K. LA MER AND KARL SANDVED

RECEIVED JULY 10, 1928 PUBLISHED OCTOBER 6, 1928

I. Introduction

This paper comprises one phase of a study of the kinetics of ionic reactions which proceed to a measurable equilibrium state, the purpose of the study being to investigate the velocity of the reaction not only in its initial stages but also in the neighborhood of equilibrium.

The reaction between ferricyanide and iodide ions yielding ferrocyanide and iodine, as follows

$$2Fe(CN)_6^{---} + 2I^- \rightleftharpoons 2Fe(CN)_6^{----} + I_2 \qquad (1)$$

possesses certain advantages for such a study since

1. The reaction reaches an equilibrium state after 2–13% conversion, depending upon the composition and the amount and character of added neutral salts. The equilibrium state is therefore accessible to experimental measurement and is well adapted for a study of salt effects.

2. The velocity of the reaction is also highly sensitive to neutral salt catalysis, a subject of considerable theoretical interest at the present time.[1]

3. Previous studies[2,3,4] have shown that the velocity of the reaction, unlike most reversible ionic reactions, is of a magnitude that can be followed.

In the investigations of Donnan and Le Rossignol,[2] Just[3] and Wagner,[4] the reaction was followed by adding measured amounts of thiosulfate and

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[1] For a critical discussion see J. N. Bronsted, "Acid and Basic Catalysis," Copenhagen, 1926, translated from the Danish by the authors for *Chemical Reviews,* September, 1928, particularly Chapters 4 and 5 and appendix.

[2] Donnan and Le Rossignol, J. *Chem. Soc.*, 83,703 (1903).

[3] Just, *Z.* phys. *Chem.*, 63,513 (1908).

[4] Wagner, *ibid.*, 113,261 (1924).

starch and noting the time of appearance of the blue color. Although this very simple technique, known as the compensation method of Harcourt and Esson,[5] has the advantage of continuously regenerating the iodide ion as fast as it is converted to iodine by ferricyanide, so that the concentration of iodide is constant throughout the course of the reaction, it is impossible to study the equilibrium state by this method since the reaction is forced to completion by the addition of thiosulfate.

We have accordingly adopted the method of titrating the liberated iodine in aliquots removed at definite time intervals. The kinetic measurements will be reported later and only data on the equilibrium state and its relation to the component potentials of the ferro–ferricyanide and iodine–iodide systems will be considered in the present paper.

II. The Equilibrium Constant in Salt Solutions

The thermodynamic mass action function for Reaction (1) may be written as follows

$$\frac{c^2_{\mathrm{Fe(CN)_6^{----}}} \cdot c_{\mathrm{I_2}}}{c^2_{\mathrm{Fe(CN)_6^{---}}} \cdot c^2_{\mathrm{I^-}}} \times \frac{f^2_{\mathrm{Fe(CN)_6^{----}}} \cdot f_{\mathrm{I_2}}}{f^2_{\mathrm{Fe(CN)_6^{---}}} \cdot f^2_{\mathrm{I^-}}} = K_a \qquad (2)$$

$$K_c \times K_f = K_a \qquad (3)$$

where c refers to the stoichiometric concentration and f to the stoichiometric activity coefficient of the participating components. K_a is a true constant for any given temperature and pressure and is independent of changes in concentration. The value of K_a is calculated in Section (V). To avoid the cumbersome quotients the abbreviated symbols given in (3) corresponding to (2) are introduced.

From what is known of the behavior of the activity coefficient as a function of valence and the total electrolyte concentration in dilute solution,[6] it is evident that the ratio

$$K_f = f^2_{\mathrm{IV}} \cdot f_0 / f^2_{\mathrm{III}} \cdot f^2_{\mathrm{I}} \qquad (4)$$

where the roman subscripts refer to the valences of the ions involved in (1) and (2), should presumably decrease with increasing salt concentration, which means that the equilibrium state will be displaced to the right. Constant values for the stoichiometric equilibrium "constant" K_c therefore can only be expected when the ratio of the coefficients in (4) is constant, that is, when a constant thermodynamic environment[7] is maintained.

Although measurements exist for computing an estimate of the change of the component activity coefficients in K_f as a function of salt concen-

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[5] Harcourt and Esson, *Phil. Trans.*, 157, **117** (1867).

[6] For a review of this subject and for references to previous literature see La Mer, *Trans. Am. Electrochem. Soc.*, 51, 507–556 (1927).

[7] See Washburn, "Principles of Physical Chemistry," 2d ed., McGraw-Hill Book Company, 1921, pp. 268, 321, for a clear presentation of the meaning and influence of this factor in both equilibrium and kinetic measurements; also Washburn and Strachan, THIS JOURNAL, 35, 710 (1913).

tration, in no case do the measurements correspond to the exact environment which is produced by the simultaneous presence of both systems, and particularly for concentrated solutions.

In their studies on the equilibrium

$$2Fe^{+++} + 2I^- \rightleftharpoons 2Fe^{++} + I_2^- \qquad (5)$$

Bronsted and Kai Pedersen[8] showed that a constant environment could be obtained by the addition of an excess of neutral salt. They found 1.65 *M* KCl + 0.1 M HCl to be sufficient for the conditions under which they studied their reaction.

In view of its importance for our further studies, it seemed desirable to determine whether or not the general principle enunciated by Brönsted,[9] namely, "That the simple gas laws hold good for ions or salts when other salt solutions are employed as solvents, the concentration being large in comparison with the concentration of the dissolved ion or ions," would also hold good for the present reaction where tri- and tetravalent ions were involved and at considerably higher concentrations than those employed in the experiments of Bronsted and Pedersen.[8] The highly specific behavior[10,11] of ferro- and ferricyanides in dilute solutions makes it especially desirable to test the principle with these ions.

III. Experimental Procedure

Weighed amounts of potassium ferricyanide corresponding to the concentrations given in Col. 2 of the tables were dissolved in boiled distilled water in a volumetric flask, calibrated to deliver 50 cc., and immersed in a thermostat at 25°. The potassium iodide and potassium chloride (also potassium ferrocyanide in Expts. 21 and 22) were weighed out, dissolved in 250 cc. of distilled water and brought to 25° in a 500cc. Erlenmeyer flask. When both solutions had acquired the temperature of the bath, the reaction was started by adding the 50 cc. of ferricyanide solution to the potassium iodide. A series of Erlenmeyer flasks containing definite amounts of *N*/100 $Na_2S_2O_3$, weighed out from a weight buret and diluted to 125 cc. with boiled water containing 0.08 g. of dissolved starch, were in readiness before the start of the reaction. Samples were withdrawn at 2.5-minute intervals in a 10cc. measuring pipet calibrated to a 0.1cc. graduation and allowed to flow rapidly into these flasks until the color change due to iodine was retained on stirring

From four to six titrations were made on the system after equilibrium was reached and the average was recorded in Col. 8 of the tables in terms of the concentration of potassium ferrocyanide formed. The maximum deviation from the average was about 0.3%. It required about forty to sixty minutes to reach equilibrium in the presence of excess potassium chloride and a somewhat longer time in its absence.

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[8] Bronsted and Pedersen, Z. *physik. Chem.*, *103*, 307 (1922).

[9] Bronsted, *Medd. Vetenskapsakad. Nobelinst.*, *5*, No. 25 (1919), (in English). See also *Kgl. Danske Videnskab. Selsk. Skrifter naturvidenskab. Math. Afdel.*, [7], XII, 241 (1914); *ibid*, *Math.-fys. Medd.*, III, 9 (1920), and reference 6, p. 519–521.

[10] La Mer and Mason, THIS JOURNAL, 49, 410 (1927)

[11] G. N. Lewis, Z. *physik. Chew.*, *70*, 212 (1909), points out that the classical dissociation constant of potassium ferricyanide changes about one million fold in passing from 0.0001 *M* to 1.0 *M*.

There are several factors which contribute to make this method an accurate one for determining the concentrations at equilibrium. The forward reaction is of the second and first orders, respectively, for iodide and ferricyanide. Fifteen-fold dilution alone is thus amply sufficient to check the reaction. Furthermore, this dilution displaces the equilibrium almost completely to the left and the instantaneous removal of iodine by the thiosulfate prevents the reverse reaction from proceeding. That this is really the case was proved by allowing samples at the titration end-point to stand overnight., No perceptible color change occurred.

All salts employed were of c. p. grade and the potassium ferricyanide was recrystallized twice from water. The potassium chloride used in Expts. 1 to 16 was recrystallized twice.

IV. Discussion of Results

The Tri-iodide Equilibrium

Cols. 5, 6 and 7 of Table I give the concentrations of the solutions, respectively, in terms of the sum of the KI and KCl, the total equivalent concentration or ΣK, and the ionic strength μ defined as $\mu = {}^1/_2\ \Sigma c_i z_i^2$. Since the concentrations of I_2 and $I-$ are influenced by the well-known equilibrium

$$I_3^- \rightleftarrows I_2 + I^- \tag{6}$$

the amount of iodine titrated is recorded in Col. 9 in terms of its stoichiometric equivalent potassium ferrocyanide.

In the most recent investigations for the constant

$$L = \frac{c_{I^-} \cdot c_{I_2}}{c_{I_3^-}} \cdot \frac{f_{I^-} \cdot f_{I_2}}{f_{I_3^-}} \tag{7}$$

is given as 0.00153 for water as solvent by Bray and MacKay,[12] whereas Bronsted and Pederson found 0.00502 at 15° and 0.00540 at 18.5°, and give an extrapolated value of 0.00611 for 25° using 1.65 M KC1 + 0.1 M HCl as solvent. The latter value appears to be quite trustworthy and was used in all the further calculations.

By applying the law of mass action to Equations 1 and 6, the following expression for the concentration of the complex ion I_3^- results

$$c_{I_3^-} = \frac{b + L - x/2 - \sqrt{(b + L - x/2)^2 - 2\,x\,(b - x)}}{2} \tag{8}$$

where b = initial concentration of KI, x = concentration of $K_4Fe(CN)_6$ formed, and $x/2$ = concentration of I_2 formed.

It is at once apparent from the I_3^- values tabulated in Col. 9 of the table that almost all of the iodine formed exists in the form of the complex ion, since the values in Col. 8 are only a little more than twice those of Col. 9. For this reason it is more convenient to compute the equilibrium constant (Col. 11)

$$K_c' = \frac{x^2 \cdot c_{I_3^-}}{(a - x)^2(b - x - c_{I_3^-})^3} \tag{9}$$

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[12] Bray and MacKay, THIS JOURNAL, 32,914 (1910).

Table I

$K_a' = 0.199 \times 10^{-3}$

(Expts. 27–33 by Mr. W. G. **Parks)**

Expt.	$C_{K_3Fe(CN)_6}$	C_{KI}	C_{KCl}	$C_{KI} + C_{KCl}$	Equiv. concn., EK	μ	$C_{K_4Fe(CN)_6} \times 10^3$ formed	$C_{I_3^-} \times 10^3$	% conv. of ferricyanide	$K_c' \times 10^3$	K_f'
1	0.10	0.25	...	0.25	0.55	0.85	5.486	2.674	5.49	0.637	0.312
2	.10	.20	...	.20	.50	.80	4.104	1.989	4.10	.500	.398
3	.075	.20	...	.20	.425	.65	3.240	1.570	4.32	.430	.463
4	.075	.15	...	.15	.375	.60	2.236	1.071	2.98	,320	,622
5	.075	.20	1.00	1.20	1.425	1.65	6.685	3.240	8.91	4.52	.0440
6	.075	.20	1.00	1.20	1.425	1.65	6.664	3.230	8.89	4.47	.0445
7	.075	.20	1.00	1.20	1.425	1.65	6.674	3.232	8.90	4.49	.0443[a]
8	.075	.175	1.025	1.20	1.425	1.65	5.864	2.829	7.82	4.43	.0449
9	.075	.15	1.05	1.20	1.425	1.65	5.087	2.433	6.78	4.45	.0447
10	.10	.25	0.80	1.05	1.35	1.65	9.763	4.754	9.76	4.26	,0467
11	.10	.25	.875	1.125	1.425	1.675	10.120	4.930	10.12	4.82	.0413
12	.10	.25	.825	1.075	1.375	1.625	9.882	4.815	9.88	4.44	.0448
13	.10	.20	.875	1.075	1.375	1.625	8.014	3.877	8.01	4.42	.0450
14	.10	.15	.925	1.075	1.375	1.626	6.113	2.927	6.11	4.43	.0449
15	.05	.20	1.125	1.325	1.475	1.625	5.230	2.533	10.46	4.86	,0409
16	.05	.20	1.075	1.275	1.425	1.575	5.103	2.474	10.20	4.48	,0444
17	.05	.15	1.125	1.275	1.425	1.575	3.915	1.876	7.83	4.51	.0441
18	.05	.15	0.50	0.65	0.80	0.95	2.711	1.302	5.42	1.38	.144
19	.05	.20	.45	.65	.80	.95	3.650	1.768	7.30	1.49	.134
20	.05	.10	.55	.65	.80	.95	1.793	0.842	3.58	1.25	.159
21	.10	.15	.925	1.075	1.387	1.705	4.402	2.110	4.40	4.29	,0464"
22	.05	.20	1.075	1.275	1.437	1.606	3.512	1.702	7.02	4.52	.0440[b]
23	.075	.20	2.00	2.20	2.426	2.65	9.963	4.824	13.28	17.8	.0112
24	.075	.10	1.90	2.00	2.225	2.45	4.775	2.240	6.37	12.9	.0154
25	.075	.15	1.95	2.10	2.325	2.55	7.448	3.568	9.93	16.2	.0123
26	.075	.20	1.00	1.20	1.425	1.65	7.214	3.497	9.60	5.84	.034[c]
27	.075	.20	2.00	2.20	2.425	2.65	9.85	4.77	13.13	17.11	.0116[d]
28	.075	.10	2.10	2.20	2.425	2.65	5.09	2.388	6.79	16.0	.0125[d]
29	.10	.20	1.925	2.125	2.425	2.725	12.00	5.808	12.00	17.8	.0112[d]
30	.10	.20	1.85	2.05	2.35	2.65	11.73	5.68	11.73	16.5	.0121[d]
31	.075	.20	1.00	1.20	1.425	1.65	6.63	3.21	8.84	4.39	.0453
32	.075	.20	1.00	1.20	1.425	1.65	7.26	3.52	9.68	5.97	.0333[e]
33	.075	.20	1.00	1.20	1.435	1.66	10.20	4.93	13.60	19.33	.0103[f]

[a] 2×10^{-4} M HCl. [b] 0.003 M $K_4Fe(CN)_6$. [c] 1.73×10^{-3} M HCl.

[d] Average of two experiments.

[e] 0.001 M HCl.

[f] 0.01 M HCl.

corresponding to the reaction

$$2Fe(CN)_6^{---} + 3I^- \rightleftharpoons 2Fe(CN)_6^{----} + I_3^- \qquad (10)$$

where a = initial concentration of ferricyanide. The mass action function for (10) will be designated by primes to distinguish it from (3); namely,

$$K_c' \cdot K_f' = K_a' \text{ where } K_f' = \frac{f_{IV}^2}{f_{III}^2} \cdot \frac{f_{I_3^-}}{f_{I^-}^3} \qquad (11)$$

The equilibrium constants for the original Equation 1 can be obtained when desired by multiplying the figures in Col. 11 with the appropriate value of L for the solvent employed. We have not done this because systematic studies on the variation of *L* for potassium chloride additions have not been made. That L changes markedly when chlorides are added is evident from the values given by Bray and MacKay and by Bronsted and Pedersen. For an accurate calculation the L value used in (8) should of course correspond with the measured value for the particular solvent employed. However, we have proved to our satisfaction that the $c_{I_3^-}$, as computed from (8), is not appreciably affected by using either the Bray or the Brönsted value. For example, $10^3K'_c$ in Expts. 1 and 23 is changed from 0.637, and 17.8 to 0.649, and 18.3 when L is assigned the values 0.00611 and 0.00143, respectively. Since the p value of 1.63 lies intermediate in our range of salt concentrations, the value L = 0.00611 is more appropriate for the calculations in Tables I and II.

A comprehensive study of the behavior of L in salt solutions, particularly the halides, by the method given by Bronsted and Pedersen, is needed since this constant enters into the interpretation of all kinetic and equilibrium studies involving iodine.

V. Determination of K_a and K'_a from e.m.f. Data

Although we cannot measure K'_c at sufficient dilution to extrapolate safely to infinite dilution to determine K'_a, we can by a combination of existing free energy data arrive at what should be very trustworthy values for K'_a and K,.

Linhart's[13] careful measurements on the cell

$$\mathrm{Hg, HgCl\,(S) + KCl\,(M)}, \left(\begin{matrix}\mathrm{K_3Fe(CN)_6(c_1)}\\ \mathrm{K_4Fe(CN)_6(c_2)}\end{matrix} + \mathrm{KCl\,(M)}\right)\mathrm{Au} \qquad (12)$$

give, when corrected for the activity of potassium chloride as Wnhart has done using the measurements of Harned, the free energy of the reaction

$$\mathrm{Hg\,(S) + Fe\,(CN)_6^{---} + Cl^- = Fe(CN)_6^{--} + HgCl\,(S)} \qquad (13)$$

$$\mathrm{E_0} = 0.2188 \pm 0.0002;\ \Delta F^{\circ}_{298.1} = -5049 \pm 5$$

In these experiments no liquid junction potential exists since the potassium chloride was in great excess and of the same concentration in both half-cells. Eight molalities of potassium chloride were used, ranging between 0.05 M and 4.284 M. The concentration ratio c_1/c_2 was varied between 2 to $^1/_2$ and $(c_1 + c_2)$ between 0.0005 to 0.02 M at the highest concentrations of potassium chloride.

When the concentration of potassium chloride was greater than 0.1 M, Wnhart found that the activities of potassium ferrocyanide and potassium ferricyanide were proportional to their concentrations, a result which Bronsted's principle demands. The greatest variation which $\mathrm{E_0}$ exhibited is only 0.4 mv. in changing from $c_1/c_2 = 2$ to $^1/_2$, which corresponds to a change of 2.5% in K'_c. Linhart speaks of this result as in accord with the view that potassium ferrocyanide and potassium ferricyanide are

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[13] Linhart, THIS JOURNAL, 39,615 (1917).

undissociated or at least that the ionization of intermediate ions is completely repressed. This is not necessarily true. Linhart's results only prove that both salts are dissociated to the same extent in potassium chloride solutions. The data may be taken equally well as proof for the hypothesis of complete dissociation as for any definite degree of incomplete dissociation.

Linhart also shows that Lewis and Sargent's[14] data yield the same average value for $\mathbf{E}_0$ when the differencesin potassium chloride concentration in the oxidation cell and normal calomel cell are taken into account. Lewis and Sargent's measurements consequently serve as a good check upon his results.

On the other hand, the measurements of Schoch and Felsing[15] involve concentrations of ferro- and ferricyanide relative to potassium chloride which are too large to determine $\mathbf{E}_0$ accurately. Nevertheless, the trend of their values is also consistent with a value $E_0 = 0.2188$.

The other data needed for the calculation are taken from Lewis and Randall's "Thermodynamics" with the exception of cell (14). For 25°

$$\mathrm{Hg\,Cl\,(S)} + \mathrm{E}^- = \mathrm{Hg} + \mathrm{Cl}^-;\ \mathbf{E}_0 = 0.2676;^{16}\ \mathrm{AF}^\circ = -6175 \qquad (14)$$

$$\mathrm{I}^- = \mathrm{E}^- + \frac{1}{2}\mathrm{I}_2\,(\mathrm{S});\ \mathbf{E}_0 = -0.5357 \pm 0.0004;\ \mathrm{AF}^\circ = 12{,}361 \pm 10 \qquad (15)$$

$$\frac{1}{2}\mathrm{I}_2\,(\mathrm{S}) = \frac{1}{2}\mathrm{I}_2\,(\mathrm{aq.});\ \mathbf{E}_0 = -0.0851;\ \Delta F^\circ = 1963 \qquad (16)$$

$$\frac{1}{2}\mathrm{I}_3^- = \frac{1}{2}\mathrm{I}^- + \frac{1}{2}\mathrm{I}_2(\mathrm{S});\ \mathbf{E}_0 = +0.0010;\ \mathrm{AF}^\circ = -23 \qquad (17)$$

By combining (13) and (14), we get (18)

$$\mathrm{Fe(CN)_6}^{---} + \mathrm{E}^- = \mathrm{Fe(CN)_6}^{----},\ \mathbf{E}_0 = +0.4864;\ \mathrm{AF}^\circ = -11{,}224 \qquad (18)$$

with an uncertainty which should be less than 1 mv.

Similarly, by combining (18) and (15)

$$\mathrm{Fe(CN)_6}^{---} + \mathrm{I}^- = \frac{1}{2}\mathrm{I}_2(\mathrm{S}) + \mathrm{Fe(CN)_6}^{----};\ \mathbf{E}_0 = -0.0493;\ \Delta F^\circ = 1137 \qquad (19)$$

or by combining (18), (15) and (16), we obtain

$$\mathrm{Fe(CN)_6}^{---} + \mathrm{I}^- = \frac{1}{2}\mathrm{I}_2\,(\mathrm{aq.}) + \mathrm{Fe(CN)_6}^{----};\ \mathbf{E}_0 = -0.1344;\ \Delta F^\circ = 3100 \qquad (20)$$

To take into account tri-iodide .formation, we have on combining (19) and (17)

$$\mathrm{Fe(CN)_6}^{---} + {}^3/_2\,\mathrm{I}^- = \frac{1}{2}\mathrm{I}_3^- + \mathrm{Fe(CN)_6}^{----};\ \mathbf{E}_0 = -0.0503;\ \Delta F^\circ = 1160 \qquad (21)$$

By introducing the well-known formula

$$-\mathrm{AF}^\circ = \mathbf{N\,F\,E}_0 = RT \ln K$$

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[14] Lewis and Sargent, THIS JOURNAL, 31,355 (1909).

[15] Schoch and Felsing, *ibid.*, 38,1928 (1916).

[16] Revised value, Randall and Young, *ibid.*, SO, 989 (1928). The older value given by Lewis and Randall **was** $\mathbf{E}_0 = 0.2700$.

we obtain the following values for the equilibrium constants K_a and K'_a, corresponding to Equations 1 and 10 for N = 2 when the activities of all components are one (hypothetical) molal; namely,

$$K_a = 2.89 \times 10^{-5} \tag{22}$$

$$K'_a = 0.199 \times 10^{-3} \tag{23}$$

which corresponds to

w $$L_a = \frac{a_{I_2} \cdot a_{I^-}}{a_{I_3^-}} = \frac{K_a}{K'_a} = 0.00143 \tag{24}$$

in substantial agreement with Bray and MacKay's value.[17]

VI. The Influence of Environment

In Col. (12), K'_f is computed by dividing K'_a by the stoichiometric quantity, K'_c, and in accordance with expectation K'_f decreases markedly with increasing salt concentration. The most striking result of the investigation is the marked dependence of K'_c, in the absence of foreign neutral salts, arising from comparatively small variations in the initial ferricyanide and iodide concentrations, and the almost complete obliteration of this dependence in the presence of excess potassium chloride. Thus Expts. 1–4 show a change in K'_c or K'_f of 35% when potassium iodide is varied from 0.15 to 0.20 M in the absence of potassium chloride and the concentration of potassium ferricyanide is held constant at 0.075 M.

In the next group of experiments (5–9), potassium chloride is added to maintain the sum of potassium chloride and potassium iodide constant at 1.20 M. K'_c now shows a variation of less than 2% which is within the experimental error. Expts. 5–9, 12–14 and 16–17 may therefore be taken as an excellent confirmation of Bronsted's principle. Expts. 18–20 indicate that 0.50 M potassium chloride is hardly sufficient to maintain a constant environment, a change in potassium iodide from 0.10 to 0.20 causing K'_c to increase by about 20%.

In Expts. 27 and 28, the same change in potassium iodide produces a 6% change in K'_c in the presence of 2.00 *M* potassium chloride. This variation is about three times as great as the probable error in K'_c and is most likely to be ascribed to the fact that the value of L employed does not correspond to this salt concentration and therefore does not yield exactly comparable results for $c_{I_3^-}$ when potassium iodide is varied as is the case for the experiments where $\mu = 1.65$ for which environment L has been determined.

Considering now those experiments in which ferricyanide is varied, it is evident that the ionic strength does not function as an entirely satis-

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[17] The minor difference between Lewis and Randall's value for L_a and Bray and MacKay's value is due to a slightly different assumption in regard to the behavior of the activity coefficients of I^- and I_3^- ions. See Lewis and Randall, "Thermodynamics," p. 527.

factory measure of the electric environment, although it is perhaps the best of all proposed measures. Comparing Expt. 10 with Expts. 5–9, and Expt. 15 with Expts. 12–14, it is seen that for constant ionic strength produced by interchanging potassium chloride for potassium ferricyanide K'_c becomes smaller as potassium ferricyanide is increased.

The principle of ionic strength assumes that the square of the valence is the appropriate function to take into account changes in the concentration of ions of different valences. The Debye-Hückel theory yields this theorem as a limiting law for extreme dilution, but it is certainly not universally true when any appreciable concentrations of high valence ions are present.[18] This inadequacy of the principle of ionic strength has already been demonstrated for other systems of high valence ions and for far more dilute solutions than those now under consideration, namely, as low as 0.0005 μ.[19]

If we compute the appropriate valence exponent in order to maintain constant values of K'_c by changing the c_{KCl} when the ferricyanide concentration changes from 0.075 M to 0.10 M, we find that an exponent of 1.75 is satisfactory for Expts. 5–9 and 12–14, but groups 12–14 and 16–17 require an exponent of 1.1 for a corresponding change in ferricyanide concentration from 0.10 to 0.05 M. It will be of interest to carry out experiments with the ferricyanide concentration at still lower values to see if in the limit the equilibrium constant is determined by the equivalent concentration which demands a valence exponent of unity.

The addition of 0.003 M potassium ferrocyanide, although of considerable influence upon the percentage conversion and the observed rate of reaction, is without influence upon K'_c, as is to be expected (Expts. 16 and 22). A qualitative experiment using 0.5 M HCl + 1.00 M KCl showed a percentage conversion about 5 times that found in the absence of hydrochloric acid, and a few experiments were accordingly undertaken to determine the influence of P_H. Expts. 7, 26, 32 and 33 show that although acidity has no effect up to a P_H of about 3.7, a very noticeable increase in the oxidizing action of ferricyanide is apparent as the hydrochloric acid is increased above 0.001 M. Kolthoff[20] states that hydroferrocyanic acid is a weak acid with a dissociation constant of about 5.10–4 and the oxidation potential of the ferro–ferricyanide system is increased

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[18] Brönsted and La Mer, THIS JOURNAL, **46**, 555 (1924).

[19] La Mer and Mason, *ibid.*, **49**, 410 (1927); Graham Cook, *Dissertation*, Columbia University, 1928. Further experimental work on this problem by F. H. Goldman and one of us shows that quite similar results are also obtained for the solubility of $La(IO_3)_3$ in sulfate solvents, and that the anomalous results obtained by La Mer and Mason in highly dilute solutions are not restricted to salts of the cobaltammine family. A theoretical explanation for these results on the basis of the Debye theory is given by Gronwall, La Mer and Sandved, *Physik. Z.*, **29**, 358 (1928).

[20] I. M. Kolthoff, *Z. anorg. allgem. Chem.*, **110**, 143 (1920).

owing to removal of ferrocyanide ion in acid solution. Our experiments are consistent with this prediction but hardly support Kolthoff's statement that ferrocyanide will *quantitatively* reduce iodine in neutral solution, except, of course, the presence of excess ferrocyanide. The validity of his empirical expression for the influence of hydrochloric acid, upon which this statement seems to be based is restricted to the concentration range studied, namely, 0.0125 N to 1.00 N HCl, and should be modified to take in the influence of the dissociation constant.[20]

We wish to acknowledge the grant of a DuPont Fellowship which enabled one of us (K. S.) to engage in this research.

Summary

The equilibrium state for the reaction

$$2Fe(CN)_6^{---} + 3I^- \rightleftharpoons 2Fe(CN)_6^{----} + I_3^-$$

has been studied analytically for the potassium salts in pure water as well as in aqueous potassium chloride solutions as solvents.

Using water as solvent the value of $K_{eq.}$ changes 35% when the concentration of potassium iodide is increased from 0.15 *M* to 0.20 M, but the corresponding change is less than 2% in the presence of 1.0 M KCl. The data confirm the principle that the law of mass action holds for ionic systems when a sufficient excess of neutral salts is present to maintain a constant electrical environment, although this law fails completely in the absence of excess of neutral salts.

The inadequacy of the principle of ionic strength for high valence ions is also evident in this system.

The equilibrium constant in the absence of salt effects has been computed from e.m.f. data and found to be $0.199 \cdot 10^{-3}$.

Addition of hydrochloric acid up to a PH value of about 3.5 is without influence upon $K_{eq.}$ but is of marked influence in more acid ranges.

NEW YORK CITY

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY, No. 584]

THE THEORY OF ACIDITY

BY LOUIS P. HAMMETT

RECEIVED JULY 14, 1928 PUBLISHED OCTOBER 6, 1928

During the past five years there has been published by Hantzsch a series of papers[1] on the nature of acidity, whose results are markedly at variance with accepted ideas on the subject. In the recent papers of Hall and Conant[2] on "superacid solutions" there is presented evidence from much more precise indicator studies and from potential measurements of the essential correctness of some of Hantzsch's conclusions. These results may be completely explained by methods which derive from Brönsted's important treatment of the problem,[3] and which will be developed in the present article.

According to the classical ionization theory the quantitative measure of acidity is hydrogen ion concentration, and a non-ionized solution cannot have the properties of an acid. The experimental evidence for this conclusion is the unquestionably close parallelism between ionization and acidity in solutions in a single solvent, and the fact that such non-ionized solutions as hydrogen chloride in benzene do not react or react only very slowly with metals and carbonates.[4] Hantzsch's conclusion, on the other hand, is that practically non-conducting solutions may be acid, even that such solutions may be much more acid than highly ionized aqueous solutions. His evidence is that dilute solutions of certain acids in non-ionizing solvents produce the same effect upon indicators as do more concentrated solutions of the same acid in water; and that the rate of decomposition of diazoacetic ester, an acid catalyzed reaction, is greater in the non-ionized solution than in an equally concentrated aqueous solution of the same acid.

The evidence for high acidity in the non-ionizing solvent depends upon homogeneous reactions; the evidence against high acidity depends upon heterogeneous reactions for which both reactant and product are insoluble in the medium. The formation of protective coatings seems almost certain, and it is clear that Hantzsch's conclusions rest upon sounder evidence than do the accepted theories.

The essential features of Hantzsch's results may be summarized as

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[1] Hantzsch, (a) *Z. Elektrochem.*, 29, 221 (1923); (b) 30, 194 (1924); *(c)* 31, 167 (1925); (d) *Ber.*, 58, 612 (1925); *(e)* 58, 941 (1925); (f) 59, 793 (1926); (g) 59, 1096 (1926); (h) 60,1933 (1927); (i) *Z. physik. Chem.*, 125,251 (1927).

[2] (a) Hall and Conant, THIS JOURNAL, 49, 3047 (1927); (b) Conant and Hall, *ibid.*, 49, 3062 (1927).

[3] (a) Bronsted, *Rec. trav. chim.*, *42,* 719 (1923); (b) *J. Chem. Soc.*, 119, *574* (1921); *(c) J. Phys. Chem.*, **30,** *777* (1926).

[4] See Stieglitz, "Qualitative Chemical Analysis," The Century Co., New York, 1922, Vol. I, Chap. 5, for a complete discussion.

follows: 1. Acids (HCl, HBr, $HClO_4$) which are both highly ionized and strongly acidic in aqueous solutions, are even more strongly acidic yet practically un-ionized in hydrocarbons and similar solvents, and differ among themselves greatly in their acidity; whereas dilute aqueous solutions of the different acids have the same acidity at the same concentration. 2. Acids (acetic, formic) which are weak in water are much weaker in the hydrocarbon type of solvent. 3. Many solvents containining oxygen, notably ether, give solutions of extremely low acidity. Some acids which are strong in water (nitric, trichloro-acetic) are quite weak in ether, and only those acids (HBr, $HClO_4$) which are the most acid in chloroform and similar solvents have an acidity in ether which approaches the value in water.

Hantzsch's explanation of the first of these results seems very probable: that water is a base in much the same way that ammonia is a base; that an acid dissolved in water exists as an oxonium salt just as an acid dissolved in ammonia exists as an ammonium salt.[5]

Strong acids are then less acid in water than in solvents of lower basicity, and still less acid in the more basic ammonia, and they all have the same acidity in a given basic solvent, because this is now the acidity of oxonium (OH_3^+) or ammonium ion regardless of the acid used. This may be better expressed in terms of Bronsted's adaptation of Werner's theory in the light of the principle of complete dissociation. The formation of ions and the resultant conductivity, according to Brönsted, are due not ~~to~~ the reaction $HClO_4 \rightleftarrows H^+ + ClO_4'$ but to the reaction $HClO_4 + H_2O — OH_3^+ + ClO_4'$. This process can take place only by virtue of the fact that oxonium ion holds its hydrogen ion more firmly than does perchloric acid, that OH_3^+ is less acid than $HClO_4$.

These conclusions are further supported by the work of Hall and Conant, and the significance of the concept of basicity of solvent for the question of acidity is very clearly presented in their diagram and discussion.[6]

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[5] Aside from Hantzsch's work, the theory that water is a base in this sense is supported by the following lines of evidence. The overwhelming similarity in the properties of water and ammonia, which shows so clearly for instance in Franklin's work on ammonia solutions, indicates strongly that the acidity relations are similar in the two solvents. But acids in ammonia solution are ammonium salts. There is evidence in the work on oxonium salts that the maximum coordination number of oxygen is three; that saturated oxygen compounds can add one hydrogen ion just as can ammonia and its substitution products. Fajans and Joos, *Z. physik*, 23, 1 (1924), have shown that the interpretation of the refractive index of aqueous acids demands the assumption of the existence of such an ion as OH^+_3. Hantzsch, *Z. physik. Chem.*, *65*, *41* (1908), has shown that the cryoscopic effect in sulfuric acid of water and ammonia is the same. Volmer, *Ann.*, 440, 200 (1924), has demonstrated by x-ray analysis the crystallographic identity of ammonium perchlorate and the monohydrate of perchloric acid, which is therefore shown to be oxonium perchlorate.

[6] Ref. 2 b, page 3069.

If, however, basicity of solvent were the only factor, all acids, and not merely the strong ones, should appear stronger in chloroform than in water, which is not true. Bronsted'' has already suggested the importance of dielectric constant in this connection, and it is possible to account for Hantzsch's results as they have been enumerated by taking this into account.

It has been clearly shown by Brönsted[3a] that the only logically consistent general measure of acidity is hydrogen-ion potential (which is proportional to PH) or the closely related hydrogen-ion activity. The use of activities instead of potentials is convenient, but it should be made very clear that this use does not express or even imply any knowledge of concentration. Hydrogen-ion activity is by definition an exponential function of hydrogen-ion potential, and hydrogen-ion potential represents the work concerned in the reversible removal of hydrogen ions (protons) from a given system, or their addition to it. High activity means loosely bound hydrogen ions, low activity firmly bound hydrogen ions. Reaction proceeds by the transfer of hydrogen ions from higher to lower activity, and we have no means of knowing whether actual protons are ever present either as an intermediary or as a by-product in such transfers. It may, however, be reasonably expected that the concentration of free hydrogen nuclei in a solution should be at least as small as the concentration of free electrons, that is, negligible; and this point of view will be taken in what follows.

Since it is only the ratios of activities that can be measured, it is necessary always to set up a purely arbitrary scale of numerical values of activity. It has been convenient when considering the variation of activity with concentration in a single solvent to set up a different arbitrary scale for each solvent, in such a way that the activity coefficient, the ratio of activity to concentration, approaches one as the solution becomes infinitely dilute. This usual convention is, however, very unsatisfactory when solutions of the same solute in more than one solvent are considered,[7] and the quite different convention is adopted in this paper that the same scale of activities is used for all solvents. It follows then that two solutions of the same hydrogen-ion potential, that is, of the same true acidity, will have the same hydrogen-ion activity, no matter what the solvent, but it follows also that the activity coefficient will not in general approach one for infinitely dilute solutions. When numerical values become available it will probably be desirable to define the scale of activities in such a way that the activity coefficient approaches one for very dilute solutions in some one solvent, say water; the activity coefficient in another solvent will then approach a value which will in general be greater or less than one.

With this understanding it is possible to attack mathematically the

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[7] *See* Scatchard, THIS JOURNAL, **47,** 2105 **(1925).**

problem of the effect of solvent upon acidity. The following symbols will be used: HX = acid, for example HCl, or $HClO_4$; S = solvent, for example water, ether, chloroform; c = concentration; a = activity; f = activity coefficient; c_a = stoichiometric concentration of HX.

Regardless of the solvent we have

$$a_{H^+} = K_{HX} \frac{a_{HX}}{a_{X'}} = K \frac{c_{HX}}{c_{X'}} \frac{f_{HX}}{f_{X'}} \tag{1}$$

but if the solvent is basic, we have also

$$a_{H^+} = K_S' \frac{a_{SH^+}}{a_S} = K_S\, c_{SH^+} \frac{f_{SH^+}}{A} \tag{2}$$

If, as seems probable, c_{H^+} may be taken as negligibly small

$$c_a = c_{HX} + c_{X'} = c_{HX} + c_{SH^+} \tag{3}$$

since the reaction between acid and solvent is $HX + S \longrightarrow X' + SH^+$. Combination of 1, *2*, and **3** gives

$$ant = \frac{1}{2} K_{HX} \frac{f_{HX}}{f_{X'}} \left\{ -1 + \sqrt{1 + 4c_a \frac{K_S}{K_{HX}} \frac{f_{SH^+}\, f_{X'}}{f_S\, f_{HX}}} \right\} \tag{4}$$

Since a_{H^+} increases with increasing K_S, this equation records the principle that *decreased basicity* of *solvent* (greater K_S) *means greater acidity, although it also means less ionization.*

In order to see more clearly the effect of changes in the f terms, which record the effect of changes in dielectric constant, it is advisable to consider the forms to which Equation 4 reduces in the two limiting cases.

When the second term under the radical sign is large compared with one, the equation becomes

$$a_{H^+} = \sqrt{c_a\, K_S K_{HX} \frac{f_{SH^+}\, f_{HX}}{f_S\, f_{X'}}} \tag{5}$$

This is the case of weak acid or weakly basic solvent; the reaction of ionization, $\mathbf{HX} + S \rightleftarrows X' + \mathbf{SH^+}$, is incomplete, and the acidity depends upon both K_S and K_{HX}, that is, upon the properties of both acid and solvent.

When the same term is small the radical may be expanded and using the linear term only we have

$$a_{H^+} = c_a K_S \frac{f_{SH^+}}{f_S} \tag{6}$$

Ionization is large and the acidity depends only upon the properties of the solvent. This represents the leveling effect of the solvent, mentioned by Hantzsch and by Conant and Hall.

We can now make at least a qualitative prediction of the effect of dielectric constant from the known effect of this property upon the activity coefficients. The activity coefficient of an ion is unquestionably greater in solvents of low than in solvents of high dielectric constant. This is demonstrated by the extremely low solubility of true salts in solvents of low dielectric constant, and is predicted by the interionic attraction theory of electrolytes. The changes in the activity coefficients for uncharged molecular species from solvent to solvent are much smaller than the changes of the ionic activity coefficients. It therefore follows of necessity that such a ratio as $f_{HX}/f_{X'}$ or f_S/f_{SH^+} will decrease with decreasing dielectric constant. We shall asume as an admittedly rough approximation that the change in this ratio between two different solvents is independent of the acid or base concerned. There is indeed some reason for believing that specific effects upon the ratio will be considerably smaller than the effect upon the individual activities. This corresponds to the impression that those acids or bases which are themselves much more soluble in organic solvents than in water will have salts which are relatively soluble in organic solvents.

It follows then that the ratio $f_{SH^+}\, f_{HX}/f_S\, f_{X'}$ in Equation 5 will be approximately one for all solvents; that *the hydrogen-ion activity of a weakly ionized acid is independent of the dielectric constant of the medium.* It follows from Equation 6 that *the hydrogen-ion activity of a highly ionized acid will be greater in solvents of low than in solvents of high dielectric constant.* For the intermediate cases decrease in dielectric constant will result in a more or less large increase in hydrogen-ion activity.

But hydrogen-ion activities cannot be measured directly unless or until we know very much more than we do at present about diffusion potentials. Verification of the theory depends upon its extension to some such measurable phenomenon as salt formation with indicators. We shall let I represent the molecular substance of some indicator base (dimethylamino-azobenzene, benzalacetophenone, etc.), and IH+ the ion which it forms with acids. Then

$$\frac{a_{H^+}\, a_I}{a_{IH^+}} = K_I \tag{7}$$

Suppose an amount of indicator be added which is insufficient to displace materially the acid solvent equilibrium. Then the salt base ratio of the indicator, which determines the color, is given by

$$\frac{c_{IH^+}}{c_I} = \frac{1}{K_I}\frac{f_I}{f_{IH^+}}\sqrt{K_{HX}\, K_S\, c_a} \tag{8}$$

for weakly ionized solutions, and by

$$\frac{c_{IH^+}}{c_I} = \frac{K_S\, f_{SH^+}\, f_I}{K_I\, f_{IH^+}\, f_S}\, c_a \tag{9}$$

for highly ionized. The same considerations already used concerning the effect of dielectric constant upon the activity coefficients lead to the conclusion *that decrease in dielectric constant will have little effect upon salt formation when ionization is large, and will decrease salt formation when ionization is small. For all except very highly ionized solutions the result of decreased dielectric constant will be a decrease in apparent acidity as measured by a basic indicator.*

We may now explain the conclusions drawn previously from Hantzsch's work. 1. Acids which are highly ionized and strong in water give increased salt formation with indicators in solvents of negligible basicity like chloroform and the hydrocarbons because these solvents are less basic than water, 2. Acids like acetic and formic which are weakly ionized in water give very little salt formation with indicators in these solvents of low dielectric constant because a reaction like $HX + I = IH^{+} + X'$ which produces ions from neutral molecules takes place to a smaller extent the smaller the dielectric constant. **3.** Acids, except the very strongest, which are presumably highly ionized in both ether and water, give less salt formation with basic indicators in ether than in water because of the low dielectric constant. Ionization is frequently much less in ether than in water, as with HCl, again because the reaction $HCl + S = SH^{+} + Cl'$ is displaced toward the left by lowered dielectric constant. Salt formation is, of course, always less in ether than in chloroform or similar solvents of about the same low dielectric constant because of the basicity of the ether.[8]

It will be seen that acidity as measured by a basic indicator does not run parallel to hydrogen-ion activity when there is a change in dielectric constant. It is only necessary to change to an acid indicator to see how unreliable indicator measurements must be for determining relative acidities in different solvents. Thus ordinary glacial acetic acid gives an intermediate shade with dimethylamino-azobenzene. From this one may estimate its P_H on the water scale to be about **3.5.** With picric acid it gives a colorless solution, indicating an acidity greater than that of molar aqueous hydrochloric acid, that is a P_H less than 0.[9]

Presumably the true acidity lies between the values indicated by the basic and by the acid indicator. For the color determining ratio acid over salt for an indicator HI (such as picric acid) is given by

$$\frac{c_{\mathrm{HI}}}{c_{\mathrm{I}'}} = \frac{1}{K_{\mathrm{HI}}}\frac{f_{\mathrm{I}'}}{f_{\mathrm{HI}}}\sqrt{K_{\mathrm{HX}}\,K_{\mathrm{S}}\,c_{\mathrm{a}}} \qquad (10)$$

for weakly ionized solutions, and by

$$\frac{c_{\mathrm{HI}}}{c_{\mathrm{I}'}} = \frac{K_{\mathrm{S}}}{K_{\mathrm{I}}}\frac{f_{\mathrm{SH^+}}\,f_{\mathrm{I}'}}{f_{\mathrm{S}}\,f_{\mathrm{HI}}}\,c_{\mathrm{a}} \qquad (11)$$

for those highly ionized. The effect is to increase the apparent acidity with decrease in dielectric constant, the change being greater the higher the ionization. A tabulation shows that the effect of decreased dielectric constant upon hydrogen-ion activity lies always between the effect upon apparent acidity by basic indicator and apparent acidity by acid indicator.

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[8] If we may drive the analogy between water and ammonia a little farther, the basicity of ether should differ from that of water to about the same extent as that of an aliphatic amine differs from that of ammonia.

[9] It is only with the strongest alkalies that the medium permits, such as sodium acetate, that the picric acid indicator gives a yellow color in acetic acid as solvent.

Ionized system	Basic indicator	Hydrogen-ion activity	Acid indicator
Weakly	Decreased acidity	No effect	Increased acidity
Highly	No effect	Increased acidity	Greatly increased acidity

The best we can say about relative acidities in water and ether and water and acetic acid, then, is that they are approximately the geometric mean of the hydrogen-ion activities estimated by the use of basic and acid indicators.

The superacid solutions of Hall and Conant are probably even more acid than their own figures indicate. Their tentative choice of a scale of P_{H} in acetic acid amounts to the same thing as the assumption that two solutions in which a basic indicator gives identical colors have the same hydrogen-ion activity regardless of the solvent. They assume that two solutions with the same ratio of concentrations of an anhydro base and the salt which it forms by addition of hydrogen ion should have the same hydrogen-ion activity. From the equation $a_{\mathrm{H}^+} = K\ (c_{\mathrm{BH}^+}/c_{\mathrm{B}})\ (f_{\mathrm{BH}^+}/f_{\mathrm{B}})$ it will be seen that of two solutions with a given ratio of salt to base $c_{\mathrm{BH}^+}/c_{\mathrm{B}}$ the solution in the solvent with lower dielectric constant has the greater hydrogen-ion activity.

If the true P_{H} relative to aqueous solutions is two to three units less than the values given by Hall and Conant, it is unnecessary to assume such abnormal values for the diffusion potential in their salt bridge,[10]

It is true that salt formation, a concrete, measurable thing, is more important than a concept like activity, which is not susceptible to direct measurement; but it remains extremely important to call the thing we measure salt formation and not hydrogen-ion activity if it is salt formation and if it is not parallel to activity.

If we were to confine our interest in acidity to aqueous solutions the subject matter of the present article would be of little value. It is only when comparing acidities in different solvents that the basicity and dielectric constant of the solvent need be considered. Probably the greatest reason for an interest in acidity outside of the bounds of aqueous solutions is the great importance of catalysis by acids and bases in organic reactions. This becomes particularly important since the appearance of Meerwein's[11] evidence that zinc chloride and aluminum ethylate have acidic properties and that their catalytic properties are probably closely related to their acidity.

According to Hantzsch there is a close and far-reaching parallelism between salt formation with basic indicators and the rate of decomposition of diazoacetic ester, a reaction which has been a classical one for the study of acidity in aqueous media. The reaction is not an ideal one for the purpose of studying acidity in different media, for the product of the

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[10] I am indebted to Professor H. A. Fales for pointing out that a diffusion potential of 0.15 volt is much greater than any previously known or suspected.

[11] Meerwein, *Ann.*, **455,** 227 (1927)

decomposition may be different with different acids and different solvents. Nevertheless it is possible, as Hantzsch supposes, that the reaction velocity depends in any case upon salt formation by addition of hydrogen ion to the ester, and that the final steps of the reaction, leading to the different possible products, do not affect the velocity. This would account for the observed parallelism of reaction velocity and indicator acidity.

It should be of great importance to investigate other, less ambiguous reactions to see if this parallelism can be generalized.

Summary

A generalized theory of acidity is proposed and given mathematical expression. In this the effect of the basicity and of the dielectric constant of the solvent are both considered.

The predictions of the theory are in agreement with the available evidence on acidity in non-aqueous solutions, notably with the work of Hantzsch and with that of Hall and Conant.

NEW YORK CITY

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY, No. 583]

A BALLISTIC GALVANOMETER METHOD OF POTENTIOMETRIC MEASUREMENT FOR HIGH RESISTANCE CELLS

BY H. T. BEANS AND GEORGE H. WALDEN, JR.

RECEIVED JULY 18, 1928 PUBLISHED OCTOBER 6, 1928

Introduction

A recent publication by Jones and Kaplan[1] contains a description of a method of potentiometric measurement for high resistance cells which uses a condenser and ballistic galvanometer as a null point indicator. A deflection method for high resistance cells which used the condenser and ballistic galvanometer was used in this Laboratory by Beans and Oakes.[2] Since then we have developed a more exact method[3] which is in many respects similar to that of Jones and Kaplan but differs in that it is a semi-deflection method. We have experimentally demonstrated that our method may be used successfully with cell resistances as high as 50 megohms. The cells which Jones and Kaplan used had internal resistances no higher than 1.6 megohms. At higher resistances the null point method, while still possible, becomes very cumbersome due to the time required to charge the condenser sufficiently to cause a noticeable throw upon discharge. Our method overcomes this difficulty, at the same time retaining an accuracy of 0.1 to 0.5 millivolt.

[1] Jones and Kaplan, THIS JOURNAL, **50,** 1845 (1928).

[2] Beans and Oakes, *ibid.*, 42, 2116 (1920).

[3] Walden, *Dissertation,* Columbia, 1924.

Apparatus

A diagram of our apparatus is shown in Fig. 1. Our circuit is the same as that of Jones and Kaplan except in two particulars. We do not use a tapping key to discharge the condenser but a discharge switch, so that the ballistic galvanometer G_b receives the total discharge of the condenser, not the instantaneous discharge. Also the discharge switch has a third contact which automatically removes the damping shunt R_d at the moment of discharge. We also have a current galvanometer G_c for comparison purposes which may be substituted for the condenser-ballistic galvanometer system by means of a double pole double throw switch. G_b has a sensitivity of about 0.0007 microcoulomb per millimeter throw. C is a mica dielectric condenser of approximately 10 microfarads capacity. All switches have mercury contacts supported on hard rubber pedestals. Connections are made with wires supported by glass insulators or silk cord.

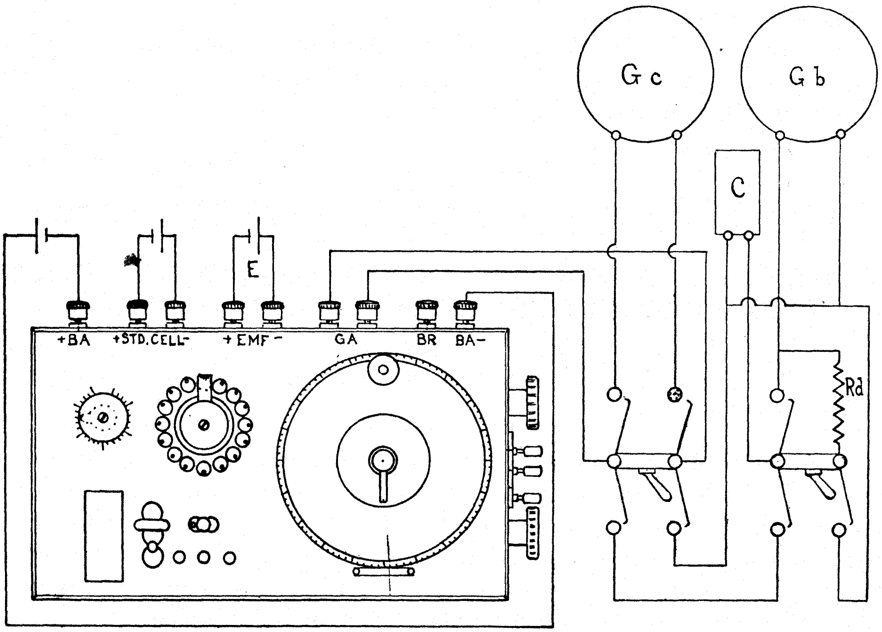

Fig. 1.—Working circuit diagram as used in connection with a Leeds and Northrup Type K potentiometer.

Method

Instead of locating the exact null point of the potentiometer by successive trials we locate it by this method within 10 millivolts. Then we measure the difference between the voltage of the potentiometer and the electromotive force of the cell by the throw of the galvanometer. To do this we need to determine the relationship between galvanometer throws and voltages between the condenser plates. This is accomplished as follows. We connect together the potentiometer binding posts marked "E.M.F." Then if the discharge switch is set to charge the condenser the applied potential difference will instantly be that of the potentiometer, since there is little resistance in the circuit. By charging and discharging with different settings of the potentiometer data are obtained with which to plot galvanometer throws against condenser voltages. Thus we empirically avoid all trouble due to a non-linear galvanometer characteristic and also from dielectric absorption. Data for this curve may be obtained in about fifteen minutes. It is necessary to check this curve occasionally since ballistic galvanometer constants change slowly. To measure the difference between the voltage of the potentiometer and the electromotive force of the cell, we may charge the condenser until it has attained its equilibrium charge nearly enough, discharge and observe the galvanometer throw, and read the difference directly from the curve. The required charging time becomes very long when cell resistances are high. For such cases we have devised a method of determining the equilibrium voltage by measuring the voltages between the condenser plates after two measured charging times. This cuts the time required to make a measurement about in half. When cell resistances are very high leakage through the dielectric of the condenser becomes a factor of importance. Our method considers this possibility and corrects for it where necessary.

Time Required to Charge a Condenser.—Let C = the capacity of the condenser; R = the resistance of the circuit; e = the charging electromotive force; v = the potential difference between the plates, of the condenser at any instant; q = the charge in the condenser at any instant; L = the resistance through the dielectric of the condenser and T = the elapsed time since the circuit was closed. As the condenser is charging

$$dq = \left[\frac{e - v}{R} - \frac{v}{L}\right] dT$$

$$T = RLC \int_0^q \frac{dq}{eLC - q(L + R)} = RC\,\frac{L}{L + R} \ln \left[\frac{e}{e - v\,\frac{L + R}{L}}\right] \qquad (1)$$

If L is very much larger than R, Equation 1 reduces to

$$T = RC \ln \frac{e}{e - v} \qquad (2)$$

If $v = 0.99e$ (corresponding to an error of 0.1 millivolt in a measurement of 10 millivolts), it has been found that if the condenser is moderately well constructed Equation 2 is a sufficiently close approximation. When R = 50 megohms, C = 10 microfarads and $v = 0.99e$; T, by Equation 2, is equal to 38.4 minutes. This large charging time is very objectionable since in the absence of exact knowledge of the resistance of the cell the only way to tell when the charging time has been sufficiently long is to obtain the same result after a longer period. Therefore, when R is large we do not measure e directly but calculate it from two measurements of v obtained after different time intervals.

Method of Calculating e when T is Large.—If v is measured after two time intervals, we have from Equation 1

$$T_1 = RC\,\frac{L}{L + R} \ln \left[\frac{e}{e - v_1\,\frac{L + R}{L}}\right]$$

$$T_2 = RC\,\frac{L}{L + R} \ln \left[\frac{e}{e - v_2\,\frac{L + R}{L}}\right]$$

Solution of these equations leads to the expression

$$e = \frac{v_2^2}{2v_2 - v_1} \times \frac{L + R}{L} \tag{3}$$

if $T_1 = 2T_2$. If e is never greater than 10 millivolts, L can be as small as $100R$ before error from neglect of the leak correction factor $(L + R)/L$ becomes greater than 0.1 millivolt. We have found that leak resistances in a well constructed condenser are sufficiently high so that this correction need not be used.

Elimination of Error from Dielectric Leakage.—If it may be assumed that the dielectric resistance L is constant, the value of the factor $(L + R)/L$ may be experimentally determined by means of Equation **3.** Two measurements of v are made after two time intervals, one twice as long as the other. Then the potentiometer setting is changed, changing e by a known amount to e', and two similar measurements of v' are made. Then

$$\frac{L + R}{L} = \frac{e - e'}{\dfrac{v_2^2}{2v_2 - v_1} - \dfrac{v_2'^2}{2v_2' - v_1'}} \tag{4}$$

from which it can be seen that if the difference between the values of e and e' calculated by Equation **3** neglecting the leak correction factor is equal to the difference between the potentiometer settings within the precision sought $(L + R)/L$ may be considered nearly enough equal to 1. If this is not the case it seems advisable to use another condenser with smaller leakage, since L may be expected to vary with the temperature and humidity. We have found that a sufficiently good condenser may be made by connecting 10 of the Western Electric Company's 1 microfarad condensers.

Error Introduced by Calculating e.—If v_1 and v_2 are measured after time intervals which are too short a very large error may be introduced. Since it is desirable to keep the charging times as short as possible in order to cut down the time required to make a measurement, some method of estimating this error is necessary. If Δv_1 and Δv_2 are the errors in the two measurements, the errors introduced by each into the calculation of e by Equation **3,** neglecting the factor $(L + R)/L$, will be

$$\frac{\delta e}{\delta v_1}\,\Delta v_1 = \frac{v_2^2}{(2v_2 - v_1)^2}\,\Delta v_1 = \frac{1}{(2 - r)^2}\,\Delta v_1$$

and

$$\frac{\delta e}{\delta v_2}\,\Delta v_2 = \frac{2v_2(v_2 - v_1)}{(2v_2 - v_1)^2}\,\Delta v_2 = \frac{2(1 - r)^2}{(2 - r)^2}\,\Delta v_2$$

where

$$r = \frac{v_1}{v_2}$$

Since the two errors are of opposite sign, the maximum error which can be introduced by this calculation is

$$\Delta e_m = \pm \Delta v \left[\frac{1}{(2 - r)^2} - \frac{2(1 - r)^2}{(2 - r)^2}\right] = \pm \Delta v\,\frac{2r - 1}{(2 - r)^2} \tag{5}$$

where Δv is the maximum error expected in measuring a. This relationship may be plotted for any given apparatus, arid the operator can then decide whether sufficiently long charging times have been taken by calculating r and finding Δe_m from the curve.

Error Caused by Leakage between the Poles of the Cell.—When electromotive force measurements are made on cells with large internal resistances very serious error may be caused by leakage between the poles of the cell. If R_L is the leakage resistance, R_I the internal resistance of the cell, E the electromotive force of the cell and AE the error caused by the leakage through R_L, it follows from Ohm's Law that $R_L = [(E - \Delta E)/E]$ R_I. If the measurement of E is to be accurate to 0.1 millivolt and if E may be as large as 1 volt, it is evident that R_L must be 10,000 times R_I. If R_I is of the order of several megohms, great care must be exercised in the design of the cell and its connections to the measuring instrument.

Experimental

Since it is not easy to construct a high resistance cell of known electromotive force, an analogous system consisting of a low resistance standard cell in series with a high resistance was used for testing purposes. The high resistance and cell were placed side by side, connected together with a short lead, and connected to the potentiometer with the same leads which were afterwards used to connect the actual high resistance cell. The high resistance consisted of the requisite number of megohm resistance units connected in series. The units were made by spattering platinum on mica.[4] The resistance of each unit was measured and found to be correct within a few per cent.

Table I shows a series of measurements made on a cell in series with resistances from 1 to 10 megohms. Over this resistance range it is not

TABLE I

RESISTANCES OF 1 TO 10 MEGOHMS

R, megohms	T, min.	E.m f., volts	Error, mv.
1	1	1 0154	0.0
2	2	1 0154	.0
3	2	1.0154	0
4	3	1.0154	.0
5	3	1.0154	.0
6	4	1.0154	0
7	4	1.0153	− .1
8	6	1.0151,	.0
9	7	1.0155	+ .1
10	7	1.0154:	0

E.m.f. (measured without series resistance) = 1.0154 v.

TABLE II

RESISTANCES OF 10 TO 50 MEGOHMS

R, megohms	T, min.	E.m.f., volts	Error, mv.
10	1 – 2	1.0188	− 0 2
10	1– 2	1.0189	− .1
20	2- 4	1.0189	− .1
20	2 – 4	1.0194	+ . 4
30	3 – 6	1.0184	− .6
30	3 – 6	1.0193	+ .3
40	5–10	1.0192	+ .2
40	5–10	1.0188	− .2
50	5–10	1.0184	− . 6
50	5–10	1.0188	− 2

E.m.f. (measured without series resistance) = 1.0190 **v.**

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[4] Furnished by the Prometheus Electric Company, New York City.

necessary to calculate e since the time required to approach equilibrium closely enough is never more than ten minutes.

Table II shows a series of measurements over a resistance range of 10 to 50 megohms. Here e was calculated by Equation 3, neglecting the correction factor for leakage through the condenser. Charging times were chosen so that Δe_m from Equation 5 was about 1 millivolt if Δv is 0.1 millivolt.

Summary

1. We have described a semi-deflection method of potentiometric measurement which may be used with cells having internal resistances as high as 50 megohms.
2. We have discussed the precautions necessary with work of this kind.
3. We have shown that when full precautions are taken measurements may be made with a precision of ±0.1 millivolt when cell resistances are as high as 10 megohms, and with a precision of ±0.5 millivolt with cell resistances as high as 50 megohms.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NEW YORK UNIVERSITY]

TERNARY SYSTEMS. VII. THE PERIODATES OF THE ALKALI METALS

BY ARTHUR E. HILL

RECEIVED AUGUST 3, 1928 PUBLISHED OCTOBER 6, 1928

Following the discovery of periodic acid and the periodates, it was observed at an early date that the acid differed widely from the analogous perchloric acid in being distinctly polybasic and in the varying degrees of hydration of its hypothetical anhydride I_2O_7. The nomenclature most commonly adopted for classifying the various acids is, with slight modification, that of Blomstrand.[1] H_5IO_6, the hydrate of greatest water content, is known as para-periodic acid, $H_8I_2O_{11}$ as di-para-periodic acid, H_3IO_5 as meso-periodic acid, $H_4I_2O_9$ as di-meso-periodic acid and HIO_4 as meta-periodic acid. Although but two, or possibly three, of these acids are definitely known, salts derived from all of them have been reported; of these, the silver salts and the salts of the common alkali metals have been most thoroughly studied.[2] It does not appear, however, that the studies have been systematic in this nature; slight modifications in the conditions of preparation have given to the various investigators salts differing in their analyses and which were on that evidence assigned to the corresponding one of the five acids enumerated above. By such

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[1] Blomstrand, *J. prakt. Chem.*, **34**, **433** (1886).

[2] See Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans Green and Co., N. Y., 1922, Vol. **2,** p. 406.

methods the possibility of mixtures being regarded as pure salts is by no means excluded, It has seemed worth while to make a systematic investigation of the periodates of the two alkali metals, sodium and potassium, in order to determine with certainty just how many of those reported are true compounds. This can be completely determined, as far as salts crystallizing from water are concerned, by a study of the three component systems consisting of water, periodic acid and sodium hydroxide or potassium hydroxide, respectively, and the finished study should leave no doubt as to the compounds existing at the temperature selected. For reasons of convenience, however, since periodic acid is not easily prepared, the studies have been made with use of the meta-periodate of sodium or potassium (the most highly acidic salts known in each series) with water and the appropriate base; these show therefore all stable periodates more basic in composition than the meta-salt chosen. The possibility of more acidic salts will be mentioned later.

Materials.—The sodium periodate used in the experiments was prepared from pure sodium hydroxide, passing through the stage of the tri-sodium-para-periodate, $Na_3H_2IO_6$, which was eventually converted into the meta-periodate, $NaIO_4$. To a solution of pure sodium iodate five equivalents of sodium hydroxide was added and the solution stirred mechanically while a rapid stream of chlorine gas was passed through. The very insoluble sodium salt begins to precipitate within a few minutes. The stream of chlorine was continued until the solution gave an odor of hypochlorites and was nearly neutral; after the treatment with chlorine was interrupted, an additional equivalent of sodium hydroxide was added and the mixture well stirred for several hours. In the presence of an excess of base, which is essential to the formation of the tri-sodium salt, the reaction occurring is represented by the equation $NaIO_3 + Cl_2 + 4NaOH \longrightarrow Na_3H_2IO_6 + 2NaCl + H_2O$; yields averaged above 80%. The solid salt was filtered on a Büchner funnel and washed repeatedly; because of its very low solubility, the loss on washing is negligible. In order to convert this salt to the meta-periodate. $NaIO_4$, it was treated with water and nitric acid in the ratio of 150 cc. of water and 45 cc. of concd. nitric acid to 100 g. of salt; the solution was heated until the salt dissolved completely, and then allowed to stand for twenty-four hours at room temperature. The crystals thus formed are of large size and even contour; because of their low rate of dissolving they could be washed rapidly on a Büchner funnel without considerable loss, and they analyze within 0.1% of the theoretical composition; the yields varied from 60 to 85%, dependent largely upon the time allowed for crystallization.

The potassium meta-periodate was likewise prepared from the iodate with four to five equivalents of base by oxidation with chlorine. Unlike the case of the sodium salt, the potassium salt is freely soluble in excess base, and does not appear in solid form until the solution has become nearly neutral. It was then, after cooling, rendered acid with a slight excess of sulfuric acid and allowed to stand until the insoluble meta-periodate, KIO_4, had precipitated. The yields obtained, after washing and drying, ran as high as 95%. As in the case of the sodium salt, the well-washed product analyzed always within 0.1% of the theoretical composition without the necessity for recrystallization.

The periodic acid used was prepared by the method used by Wells, Lamb[3] and others: the sodium salt was converted into (supposedly) Ag_3IO_5 by long stirring with

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[3] (a) Wells, *Am. Chem. J.*, 26, 278 (1901); (b) Lamb, *ibid.*, 27, **134** (1902).

three equivalents of silver nitrate solution, and the precipitate decomposed, after thorough washing, by a slow stream of washed chlorine gas passed into a cold aqueous suspension. After filtration from the silver chloride, the solution was evaporated to a small volume over a free flame and finally in a desiccator over sulfuric acid; the periodic acid crystallizes in the form of its hydrate $HIO_4 \cdot 2H_2O$, which may be dried over sulfuric acid without loss of water. Since no data have been recorded as to the solubility of this acid, it may be of use to state that analysis of the mother liquor shows the solubility to be about 53% at room temperature, and the density about 2.3.

The sodium hydroxide and potassium hydroxide used were Kahlbaum preparations, which were dissolved in water to a suitable concentration and standardized by titration against analyzed hydrochloric acid solutions, using methyl orange as indicator. The small carbonate content of the base was left out of consideration as having but a negligible influence upon the solubilities measured.

The periodates were analyzed by measuring their oxidizing action upon potassium iodide in acid solution; the thiosulfate solutions used were standardized against recrystallized potassium iodate. The free alkali present in the ternary solutions was determined by titration with standard sodium hydroxide solution, using methyl orange as indicator; the meta periodates are neutral to that indicator, as previously shown by others,[4] so that any excess alkali can be accurately determined.

The Periodates of Potassium

The determination of the periodates of potassium consisted in the study of the action of potassium hydroxide upon the solubility of potassium meta-periodate. The experiments were conducted in a thermostat at 25°; weighed quantities of the meta-periodate were treated with measured quantities of potassium hydroxide solution and of water and rotated in glass stoppered test-tubes of Pyrex glass until equilibrium was attained; the time required did not exceed twenty-four hours in any case. Pipetted samples of the clear supernatant liquid were analyzed for periodate and for free base; from the volume of the pipetted liquid, density determinations of moderate accuracy could be calculated. The results are given in Table I.

TABLE I

TERNARY SYSTEM KIO_4–KOH–H_2O AT 25°

Complex taken		Saturated solution			
KIO_4, %	KOH, %	KIO_4, %	KOH, %	Density	Solid phases
5.0	0.0	0.51	0.0	1.00	KIO_4
5.0	1.0	4.12	1.01	1.044	KIO_4
8.0	2.0	8.03	1.99	1.087	KIO_4
16.0	4.0	10.32	2.55	1.116	$KIO_4 + K_4I_2O_9 \cdot 9H_2O$
20.0	6.0	13.15	4.55	1.165	$K_4I_2O_9 \cdot 9H_2O$
18.0	6.4	16.12	6.03	1.221	$K_4I_2O_9 \cdot 9H_2O$
21.6	8.3	20.8	8.0	1.326	$K_4I_2O_9 \cdot 9H_2O$
25.1	9.9	24.1	9.7	1.377	$K_4I_2O_9 \cdot 9H_2O$
31.0	12.0	28.9	11.9	1.484	$K_4I_2O_9 \cdot 9H_2O$
36.6	14.4	35.2	14.5	1.64	$K_4I_2O_9 \cdot 9H_2O$
44.0	16.0	39.0	16.4	...	$K_4I_2O_9 \cdot 9H_2O$
51.0	18.5	44.6	19.1	...	$K_4I_2O_9 \cdot 9H_2O$

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[4] Rosenheim and Loewenthal, *Kolloid. Z.*, 25, 53 (1919); Loewenthal, "Inaugural Dissertation," Berlin, 1918.

From Table I and Fig. 1 the facts as to the periodates of potassium which are stable in contact with solution can easily be deduced. The sparingly soluble salt KIO_4 has its solubility rapidly increased by the addition of potassium hydroxide; no common-ion effect in lessening its solubility can be detected. At the point *b* in Fig. 1, representing line 4 in the table, there is a change of solid phase, giving an isothermally invariant point. Further additions of potassium hydroxide give increasing concentrations of the second solid, which will be shown to be the ennea-hydrated potassium di-meso-periodate, $K_4I_2O_9{\cdot}9H_2O$. The increase in solubility of this salt upon addition of potassium hydroxide is striking; in line 13 we have a total solubility increased to 87 times that of the original saturating salt.

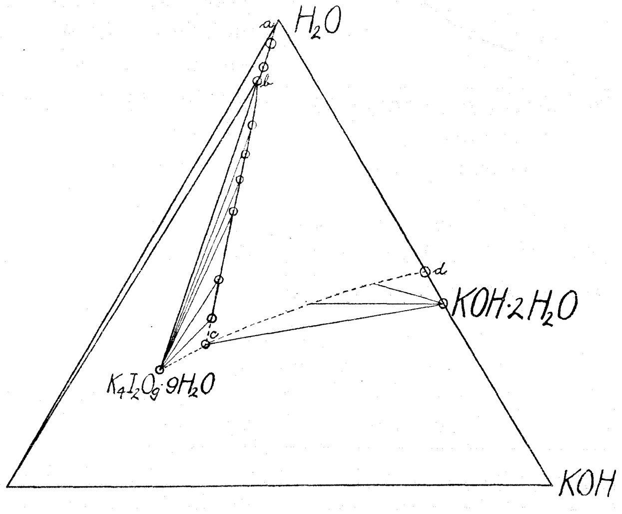

Fig. 1.—25° isotherm, KIO_4–KOH–H_2O.

Further additions of base caused the system to gelatinize, which of course put an end to further solubility measurements. It is clear, however, that the last experiment indicates a solution not far from the saturation point with respect to potassium hydroxide, which is shown schematically as the point c, with the solubility curve c-d drawn schematically for the hydrated base. It is accordingly clear that two and only two periodates of potassium can be formed from aqueous solutions at 25°, and it is probable that at higher temperatures the same limitation exists as far as aqueous solutions are concerned. Kimmins'[5] salt, $K_3HI_2O_9$, and Ihre's[6] $K_3IO_5{\cdot}4H_2O$ are not confirmed; it is probable that both are mixtures represented by the point *b* in Fig. 1, since they were formed in solutions in which the concentration of free base was not accurately known.

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[5] Kimmins, *J. Chem. Soc.*, 51, 356 (1887); 55, 148 (1889).

[6] See Blomstrand, *Ber.*, 3, 316 (1870).

Some study was given to each of the two potassium salts prepared. The meta-periodate, KIO_4, has a strikingly low solubility for a potassium salt; the figure at 25°, calculated as moles per liter, is 0.0238; that of the corresponding perchlorate, $KClO_4$, is 0.152,[7] over six times as great. The advantages of the use of this salt for the determination of potassium are clearly evident, especially because of the ease with which the periodate radical can be determined volumetrically and because of the high solubility of the corresponding sodium salt, which will be discussed later. It is understood that the details of such a method have been worked out at the laboratories of the University of Michigan. The solubility of the salt at a number of temperatures is given in Table II and shown in Fig. 2; measurements were made from solutions stirred by hand for brief periods, immersed in a water-bath with hand controlled temperature regulation.

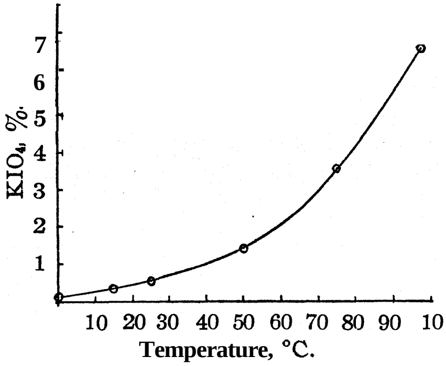

Fig. 2.—Solubility of KIO_4.

TABLE II

SOLUBILITY OF KIO_4 IN WATER

Temp., °C.	0.2	5.4	15.0	25.0	50.0	75.0	97.0
KIO_4, %	0.169	0.21	0.334	0.510	1.44	3.59	6.83

The di-meso-periodate, $K_4I_2O_9{\cdot}9H_2O$, should be congruently soluble according to Fig. 1, and therefore capable of recrystallization, which was found to be the case. For the analysis of the salt, including the water of hydration, the crystals were dried to constant weight in a miniature desiccator over the anhydrous salt;[8] the water content was then determined by heating in an electric oven at 110°, KIO_4 by the usual iodimetric method, and the excess base by titration with standard acid. The results follow.

Anal. Calcd. for $K_4I_2O_9{\cdot}9H_2O$: KIO_4, 64.21; K_2O, 13.15; H_2O, 22.63. Found: 64.32, 13.23, 22.34.

There can be no question therefore, as to the composition of the salt. Its solubility was then determined as shown in Table III and in Fig. 3, the temperatures above 25° being hand controlled.

It is evident that the di-meso salt has both a high solubility and a high temperature coefficient of solubility. The figure found at 25° for the pure salt is in reasonably close agreement with the point b of Fig. 1, indicating

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[7] Seidell, "Solubilities," D. Van Nostrand Co., New York 1919, p. 515.

[8] See Hill and Smith, THIS JOURNAL, 44, 548 (1922).

TABLE III

SOLUBILITY OF $K_4I_2O_9$ IN WATER

Temp, °C.	$K_4I_2O_9$, %	Density of soln.	Solid phases
0.3	3.5	1.032	$K_4I_2O_9 \cdot 9H_2O$
15.0	7.7	1.073	$K_4I_2O_9 \cdot 9H_2O$
25.0	12.3	1.116	$K_4I_2O_9 \cdot 9H_2O$
37.5	22.0	1.216	$K_4I_2O_9 \cdot 9H_2O$
50.0	35.0	1.395	$K_4I_2O_9 \cdot 9H_2O$
65.0	50.1	...	$K_4I_2O_9 \cdot 9H_2O$
78	61.7	...	$K_4I_2O_9 \cdot 9H_2O + K_4I_2O_9$
98.6	61.1	...	$K_4I_2O_9$

that the salt does not form as a solid phase until the ratio of base to acid in the solution is almost exactly that which occurs in the salt itself. The solubility curve shows a sharp break at about 78°, which is the temperature of the transition $K_4I_2O_9 \cdot 9H_2O \rightleftarrows K_4I_2O_9$ + solution. This temperature was obtained by a study of cooling curves, but could not be obtained with high precision, owing to delayed transformation and also possibly to slight decomposition, since the hot solutions gradually acquired a slightly yellow tinge, although free iodine could not be detected in them by the starch test. That the compound existing above 78° is the anhydrous form and not some lower hydrate is indicated by the evidence (just short, it may be claimed, of proof) that the moist ennea-hydrate, placed over the anhydrous form, does not lose water to form any lower hydrate, as shown above. If this evidence be accepted, it follows that the ennea-hydrate is to be regarded as a true salt-hydrate, and not in any sense an acid salt of the para series, as has been sometimes proposed.

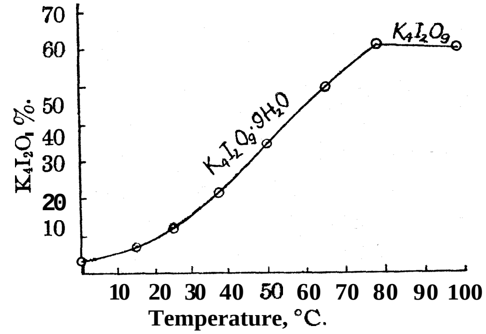

Fig. 3.—Solubility of $K_4I_2O_9$.

The Periodates of Sodium

To determine the periodates of sodium which are stable in contact with aqueous solution, the 25" isotherm was studied by the same method used for the potassium salts. The results are given in Table IV.

The results are in striking contrast with those of Table I. First, with regard to the experiments themselves, it was found that a very long time is required for equilibrium to be attained; from one to three weeks' stirring was used for the experiments in which $Na_2H_3IO_6$ is the solid phase and it is by no means certain that complete equilibrium was always reached. For this reason the figures for $NaIO_4$ content of the solution, while showing a

TABLE IV

TERNARY SYSTEM $NaIO_4$–$NaOH$–H_2O AT 25°

Complex taken		Saturated solution			Solid phases	
$NaIO_4$, %	$NaOH$, %	$NaIO_4$, %	$NaOH$, %	Density	NaOH content, %	Formula
14.0	0.0	12.62	0.0	1.103	...	$NaIO_4 \cdot 3H_2O$
14.0	.1	12.51	.0	1.103	5.4	$NaIO_4 \cdot 3H_2O + Na_2H_3IO_6$
12.35	.1	11.59	tr	1.094	9.5	$Na_2H_3IO_6$
15.19	1.5	7.63	.02	1.057	14.26	$Na_2H_3IO_6$
4.5	0.5	1.85	.01	1.011	14.32	$Na_2H_3IO_6$
4.2	.8	0.22	.045	0.999	14.96	$Na_2H_3IO_6$
2.4	.6	.15	.17	1.000	15.01	$Na_2H_3IO_6$
2.2	.8	.31	.45	1.002	14.90	$Na_2H_3IO_6$
3.8	1.2	.30	.55	1.006	15.04	$Na_2H_3IO_6$
1.92	1.08	.33	.57	1.004	24.64	$Na_2H_3IO_6 + Na_3H_2IO_6$
3.3	1.7	.17	.57	1.006	26.90	$Na_3H_2IO_6$
1.82	1.18	.19	.60	1.006	26.29	$Na_3H_2IO_6$
1.60	1.4	.15	.89	1.009	27.06	$Na_3H_2IO_6$
3.00	2.0	.15	1.00	1.010	26.67	$Na_3H_2IO_6$
5.16	3.99	.08	2.41	1.032	24.54	$Na_3H_2IO_6$
3.1	10.7	.02	10.04	1.111	25.95	$Na_3H_2IO_6$
3.0	22.0	.004	22.2	...		$Na_3H_2IO_6$
3.0	30.75	tr	30.75	1.319		$Na_3H_2IO_6$

high absolute accuracy, do not show a high relative accuracy. Since the solutions were made up from the side of supersaturation, the result showing the lowest solubility was taken in all cases as most nearly correct. With

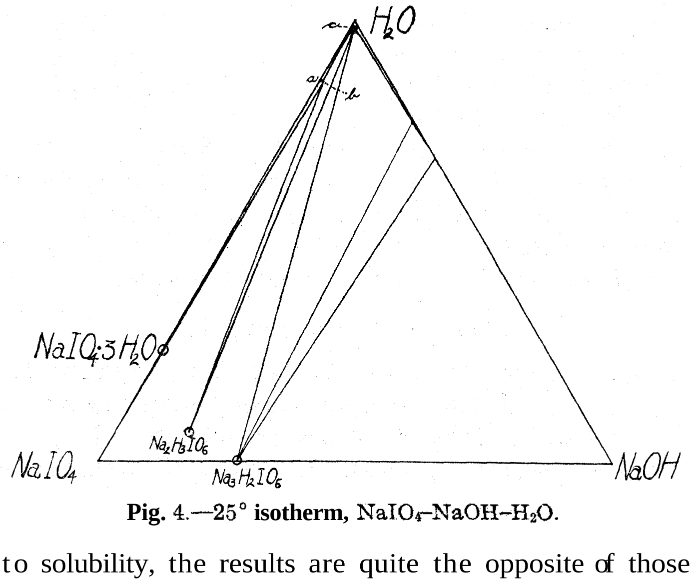

Fig. 4.—25° isotherm, $NaIO_4$–$NaOH$–H_2O.

respect to solubility, the results are quite the opposite of those for the potassium salts; the meta salt, $NaIO_4$, has a relatively high solubility, as shown in line 1, and is changed to the very insoluble para-periodate,

$Na_2H_3IO_6$, upon addition of the smallest quantity of sodium hydroxide (line 2). In the solution obtained no free base could be detected, although the titration would easily show amounts smaller than 0.01%. The isothermally invariant point *b*, shown in Fig. 4, is therefore too close to the side of the triangle to be shown to scale. Further additions of base give $Na_2H_3IO_6$ as the solid phase until the point *c* of Fig. 4 is reached, corresponding to line 10 of Table IV, beyond which the stable phase is the more basic para-periodate, $Na_3H_2IO_6$. The experiments were discontinued at the point where there was present 30% of sodium hydroxide, without the appearance of any new phase; there are, therefore, three and only three sodium periodates found by precipitation from aqueous solution, namely, $NaIO_4{\cdot}3H_2O$, $Na_2H_3IO_6$ and $Na_3H_2IO_6$. Col. 6 of Table IV shows the sodium hydroxide content of the salts, by algebraic extrapolation of the tie lines; the results are in good agreement with the calculated values of 14.71% and 27.22% for the two salts, taking into consideration the great length of the lines extrapolated. The partial isotherm shown in Fig. 5 shows in greater detail the pitch of the tie lines for the two compounds.

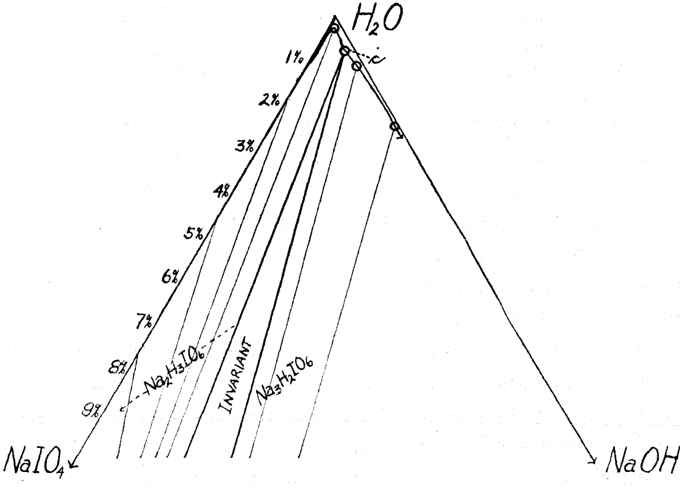

Fig. 5.—Partial isotherm at 25°, $NaIO_4$–$NaOH$–H_2O.

Each of the three sodium salts has been studied. The meta-periodate exists as a trihydrate and in anhydrous form as shown in Table V.

It was found that this salt is very slow in coming to equilibrium with its aqueous solutions and that the transition from the anhydrous form to the hydrate is also greatly delayed; the experiments, therefore, were conducted in the usual thermostat at the lower temperatures and at the higher temperatures in an electric oven, containing a large vessel of glycerin as a temperature buffer, into which the test-tube of solution was dipped and stirred mechanically from outside the oven. By making the heating

TABLE V

SOLUBILITY OF $NaIO_4$ IN WATER

Temp., °C.	$NaIO_4$, wt., %	Density of soln.	Solid phases
5.8	3.93	1.048	$NaIO_4 \cdot 3H_2O$
15.0	7.2	1.060	$NaIO_4 \cdot 3H_2O$
20.0	9.3	1.073	$NaIO_4 \cdot 3H_2O$
25.0	12.62	1.103	$NaIO_4 \cdot 3H_2O$
30.0	16.6	1.143	$NaIO_4 \cdot 3H_2O$
31.5	18.2	1.161	$NaIO_4 \cdot 3H_2O$
33.0	19.6	1.175	$NaIO_4 \cdot 3H_2O$
[34.5]	[21.3]	... .	$NaIO_4 \cdot 3H_2O + NaIO_4$
31.5	19.8	1.173	$NaIO_4$ (metastable)
33.0	20.6	1.185	$NaIO_4$ (metastable)
35.0	21.5	1.192	$NaIO_4$
36.0	21.8	1.196	$NaIO_4$
38.0	22.6	1.202	$NaIO_4$
44.2	24.9	1.218	$NaIO_4$
51.5	28.0	1.251	$NaIO_4$

element of the oven appropriate in size, the temperature changes in the glycerin bath were kept within 0.1'. The time required for equilibrium, if the stable solid phase is present, varies from one to two days; but if a change of phase is to be completed, a week or more may be necessary. The results of lines 9 and 10 were obtained after twenty-four hours and forty-eight hours' stirring, respectively; in line 9 the solubility is in perfect alignment with the results for the anhydrous salt, though metastable at this temperature, while in line 10 there has been a slight fall from that required for the metastable curve, indicating the very slight transformation to the hydrate which has occured in two days. The transition temperature, 34.5°, is obtained from the intersection of the two curves, using the equation Solubility $= 8.53 + 0.37t$ for the anhydrous form and Solubility $= 4.017 - 0.0758t + 0.0167t^2$ for the hydrate. Efforts to find the transition by cooling or warming curves gave no indication of the transition at any temperature, however carefully managed.

The composition of the hydrate, as previously shown by Barker,[9] was confirmed by bringing a sample of moist crystals to constant weight over the anhydrous form. Analysis gave the water by loss on heating as 20.0%; calcd. for $NaIO_4 \cdot 3H_2O$, 20.17%.

The secondary sodium para-periodate, $Na_2H_3IO_6$, has a very low solubility; by independent experiments made with a recrystallized sample, the solubility at 25° was found to be 0.23%, somewhat higher than the figure (0.157%) given by Rosenheim and Loewenthal.[4] This is, as far as I am able to find, the least soluble sodium salt known, and its use for the detection and estimation of sodium is easily possible; the sharp contrast with the solubilities of the potassium salt is favorable for such a separation,

[9] Barker, *J. Chem. Soc.*, 93, 15 (1908).

since in neutral or acid solution the potassium salt (KIO_4) is insoluble and the sodium salt ($NaIO_4$) soluble, while in alkaline solution the potassium salt ($K_4I_2O_9$) is freely soluble and the sodium salt ($Na_2H_3IO_6$) very insoluble.

In the study of the properties of this secondary sodium salt, some interesting facts as to its hydration were observed. When formed by precipitation from $NaIO_4$ and NaOH solutions, the precipitate is usually amorphous in part, and upon drying over sulfuric acid to a constant weight it is found to contain from 2 to 3% of water in excess of that calculated by formula. This finding is in accordance with the results of Rammelsberg,[10] whose analysis shows the salt to be low in periodate and therefore high in water, but not in accord with the analyses of Loewenthal,[4] who worked, however, with exceedingly small samples of the salt (0.030 to 0.099 g.), which may have resulted in obscuring the fact of high water content. On putting the samples in a drying oven at 100°, it was observed that there was a somewhat rapid loss of water for the first two days (0.4 to 0.6%), and following that a quite regular loss continuing for at least three months, at a rate of about 0.01% per day, during which time the composition passed through that of the para-periodate and evidently the formation of a pyro salt began. The results of analyses of two 10g. samples are given in Table VI. Sample 1 was apparently amorphous, and showed continuous loss of water while Sample 2, more definitely crystalline, lost water only up to the point of the composition of the di-sodium salt.

TABLE VI

DEHYDRATION OF $Na_2H_3IO_6$

Sample No. 1 (amorphous)

	Calcd., %	Dried over H_2SO_4, %	Dried at 100°, days			
			10	50	75	100
$NaIO_4$	78.66	76 91	...	78.61	79.17	80.09
NaOH	14.72	14.74	...	14.91	15.23	15.56
H_2O	662	(8.35)	...	(6.48)	(5.60)	(4.35)
Water lost at 100°	...	...	...	1.56	2.23	3.86
	Sample No. 2 (partly crystalline)					
$NaIO_4$	78.66	...	77.75	78.24	78.38	78.36
NaOH	14.72	...	14.87	15.01	15.03	15.24
H_2O	6.62	...	(7.38)	(6.75)	(6.57)	(**6.40**)
Water lost at 100°	...	...	0.68	1.12	1.30	1.30

During this entire period the samples were weighed weekly. It is apparent, therefore, that the salt (at least in its amorphous form) can contain more than the stoichiometrical proportion of water, that the loss of water (both the excess and that of the stoichiometric compound) is appreciable at 100° under atmospheric conditions of aqueous pressure and that the vapor pressure of the excess water and that of the true

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[10] Rammelsberg, *Pogg. Ann.*, 134, 368 (1868).

compound are sensibly the same. The loss of water was not observed by Rammelsberg[10] to occur until a temperature of 185° had been reached. With well crystallized samples of the salt, however, no excess of water, within the limits of the analysis, could be found. Recrystallization was accomplished by dissolving the salt by lengthy boiling in water (its solubility at 100° being about 0.4%) and evaporating the saturated solution to about one-fourth its original volume; because of the well-developed property of forming supersaturated solutions, this could be accomplished without any precipitation. On standing at room temperature for a period of days, the salt precipitated in well-formed, small crystals; analysis of these samples gave the calculated stoichiometric composition for all three components within ± 0.1%. It is also to be deduced from the low vapor tensions here indicated that the water in the stoichiometric compound is held by primary valence as water of composition, and not by secondary valence as water of hydration; the compound is therefore to be classed as a para-periodate and not as a hydrated di-meso-periodate, as has sometimes been proposed.[11]

In order to determine whether the ratio of the two components, $NaIO_4$ and NaOH, varies in the compound, through adsorption from an excess in solution, four experiments were conducted similar to those of Table IV, but with quantities of the components chosen so that the extrapolation of the tie lines should be subject to smaller error, that is, with a larger proportion of solid phase in the complex. Arranging to have about 10% of solid present, the four tests were made to contain the following molar ratios of NaOH to $NaIO_4$: 0.8, 1.0, 1.1 and 1.2, respectively. After agitation in the thermostat for ten days, the liquid phases were carefully analyzed; algebraic extrapolation of the tie lines showed that the solid phases contained the following slight variations from the theoretical quantities of NaOH: −0.40%, + 0.24%, + 0.07%, −0.07%. These figures contain the error of the analysis of the solution multiplied nearly ten times, and because of their small magnitude and irregular direction seem to me to be negligible and to prove that there is no sensible variation of these two components in the compound. Analysis of these solids, and of others, gave a molar ratio of $NaIO_4$ to NaOH of 1 to 1 ± 2%. These findings are in agreement with those of Loewenthal.[4]

Passing to the tertiary sodium salt, $Na_3H_2IO_6$, it will be seen from Fig. 5 that the salt does not possess congruent solubility. It can be formed only when there is excess sodium hydroxide in the solution, which excess can be calculated from the results of Table IV, line 10; expressed as a molar ratio of $NaIO_4$ to NaOH, it has the high value 1:9.2. The pure salt, therefore, cannot be recrystallized from water; depending upon whether the amount of water is greater or less, it will either be completely

[11] Rammelsberg, *Ber.*, **1**, 70 **(1869).**

hydrolyzed to the secondary salt, or (if the total complex falls within the invariant area of Pig. 5) to a mixture of the two salts. This fact as to influence of the excess base explains why the preparation of sodium periodate by action of chlorine upon sodium iodate in presence of sodium hydroxide has sometimes given the secondary sodium salt,[12] sometimes the tertiary,[13] and sometimes a mixture;[5] no other explanation is needed to clear up the discrepancies. In order to confirm these conclusions as to the hydrolysis of the tertiary salt, independent experiments were carried out; a sample complex of $Na_3H_2IO_4$ and water falling within the area of saturation for the salt $Na_2H_3IO_6$ (Fig. 5) was agitated for a week's time at 25°; the supernatant liquid showed upon analysis a ratio of 2.3 moles of NaOH to 1 of $NaIO_4$, indicating that the hydrolysis had occurred. Since it was found that the hydrolysis was slow at room temperature, a similar complex was boiled with water for two and one-half hours and then allowed to stand overnight at room temperature; the liquid phase showed upon analysis substantially the same ratio of the components as given above, and the solid phase, filtered and dried, was found to contain 78.16% of $NaIO_4$, corresponding to a 91.5% conversion into $Na_2H_3IO_6$.

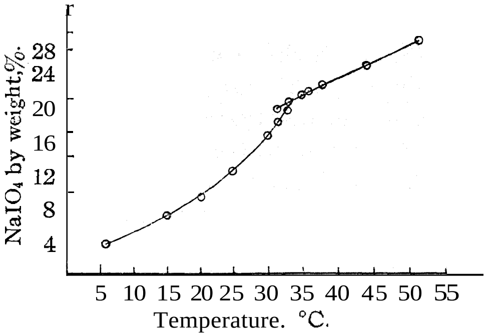

Fig. 6.—Solubility of $NaIO_4$.

The water content of the tertiary salt was found, as in the case of the secondary salt, to depend upon the crystalline character of the solid. If precipitated rapidly and in amorphous condition, it may contain up to 2% of water, which is not lost over sulfuric acid; moreover, it is driven off at 100° much more slowly than in the case of the secondary salt. Experiments continued over several months gave an average daily loss of only 0.002%. If the salt is allowed to precipitate from only moderately supersaturated solutions, formed from $NaIO_4$ and NaOH, a crystalline form occurs which has the stoichiometrical composition. As a matter of interest, the preparation of the salt by action of chlorine upon the iodate, as given earlier in the paper, apparently occurs at a rate giving a crystalline precipitate, which analyzes as practically 100% pure. The ratio of NaOH to $NaIO_4$ in various samples was found to be stoichiometric within the errors of the analysis. It was found also, in accordance with the experiments of Loewenthal,[4] that there is no detectable adsorption of sodium

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[12] Rosenheim and Liebknecht, *Ann.*, 308, **53** (1899).

[13] Ihre (Blomstrand), Her., **3,** 316 (1870).

hydroxide from solution containing the base in excess; the figures of Col. 6 of Table IV indicate, indeed, a deficiency of base, but this variation is probably due to the method of experimentation necessary for solubility determinations; an excess of the solid meta-periodate was present, which on treatment with sodium hydroxide solution doubtless became crusted with the very insoluble trisodium salt, preventing further action upon the interior parts of the crystals. Material formed by precipitation, however, never showed variation in this direction.

It is also to be deduced that the trisodium salt, which shows so very low an aqueous tension, is to be regarded as a salt of the para series, and not a hydrated meso salt ($Na_3IO_5 \cdot H_2O$). It appears, then, that the only stable sodium periodates forming from aqueous solution are the meta-periodate (as a trihydrate and in anhydrous form) and the disodium salt and the trisodium salt of para-periodic acid; the several others listed in Mellor's "Treatise"[12] cannot be confirmed. In view also of the very low aqueous tension of the two last named salts, it seems necessary to classify them as stated, and Mellor's preference for regarding them as hydrated di-meso salts or meso-salts cannot be sustained. Walden's[14] measurements of the electrical conductivity of solutions made from periodic acid and sodium hydroxide are in solutions supersaturated with respect to the two salts described above and illustrate the marked metastability of these solutions; however justified may be his deductions as to the condition of the dissolved salts, they have no bearing upon the composition of the solid phases and there is therefore no evidence for the existence, as a solid, of the salt Na_5IO_6.

Acid Periodates

It being well known that the nearly related alkali salts of iodic acid form double compounds or acid salts with free iodic acid, such as $KIO_3 \cdot HIO_3$, experiments were conducted to determine whether a similar condition exists in the case of the periodates. Samples of the two meta-periodates were agitated in the thermostat with varying amounts of periodic acid and the solutions analyzed after equilibrium had been attained, as shown in Table **VII.**

TABLE VII

SOLUBILITY OF META-PERIODATES IN THE PRESENCE OF PERIODIC ACID AT 25°

Saturating salt	Complex taken		Saturated solution		
	Wt. % of salt	Wt. % of HIO_4	Wt. % of salt	Wt. % of acid	Density
KIO_4	Excess	0.0	0.51	0.00	1.000
KIO_4	0.982	1.171	0.355	1.157	1.014
KIO_4	1.04	2.81	0.261	2.83	1.023
$NaIO_4$	Excess	0.0	12.62	0.0	1.103
$NaIO_4$	13.77	4.93	11.43	5.23	1.150

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[14] Walden, Z. *physik. Chem.*, 2, 49 (1888).

It will be seen that the addition of free acid produces a marked diminution in the solubility of potassium periodate, qualitatively in accord with the common-ion effect of the periodate ion but in direct contrast with the effect of free base previously shown to cause an increase in solubility. Such a decrease in solubility indicates the probable non-existence of a double compound of the nature of an acid periodate of potassium. The results in the case of the sodium salt are to be interpreted in the same fashion. It did not seem worth while, with this evidence, to complete the isotherms through all possible concentration ranges.

The Periodates of Lithium and Ammonium

Periodates of lithium have previously been prepared only by action of periodic acid upon lithium hydroxide. Attempts were made[15] to prepare such salts by action of chlorine upon lithium iodate in the presence of lithium hydroxide, in imitation of the methods so successful for the sodium and potassium salts. The products of the reaction were certain very insoluble substances, proved to be periodates by the correct ratio of oxidizing oxygen to iodine content, but containing large and irregular quantities of lithium hydroxide, so that stoichiometrical formulas were not to be thought of. The explanation probably lies in the fact, clearly demonstrated by Rosenheim and Loewenthal,[4] that lithium periodate adsorbs the hydroxide very strongly from its solutions. It appears, therefore, that this method of preparing lithium periodate is not possible, unless devices for maintaining a correct concentration of base during the preparation were worked out, which would be a matter of some difficulty.

Attempts[16] to prepare ammonium periodate by action of chlorine on ammonium iodate in the presence of ammonium hydroxide were wholly unsuccessful; no periodate was obtained and the iodate remained unchanged. It seems probable that in ammonia solutions the hydroxyl-ion concentration is insufficient to permit the oxidation of iodate ion to periodate ion, a reaction which thus far has been found to occur only in strongly basic solutions.

The conditions for the formation of pyro-salts of sodium periodate, by dehydration of the para-periodates, are being studied in this Laboratory, and the composition of the periodates of silver is also under investigation.

Summary

1. A 25° isotherm has been studied for the system consisting of KIO_4, potassium hydroxide and water. The stable salts of potassium found to

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[15] Experiments by Mr. H. E. Wolf, thesis for the B.S. degree, New York University, 1928.

[16] Experiments by Mr. San W. Wong, thesis for B.S. degree, New York University, 1928.

form from aqueous solutions are two only, and of the formulas KIO_4 and $K_4I_2O_9 \cdot 9H_2O$.

2. The solubility of the two potassium salts in water has been measured between the temperatures of 0 and 100°. The latter salt undergoes a transition to the anhydrous form at about 78°.

3. A 25° isotherm has been studied for the system consisting of $NaIO_4$, sodium hydroxide and water. The stable sodium salts which form from aqueous solution are three only, and of the formulas $NaIO_4 \cdot 3H_2O$, $Na_2H_3IO_6$ and $Na_3H_2IO_6$.

4. The solubility of sodium meta-periodate, $NaIO_4$, has been measured between the temperatures of 5 and 50°. A transition point between the hydrate and the anhydrous form occurs at 34.5°.

5. The wide difference in the solubilities of the sodium and potassium salts may be used as a means for the analytical separation of potassium and sodium.

6. The secondary sodium periodate, $Na_2H_3IO_6$, is found, when in an amorphous condition, to hold a few per cent. of water with a vapor tension apparently as low as that of the compound; at 100° the rate of loss of water, adsorbed or of composition, averages about 0.01% per day under atmospheric aqueous pressures. The tertiary sodium salt also adsorbs water, and the rate of loss of water adsorbed or of composition is about one-fifth as great.

7. Action of periodic acid upon the meta-periodates was not found to produce acid salts.

8. Lithium periodate could not be formed in a pure state, and ammonium periodate could not be formed at all by the oxidation of the iodates by chlorine in presence of the appropriate base.

NEW YORK CITY

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

THE FREEZING POINT-SOLUBILITY RELATIONS OF GEOMETRICAL ISOMERS. I. THE β-CHLOROCROTONIC ACIDS[1]

BY EVALD L. SKAU[1a] AND BLAIR SAXTON

RECEIVED AUGUST 3, 1928 PUBLISHED OCTOBER 6, 1928

If the freezing point-solubility data of any component of an ideal solution are plotted $1/T$ against log N, the slope of the line at any point is proportional to the molal heat of fusion of the component.[2] Alternately, we may take as our criterion that the activity, *a*, or N calculated by means of this equation from a calorimetrically determined value of ΔH, should be equal to the actual value of N. With these criteria of ideality, a number of cases have been cited in which two substances are substantially mutually ideal and these seem to show that ideality is realizable when, and only when, the substances are quite similar in chemical constitution,[3] but not similar enough, especially in crystallography, to form mixed crystals to a pronounced extent.[4] For example, certain isomeric *ortho*, *meta* and para disubstituted benzenes form practically ideal binary and ternary systems.[5]

It seemed reasonable to suppose that isomers of the cis-trans or the *syn-anti* type might form ideal solutions of the simple eutectic type, since there appears to be a marked resemblance in structure between the *cis* and *ortho* on the one hand and the *trans* and para on the other.[6] Further, it appears from the rather meager data which are available that geometrical isomers show substantially the same percentage differences between their heats of combustion as are shown by *ortho*, *meta* and para isomers. At their melting points the molal heat capacities of the geometrical isomers studied in this paper do not show a greater difference than the differences

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[1] From a dissertation submitted by Evald L. Skau to the Graduate School of Yale University, June, **1925,** in candidacy for the Degree of Doctor of Philosophy.

[1a] Du Pont Fellow, **1924-1925.**

[2] From the equation $(d \log N_A)/[d(1/T)] = -\Delta H_A/4.575$, where log N_A is the common logarithm of the mole fraction of *A*, the component crystallizing at temperature T, and ΔH_A is its molal heat of fusion at that temperature. For a bibliography and discussion of this equation see Johnston, *J. Phys. Chem.*, 29, 882 **(1925).**

[3] For a more detailed discussion see Hildebrand, "Solubility," The Chemical Catalog Co., New York, 1924, p. **59** ff.

[4] In such a case the equation must be modified. For example, see Van Laar, *Z. physik. Chem.*, *55*, *435* **(1906); 63, 216 (1908); 64, 257 (1908).** In some cases where limited solid solutions are formed nearly straight lines are obtained by plotting log N against $1/T$, but this alone is not a criterion of ideality in the liquid phase.

[5] Narbutt, *Z. physik. Chem.*, *53*, **697 (1905);** Holleman, Hartogs and van der Linden, *Ber.*, 44, **704 (1911);** Andrews, *J. Phys. Chem.*, 29, **1041 (1925);** Kohman, *ibid.*, **1048.**

[6] See Werner, "Lehrbuch der Stereochemie," Gustav Fischer, Jena, 1904, p. 211.

calculated for the *ortho, meta* and para isomers investigated by Andrews, Lynn and Johnston.[7] Indeed, Andrews[8] found practically no differences in the molal heat capacities of the solid isomers of the type C_6H_4XY from 30° below the lowest melting isomer to 110°K. Hence he concluded that they would give substantially the same free energy change of formation. Probably this can also be said for geometrical isomers. Furthermore, it was hoped that a study of such systems might aid in the solution of the nature of this type of isomerism, which, following Wislicenus, has been called geometrical isomerism. If it could be shown that the *cis-trans* isomers of a substance form systems of the simple eutectic type, whereas the *cis-cis* or the *trans-trans* forms of two closely related substances form solid solutions,[9] the structure of such isomers might be referred to fumaric and maleic acids, whose structures are conceded to be reasonably well established.

A search of the literature reveals only one system of geometrical isomers for which the temperature–composition diagram has been constructed with sufficient accuracy for use in testing ideality by these methods. This is the system crotonic acid–isocrotonic acid as given by Morrell and Hansen.[10] These investigators undoubtedly used pure acids but their experimental method is open to criticism. They made their solutions of different compositions by starting with a known amount of each pure component and adding, successively, small amounts of the other form. The freezing points were determined in the usual way without correcting for the amount of solid separating. Thus the error in composition was accumulative and the freezing points were all lower than the true values. In the course of one series of determinations "it was necessary to substitute a mercury thermometer for the alcohol thermometer." Although correction was made for the solid removed by the thermometer, a considerable error must have been introduced since there is a break in the solubility curve between the points in question. Using their data, we have plotted $(1 + \log N)$ against $1000/T$. On the crotonic acid branch of the plot, the points lie both above and below a nearly straight line drawn from $1000/T_f$ (T_f is the freezing point of pure crotonic acid) with an initial slope calculated

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[7] Andrews, Lynn and Johnston, THIS JOURNAL, 48, 1274 (1926).

[8] Andrews, *ibid.*, 48, 1287 (1926).

[9] This does not seem improbable since, judging from a survey of the literature and from results obtained in this Laboratory by E. P. Jones [Johnston and Jones, *J. Phys. Chem.*, 32, *593* (1928)] and by Myer Solomon (unpublished), the disubstituted derivatives of benzene seem to form solid solutions only in the *meta-meta, ortho-ortho* or *para-para* systems. Further, Bruni [Bruni and Gorni, *Atti. accad. Lincei* (5) *8*, 454, 570 (1899); Bruni, *Gazz. chim. ital.*, *I*, 30, 64 (1900)] claims to have shown that the *trans* form of two geometrical isomers forms a solid solution with the corresponding saturated compound, whereas the cis form gives a freezing point–solubility diagram of the ordinary eutectic type.

[10] Morrell and Hansen, J. Chem. *Soc.*, 85, 1520 (1904).

from the molal heat of fusion.[11] Though the experimental points show considerable divergence from this line, the fact that the deviation is not in one direction indicates that experimental error rather than non-ideality is the cause. The points on the isocrotonic acid branch fall remarkably close to a straight line corresponding to a calculated heat of fusion of 3100 cal. per mole. Although this heat has not been determined calorimetrically, we may conclude that the two forms of crotonic acid probably form a nearly ideal solution.

The temperature–composition diagram of another system, *syn*- and anti-benzaldoxime, has been constructed by Cameron,[12] but due to the partial transformation on heating above the melting point, the freezing points could be determined only roughly by means of the capillary tube method. On plotting the values of $(1 + \log N)$ against $1000/T$ for this system, decidedly curved lines, concave upwards, are obtained for both branches, which would ordinarily point toward non-ideality.[13] Due to the inaccuracy of the data, however, and since the true heats of fusion are unknown, it would be unsafe to draw any conclusions from this evidence.

In order to secure some definite evidence concerning the ideality of cis-trans systems, it was decided to construct accurately the freezing point–solubility diagram for the system β-chlorocrotonic acid-β-chloro-isocrotonic acid and to determine their heats of fusion. These compounds can be synthesized with relative ease; furthermore, proof of the ideality of this system would strengthen the indications as to the ideality of the crotonic acid–isocrotonic acid system, since they are structurally quite similar to the latter.

Experimental Part

Method of Synthesis

Preparation of *cis* and *trans* Forms.—A mixture of the two forms of β-chlorocrotonic acid was prepared from acetoacetic ester by Geuther's method as modified by

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[11] Determined in this Laboratory by Lynn (*Dissertation*, 1925) using the method described by Andrews, Lynn and Johnston (ref. 7). In the neighborhood of the melting point this can be expressed by the empirical equation $\Delta H = 3695 - 13.56t + 0.0736t^2$. At the melting temperature, 71.4°, this becomes 3100, or 924 cal. higher than the value obtained by Bruner [Ber., 27, 2102 (1894)], who probably used impure acid since he gave the melting point as 67.4°. The new value for the heat of fusion corresponds to an entropy of fusion of 9.0 cal. per degree at the melting point instead of 6.4 from Bruner's data. Crotonic acid can no longer be cited as the organic compound with the lowest entropy of fusion (Roozeboom, "Die Heterogenen Gleichgewichte," II, 1, 279). As far as the present authors are aware this position should now be assigned to cyclohexane with a value of 1.75 cal. per degree.

[12] Cameron, J. Phys. *Chem.*, 2, 413 (1898).

[13] The change in slope of such a curve is determined by $d\,\Delta H/dT$; hence this evidence alone does not exclude ideality.

Michael, Wislicenus, Jr., and Scheibler.[14] The ester, in benzene solution, was treated with phosphorus pentachloride and the reaction mixture was added to water. The acids were removed from the benzene layer as their sodium salts by extracting with sodium carbonate solution and were then precipitated by acid and extracted with ether. In removing the ether it was found advisable to use a fractionating column to hold back the volatile β-chloro-isocrotonic acid; the last portions are best removed by evaporation at room temperature from a shallow crystallizing dish. The yield was 36.5%. The two acids were then separated as well as possible by fractional steam distillation.

Purification

β-Chlorocrotonic Acid.—The crude residue from the steam distillation was decolorized with Norite and was then recrystallized once from water and fractionally crystaliized from carbon disulfide. It was finally sublimed[15] at 105° at atmospheric pressure. The melting point was at first followed by means of the ordinary capillary tube method and later by means of cooling curves. The final product froze at 93.6°.

β-Chloro-isocrotonic Acid.—The crude product was first fractionally steam distilled. Subsequent sublimation[15] at 105° and atmospheric pressure gave a pure product which gave a "flat" on a cooling curve at 60.5°.

The Freezing Points

The freezing point determinations were made by means of the apparatus described by Andrews, Kohman and Johnston,[16] with some further refinements developed in this laboratory since the publication of their work. The apparatus is sketched in Fig. 1. A cylindrical copper tube or shield (14 cm. long, 5cm. outside diameter, 2.5cm. inside diameter) closed at one end is set on a cushion of asbestos in the silvered pint Dewar flask A. K is a heating coil consisting of a 25-ohm nichrome resistance wound tightly around the metal cylinder and insulated from it by means of a thin layer of mica. A thin-walled freezing point tube G (65 mm. long, 8 mm. diameter) containing the sample, H, fits quite snugly over the end of a thin glass tube. The latter extends up through the cork stopper from which the small unsilvered Dewar tube C[17] is suspended by means of a wire not shown in the diagram. I is an inlet for a stream of hot air,[18] used in melting the sample *in situ,* and E an outlet. The temperature of the shield B is measured by means of the copper–constantan thermoelement J set in hard solder in a hole drilled for the purpose. A plug of cotton wool prevents too rapid radiation from the top of the shield. The thermoelement D, in the melt, is constructed of No. 46 (B. and S. gage) copper and No. 40 constantan wire, the copper being wound around the insulated constantan for a distance of about 4 cm. above the junction In order to minimize the heat conductivity. It is of course an advantage to have the thermoelement directly in the melt but in some cases this is impossible due to the solvent action of the liquid. However, the element responds to *a* change in temperature with no appreciable lag when

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[14] Geuther, *Z. Chem.,* **14,** 237 (1871); Michael and Schulthess, *J. prakt. Chem.,* [2] **46,** 236 (1892); Wislicenus, Jr., *Dissertation,* Leipzig, **1892,** *Chem. Zentr., I,* 413 (1893); Scheibler, *Ber.,* 53, 381 (1920).

[15] Rejecting and resubliming all but the long needle-like crystals that projected from the sides of the sublimation tube.

[16] Andrews, Kohman and Johnston, *J. Phys. Chem., 29,914* (1925).

[17] Later work showed this tube to be superfluous.

[18] Produced by passing air through a small iron pipe loosely filled with copper turnings and wound with a heating element. The sample may also be melted by using a small resistance heater fitting loosely around tube G.

protected by a thin-walled capillary tube containing vaseline or some high-boiling liquid (for example, benzophenone). We have therefore used this method exclusively since it has the added advantage that the glass around the thermoelement is much more easily cleaned than the bare thermoelement.

The thermocouples were calibrated at the ice point and at the boiling points of water, naphthalene and benzophenone. Temperatures were read to the nearest microvolt (ca. 0.02°) by means of a Leeds and Northrup type K potentiometer. The freezing points were corrected by using the extrapolation method of Andrews, Kohman and Johnston.[16] The freezing points of the pure substances are correct to within about ±0.05° and, with the solutions, the maximum error, near the eutectie point, is about 0.25°.

The freezing point data for the system are given in Table I, the points marked with an asterisk being values interpolated from the $(1 + \log N)$ *vs.* $1000/T$ plots. In this table are included the ideal values of N, or the activities, a, calculated from the heats of fusion and the changes in heat capacity as measured by us. The ratio a/N, given in the last column for each component, represents the deviation from ideality at the temperature t and mole fraction N.

The system is of the simple eutectic type and on plotting $(1+ \log N)$ against $1000/T$ for the two branches on a large scale it is found that, within the accuracy of our experimental values, straight lines are obtained in both cases. The values of $(d \log N)/[d(1000/T)]$ for these lines are 1.1427 for the β-chlorocrotonic acid branch and 0.0009 for the β-chloro-isocrotonic acid branch, from which the calculated heats of solution are 5220 and 4120 cal. per mole, respectively.[19]

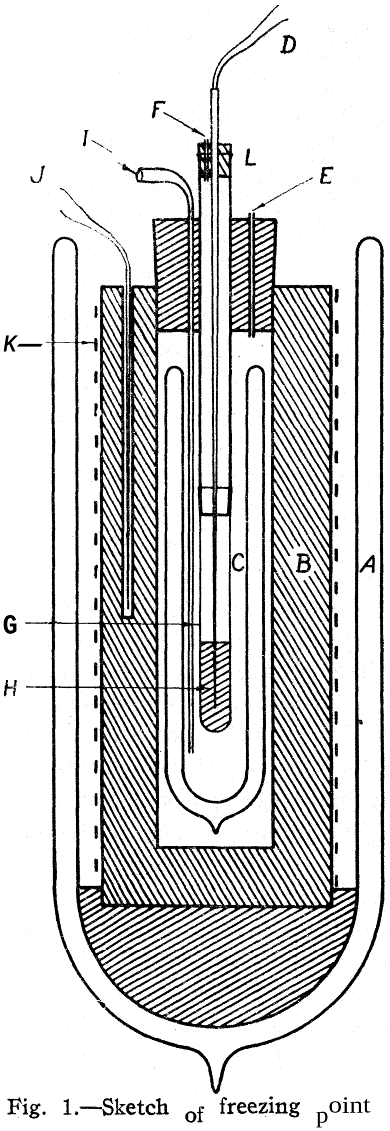

Fig. 1.—Sketch of freezing point apparatus.

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[19] Since $(1 + \log N)$ is plotted against $1000/T$, $s = \dfrac{d \log N}{1000\ d(1/T)} = -\Delta H/4575$, from which $\Delta H = -4575\,s$.

TABLE I

FREEZING POINT–SOLUBILITY DATA FOR THE SYSTEM β-CHLOROCROTONIC ACID–β-CHLORO-ISOCROTONIC ACID

	β-Chlorocrotonic acid				β-Chloro-isocrotonic acid		
t	*N*	a	*a/N*	*t*	N	*a*	*a/N*
93.6	10000	1.000	1.000	60.5	1.0000	1,000	1.000
*88 3	0.9000	0.905	1.006	56.4	0.9250	0.940	1.017
*82.5	.8000	.811	1013	*53.6	.8800	.902	1.025
75.6	.6848	.708	1.033	49.6	.8167	.848	1.038
*60.3	.5000	.527	1.054	*46.3	.7600	.806	1.061
53 2	.4148	,441	1.062	43.2	.7128	.768	1.077
*46.8	.3500	.381	1.088	41.5	.6920	.747	1.080
41.5	,3080	.335	1.088				

The Heats of Fusion

Direct calorimetric measurements of the differences between the heat contents of each form[20] at several temperatures and that of the solid at 22° were made by the method described by Andrews, Lynn and Johnston.[7]

Following their usage, we have expressed the heat content of the solid and of the liquid by empirical equations, valid over a short temperature range in the neighborhood of the melting point, of the form $H = a + bt + ct^2$. In these equations H is expressed in gram-calories per mole at t°, referred to the heat content of the solid at 22° as zero. The value of *H* for the liquid minus that for the solid is the heat of fusion, ΔH. For β-chlorocrotonic acid this is $\Delta H = 20{,}300 - 94.15\ T + 0.1426\ T^2$; and for β-chloro-isocrotonic acid it is $\Delta H = 11{,}660 - 61.26\ T + 0.1085\ T^2$. These equations have been used in calculating the activities given in Table I. This involves the assumption that the heat content equations for the liquids are valid down to the eutectic temperatures, but this seems preferable to considering the heats of fusion as constant. The values of ΔH, calculated to the freezing temperatures, are given in Table II.

By differentiating the heat content equation with respect to temperature, C_p can be expressed over a limited temperature range. Since the heat content equations are necessarily empirical, the heat capacity equations derived from them are only approximate. The heat capacities of the solids and liquids have been calculated to the freezing temperatures and are given in Table II. The difference, $C(l) - C(s) = \Delta C_p$, approximately expressing the variation of ΔH with temperature in the neighborhood of the freezing point, is about the same for the two isomers. The

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[20] The sample of β-chlorocrotonic acid was not quite so pure as that used in the freezing point experiments, hence its freezing point was about 0.3° lower. In attempting to carry the curve to higher temperatures, it was found that decomposition of some kind took place, as was shown by the heat content values of the sample when redetermined at lower temperatures. The β-chloro-isocrotonic acid, on the other hand, was of the highest purity and the heating curves run on this sample afterwards proved that there had not been the slightest decomposition.

values **are** of the same order of magnitude as those found by Andrews, Lynn and Johnston[7] for the organic acids studied by them. The results are summarized in Table II. In addition to the quantities above described we have included A , and A„ expressing the maximum and the average (disregarding sign) differences between the experimental values of H and those calculated from the empirical equations.

TABLE II

HEAT CONTENTS OF THE β-CHLOROCROTONIC ACIDS

	No of obs.	Temp. range, °C.	*a*	*b*	*c*	A	A,	ΔH_f at t_f	C_p at t_f	ΔC_p
β-Chlorocrotonic acid										
solid	9	33	—756	36 68	0 0303	62	**31**	4950	39.4	
liquid	4	121	4470	17.42	.1729	14	9		49 8	10 4
β-Chloro-isocrotonic acid										
solid	6	33	—712	31 45	0 0416	48	22	3300	36 5	
liquid	9	121	2308	29 44	1501	71	24		47 6	11.1

It will be noted that the values for the heats of fusion calculated from the freezing point data and those experimentally determined differ by 270 cal. per mole in the case of the β-chlorocrotonic acid and by 820 cal., per mole in the case of the β-chloro-isocrotonic acid, both deviations being in the same direction. That these differences are due to experimental error is out of the question. The freezing points calculated from the experimentally determined heats of fusion are ***lower*** by **3** and 5°, respectively, near the eutectic composition, than the observed freezing points. This is many times the probable error in the freezing point determinations. The experimental accuracy in the calorimetric determinations is about 50 cal. per mole, so that the error in the heats of fusion so determined would be 100 cal. per mole at the greatest. Inasmuch as the experimental measurement of the heat of fusion involved the sudden cooling of the molten sample to about 22°, it seemed possible that under these conditions the substances may have solidified in some unstable crystalline modification whose heat of fusion was smaller. In order to test this possibility three successive heating curves were run on the same sample of β-chloro-isocrotonic acid and for the data so obtained the relative heats of fusion in the three cases were calculated, by evaluating the appropriate area under the temperature–time curves,[21] with a reproducibility of about 5%. The first and third curves were run on the sample after melting it and chilling it suddenly to room temperature; the second after inoculating it just below the melting point and then allowing it to cool very slowly, thus duplicating the conditions in the freezing point determinations. The results are as follows.

[21] See Andrews, Kohman and Johnston, who have applied this method to cooling curves (ref. 16).

TABLE III

EFFECT OF RATE OF COOLING ON HEAT OF FUSION OF β-CHLORO-ISOCROTONIC ACID

No.	Previous treatment	% deviation from mean of I and III
I	Suddenly chilled	+3.8
II	Seeded and slowly cooled	– 1.9
III	Suddenly chilled	– 3.8

Since the difference to be accounted for is of the order of 20%, this evidence shows that only one modification of β-chloro-isocrotonic acid was involved. Further, inasmuch as no break was detected in the heat content–temperature curve of the solid until the melting point was reached, it seems reasonable to conclude that it undergoes no transition above 22°.

Conclusion

The only plausible conclusion to be drawn from the data, therefore, seems to be that the system is not entirely ideal. That no complexes are formed in appreciable amounts by association or reaction seems to be probable since the $(1 + \log N)$ *vs.* $1000/T$ plots are substantially straight lines throughout the whole range considered for both branches of the freezing point diagram. Neither would mixed crystal formation explain the discrepancies satisfactorily. On the other hand, the non-ideality might be explained by a slight difference in the internal pressures or polarity of the two substances.[22] That is, there may be a slight heat of mixing in the liquid state for the two forms which deviates from constancy at the various compositions in such a way that when it is added to the heat of fusion, which also changes, it gives practically a straight line for the $(1 + \log N)$ vs. $1000/T$ plot.

If this explanation is correct, one would predict a slight volume change on mixing the two liquids.

Summary

A modification of the freezing point apparatus as given by Andrews, Kohman and Johnston[16] has been described.

Accurate freezing point measurements for the system β-chlorocrotonic acid–β-chloro-isocrotonic acid have been made and calorimetric data, including heat contents, specific heats and heats of fusion, have been determined for each of these two compounds. The heat of fusion of crotonic acid has been reported. An examination of these data and those existing for the crotonic acid–isocrotonic acid system has been made to test the ideality of these two systems. It was found that in the former system the values for the heats of solution based on freezing point measurements are higher than those determined calorimetrically and the activities calculated from the thermal data are, for each component, greater than the corre-

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[22] See, for example, Hildebrand "Solubility," The Chemical Catalog Co., New York, 1924, p. 69 ff.

sponding mole fraction to the maximum extent of about 8% at the eutectic point. Judging from our present knowledge of such systems, geometrical isomers seem to show slight deviations from mutual ideality but not such as would indicate complex or mixed crystal formation.

It is possible that similar studies made on less polar isomers of this type may show them to be more nearly ideal than those discussed in this paper.

NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE PHYSICAL CHEMICAL LABORATORY OF MCGILL UNIVERSITY]

THE SURFACE ENERGY OF SOLID SODIUM CHLORIDE. III. THE HEAT OF SOLUTION OF FINELY GROUND SODIUM CHLORIDE

BY S. G. LIPSETT, F. M. G. JOHNSON AND O. MAASS

RECEIVED AUGUST 6, 1928 PUBLISHED OCTOBER 6, 1928

In previous papers[1] it was shown that finely divided sodium chloride had a heat of solution different from that of coarsely ground sodium chloride. This difference was attributed to the energy bound up in the surface of the finely divided salt, and from the measurement of the difference in the heat of solution, the actual value of the surface energy of solid sodium chloride was calculated. In these experiments the finely divided salt had been obtained by sublimation.

In the present paper an account is given of similar measurements but here the finely divided salt is obtained by grinding. It has been found in this case also that the finely divided material had a lower (negative) heat of solution than the coarsely ground sodium chloride.

Experimental Procedure

Pure sodium chloride was ground in a mechanically driven agate mortar for fifteen minutes. The ground salt was then placed at the bottom of a vertical glass tube about 1 m. long and 4 cm. in diameter and dry air, at a constant pressure, was blown into the tube through a fine nozzle at the bottom. The air was admitted so as to impinge on the ground salt. The current of air carried up the fine particles of salt which then passed into a series of settling chambers[1b] where they were sorted out according to size. The vertical glass tube was jarred continuously by an automatic tapper to prevent salt from adhering to the walls of the tube. The salt in the tube was recharged every fifteen minutes.

In order to see whether the salt was contaminated by silica rubbed off the agate mortar, samples of the product were analyzed but no weighable amount of silica was found in them.

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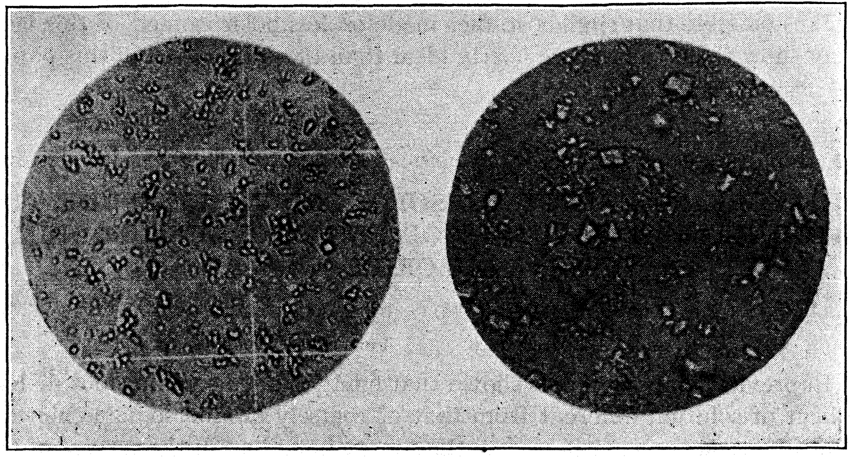
[1] *(a)* Lipsett, Johnson and Maass, THIS JOURNAL, 49, 925 (1927); (b) 49, 1940 (1927).

The heat of solution of the finely divided salt was determined using the apparatus described previously[1b] and the diameter of the particles was measured by means of photomicrographs.[1b]



Sublimed. Ground.

Fig. 1.—Finely divided sodium chloride. (805 diameters).

Experimental Results

The heat of solution was determined at 25° at a concentration of 4.62% with three different samples of salt. The results are given in Table I.

TABLE I

HEAT of SOLUTION OR FINELY GROUND SODIUM CHLORIDE:

Sample	Heat of soln., cal. per mole	Diff. in heat of soln., cal. per mole	Diameter of average particle, μ
I	−903.7	24.9	1.3
II	−903.6	25.0	1.2
III	−887.9	40.7	1.4

In Col. 3 is given the difference between the heat of solution of coarsely ground sodium chloride (−928.6 cal. per mole) and of the finely ground salt measured, of course, at the same temperature and concentration. This difference is far larger than that obtained with finely divided salt obtained by sublimation. It may be calculated from the previous work[1b] that sublimed salt whose particles were 1.3μ in diameter would have approximately a heat of solution only 11 cal. less than that of coarse salt. The exceptionally large difference obtained with the finely divided salt obtained by grinding is probably due to the uneven surface of the ground salt whereby the actual surface of the particles is much larger than the apparent surface.

The fine salt obtained by sublimation, when examined under the microscope, is seen to be definitely cubic in appearance. It is reasonable to suppose that crystals of salt formed by sublimation would have smooth surfaces and be fairly regular in shape. On the other hand, the fine salt obtained by grinding is distinctly irregular in appearance under the microscope and the crystals show many jagged fractures. This is shown in the accompanying photomicrographs of the finely divided salt prepared by the two methods. Calculation of the surface area of the finely divided ground salt from the measurement of the diameter of the particles, assuming that the particles are cubic in shape, will almost certainly give a result which is less than the actual surface, since no account will have been taken of the irregularities in the surface and the small projecting fragments which may be assumed to be present even when not visible under the microscope.[2]

For the above reason, the results obtained by using the ground material have been taken as more or less qualitative in nature and as supporting the previous work, but the actual calculation of the surface energy is believed best to be derived from the results obtained using the finely divided sublimed salt, since in the latter case the surface area is probably more accurately obtained.

The present work shows, however, that finely divided salt whether obtained by sublimation or by grinding has a lower (negative) heat of solution than coarsely ground salt.

Grateful acknowledgment is made to the National Research Council of Canada for a grant to aid in this work and also for a Studentship held by one of us, during the tenure of which this work was carried out.

Summary

The heat of solution of finely divided salt prepared by grinding has been determined and has been found to be less in magnitude than the heat of solution of coarsely ground sodium chloride.

MONTREAL, CANADA

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[2] D. Balarew, *Z. anorg. Chem.*, 154, 170 (1926).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

THE OXALATE METHOD FOR SEPARATING CALCIUM AND MAGNESIUM

BY WILLIAM T. HALL

RECEIVED AUGUST 27, 1928 PUBLISHED OCTOBER 6, 1928

The use of the oxalate anion for the quantitative precipitation of calcium in the presence of magnesium cations probably dates from Bergmann, the father of analytical chemistry, for it is mentioned in a Latin paper covering the work of Bergmann, which was published in 1778. Bucholz in a paper written in 1812 casually mentions the reaction as if it were well known to chemists at that time.

C. R. Fresenius, in his classic text on analytical chemistry, recommended, at about 1850, a dilute solution, the presence of sufficient ammonium chloride to prevent the precipitation of magnesium hydroxide and sufficient ammonium oxalate to combine with both calcium and magnesium. Fresenius stated that more oxalate than that required by the calcium is necessary because magnesium tends to prevent the precipitation of calcium oxalate. He recommended that the precipitate be allowed to stand twelve hours to insure complete precipitation of the calcium and that the precipitate be dissolved in hydrochloric acid and again treated with ammonia and oxalate in order to obtain a pure precipitate free from magnesium.

Down to the beginning of the nineteenth century, the statements of Fresenius regarding the oxalate precipitation of calcium were for the most part regarded as authoritative, although a number of chemists criticized the method, notably Sherer, who in 1858 preferred to separate calcium and magnesium ions by means of dilute sulfuric acid and considerable alcohol.

In 1901, Richards, McCaffrey and Bisbee[1] studied the ammonium oxalate separation from the standpoint of the physical chemist, and succeeded in avoiding the double precipitation. According to Richards, the hot, slightly acid solution of calcium and magnesium chlorides is first treated with an excess of oxalic acid and is then neutralized slowly during about fifteen minutes. Then the solution is made distinctly ammoniacal and a large excess of ammonium oxalate is added.

A careful study of Richards' paper fails to show exactly what is meant by a "large excess of ammonium oxalate" and the reason for the excess appears to be the idea of making the calcium oxalate less soluble in accordance with the solubility product principle and the common ion effect.

Blasdale[2] subsequently modified the procedure of Richards and obtained good results with much less oxalate. For a solution containing the equiv-

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[1] Richards, McCaffrey and Bisbee, *Proc. Am. Acad. Arts Sci.*, **36**, 375 (1901); *Z. anorg. Chem.*, 28, 71 (1901).

[2] Blasdale, THIS JOURNAL, 31, 917 (1909).

alent of not more than 0.6 g. of the mixed oxides in a volume of 300 cc. Blasdale recommended adding to the boiling solution 3.5 g. of ammonium chloride and only one gram of oxalic acid. If the content of magnesium is very high, only enough oxalate to precipitate the calcium is added at the start and the rest only after the solution has been slowly neutralized and allowed to stand for ten minutes. A double precipitation is advised when ten times as much magnesium as calcium is present and when the content of ammonium salts is high it is advised to remove them before precipitating the magnesium.

Dede[3] determined the calcium content of burnt magnesia and held that the addition of 2 g. of ammonium oxalate was necessary. Luff[4] avoided the use of excess ammonium oxalate and Bach[5] states that a bad separation of a little calcium from considerable magnesium always results if the ammonium chloride content is low or the ammonium oxalate content is high.

Recently two very contradictory papers have been written on the separation of small quantities of calcium from considerable magnesium. Hahn and Weiler[6] claim that a good separation is obtained when only a *slight excess* of ammonium oxalate is used while Bobtelsky and Frau Malkowa-Janowskaja[7] obtained excellent results by adding 20 g. of ammonium oxalate to 100 cc. of hot solution containing calcium and magnesium. In this way, prompt precipitation of 20 mg. of calcium was obtained in the presence of 2.70 g. of magnesium chloride.

The above citations represent but a very small part of the voluminous literature on the separation of calcium and magnesium. It is clear that chemists differ widely with respect to how much ammonium oxalate should be used to accomplish the best results. In order to settle this matter in our own minds, we have made quite a number of experiments, the enumeration of which would be very boring but the results seem quite clear.

The statement by Fresenius that more oxalate is required when magnesium is present than would be necessary in a solution of pure calcium chloride is true. Thus, with a sample of pure calcium carbonate weighing 0.5 g. (10 milliequivalents), correct results were obtained by using 50 cc. of 0.5 *N* ammonium oxalate solution as precipitant. When, however, 0.5 g. of calcium carbonate was present together with 0.5 g. of basic magnesium oxalate, only 4.06 and 4.12% of calcium were obtained when 7.40% of calcium was present by using 5 cc. of the reagent. In fact, with only 0.05 g. of calcium carbonate in the mixture, the results were low with 50 cc. of reagent. Correct results were obtained when one milliequivalent of cal-

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[3] Dede, *Chem.-Ztg.*, **36, 414 (1909).**

[4] **Luff,** *Z. anal. Chem.*, **65,** 439–448 **(1925).**

[5] Bach, *Chem.-Ztg.*, **49, 514** *(1925).*

[6] **Hahn and Weiler,** *Z. anal. Chem., 70,* **1–22 (1926).**

[7] Bobtelsky **and** Malkowa-Janowskaja, *Z. angew. Chem., 40,* **1434–1437 (1927).**

cium was present together with five milliequivalents of magnesium only by adding 35 milliequivalents of oxalate. In every case the precipitate was allowed to stand overnight before filtering.

Fresenius' statement that magnesium oxalate is likely to be formed if considerable ammonium oxalate is added, does not appear to be true when the solution is fairly dilute and the precipitation is accomplished as recommended by Richards or by Blasdale. With a sample weighing 0.5 g. and containing 24.5% of magnesium, the magnesium results were high when the precipitation of calcium was incomplete but were correct when 25–125 milliequivalents of ammonium oxalate was added to precipitate one milliequivalent of calcium.[8] The method of Bobtelsky and Frau Malkowa-Janowskaja is based on some solubility studies which show that ammonium chloride solutions dissolve more magnesium oxalate than pure water does and that the solvent effect of ammonium oxalate on magnesium oxalate is much more marked. A number of experiments were made[9] using 20 grams of ammonium oxalate to precipitate a small quantity of calcium in the presence of considerable magnesium. The results obtained were in close agreement with those obtained by the method of Richards or by a double precipitation of calcium. The statement that there is no precipitation of magnesium when this very large excess of oxalate is used to precipitate a little calcium appears to be correct.

The presence of this large excess of ammonium oxalate has, however, a decidedly unfavorable effect upon the subsequent determination of magnesium. In the first experiment by Mr. Gardner in which 20 g. of ammonium oxalate was used, there was absolutely no precipitation of magnesium ammonium phosphate by the method of Smitz, although the solution was allowed to stand for several days. In another experiment a solution was used from which 0.1775 g. of magnesium pyrophosphate should have been obtained, as it was when only 5 g. of ammonium oxalate was used. This solution, when 20 g. of ammonium oxalate was present, yielded only 0.0154 g. of magnesium pyrophosphate by the Smitz method but after evaporating the filtrate to dryness, expelling ammonium salts and taking up in dilute acid, an additional 0.1618 g. of magnesium pyrophosphate was obtained on repeating the precipitation.

Recently it has been recommended to determine magnesium by precipitation with *o*-hydroxyquinoline.[10] This precipitant gives a crystalline precipitate, easy to handle, in solutions which are slightly alkaline. Our

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[8] These conclusions are based on the results of twenty-two experiments by Arnold A. Smith. The experiments were carried out in duplicate and consistent values obtained with each duplicate.

[9] Experiments of Howard S. Gardner.

[10] R. Berg, *J. prakt. Chem.*, **115**, 18, 178–185 (1927); Hahn and Vieweg, *Z. anal. Chem.*, 71, 122–130 (1927).

experiments[11] show, however, that the presence of a large excess of ammonium oxalate prevents the complete precipitation of this organic salt of magnesium. All the results were too low when much oxalate was present.

Neubauer,[12] Gooch and Austin,[13] Järvinen,[14] and Smitz have all found that the precipitation of magnesium succeeds in the presence of considerable ammonium salt, but it is evident that they never tried the experiment with as much ammonium oxalate present as recommended by Bobtelsky. In giving beginners a sample of dolomite to analyze for calcium and magnesium, the results obtained are usually good when the directions of Richards or of Blasdale are followed and a single precipitation of calcium oxalate made, or when, according to the directions of Fresenius,[15] a double precipitation of calcium oxalate is made. Occasionally, however, we have noticed that a student fails to get all of the magnesium precipitated as magnesium ammonium phosphate. In the light of these experiments it seems probable that this is the result of using too large an excess of ammonium oxalate. These experiments indicate that 75 cc. of 0.5 N ammonium oxalate solution is sufficient for the precipitation of 0.3 g. of calcium ions in a volume of 500 cc., but the same quantity of reagent should be used when only 0.02 g. of calcium is present in the presence of considerable magnesium (0.12 g.).

Summary

For the precipitation of calcium oxalate in the presence of magnesium ions an excess of ammonium oxalate is necessary. If this excess is properly regulated, it is possible to precipitate pure calcium oxalate. If, however, a very large quantity of ammonium oxalate is present, the precipitation of magnesium ammonium phosphate is incomplete even after long standing.

CAMBRIDGE, MASSACHUSETTS

NOTE

The Rate of Reaction of Liquid and Gaseous Zinc with Carbon Monoxide.[1]—The data of Maier and Ralston[2] on the free energy of zinc oxide and Lewis and Randall's[3] equation for the free energy of carbon monoxide indicate that at all except extremely small partial pressures,

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[11] Performed by Mr. Waite.

[12] Neubauer, *Z. angew. Chem.*, *9*, 435 (1896).

[13] Gooch and Austin, *Am. J. Sci.*, [4] 7, 187 (1899).

[14] Jbrvinen, *Z. anal. Chem.*, *44*, 333 (1905).

[15] Cf. Hillebrand, "Analysis of Silicate and Carbonate Rocks."

[1] Published by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.)

[2] Maier and Ralston, THIS JOURNAL, 38, 364 (1926).

[3] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Rook Co., New York, 1923, p. 576.

zinc vapor and carbon monoxide should react to give zinc oxide and carbon at about 700°, the temperature of the condenser in zinc smelter practice. Viewed otherwise, carbon monoxide should at 700° change to carbon dioxide and carbon almost completely, and the carbon dioxide should oxidize the zinc to zinc oxide. As the formation of carbon dioxide and carbon from carbon monoxide is, in the absence of a catalyst, extremely slow at 700°, it appeared to be of interest to determine whether or not the rate of the direct reduction of carbon monoxide by zinc was appreciable. The appearance of some carbon during experiments of Maier and Ralston at higher temperatures suggested that zinc oxide might catalyze the decomposition of carbon monoxide into carbon and the dioxide.

Pure zinc was made by fractional distillation of electrolytic zinc in *vacuo*. Pure carbon monoxide was made from concentrated sulfuric acid and 60% formic acid, passed over soda lime, and allowed to stand for two days in contact with molten sodium at 130°.

In a system of about 200 cc. in volume, 20 g. of zinc was distilled in two hours through carbon monoxide at 0.5 atm. Vaporization took place in the center of a horizontal silica tube furnace, the gas passed through about 20 cm. of the tube kept at 750° by a separate winding, and condensation took place near the end of the furnace. The distilled zinc contained no free carbon detectable when 1 g. was dissolved in hydrochloric acid, and no zinc oxide could be found on the walls of the tube. The hydrogen evolved was not tested for hydrocarbons. The pressure did not drop.

About 5 g. of zinc was refluxed in a silica tube in 0.5 atm. of carbon monoxide for five days. The volume of the system was about 100 cc. and the temperature was 690°. A total decrease in pressure of 0.006 atm. occurred. Some zinc condensed in the section of the tube at the upper end of the furnace, changing to a finely divided solid in the colder part of the tube and to large crystals in the hotter part.

A silica tube containing 0.1 g. of zinc and 3 pieces of red fire brick about 1 mm. in diameter was evacuated, heated to 680°, and filled with carbon monoxide at 0.4 atm. The volume of the system was about 100 cc. In five days the pressure dropped 0.06 atm. The fire brick became sooty, and a coating of zinc oxide covered the inner wall of the tube. Fire brick freed from iron showed no catalytic effect whatever; negative results were also obtained with aluminum oxide and zinc oxide.

Zinc containing 0.04% of iron was refluxed in carbon monoxide in the same way as the pure zinc, with the same result.

These experiments indicate (1) that the reaction $CO + Zn_{(l \text{ or } g)} = ZnO + C$ is extremely slow at 600 to 700° in the absence of a catalyst, (2) that it is possibly slower than the reaction $2CO = CO_2 + C$ under the same conditions and (3) that zinc reduces carbon dioxide rapidly at the given temperatures.

The production of zinc oxide in the zinc condenser is due, then, to the oxidation of the zinc by carbon dioxide, or water vapor, both of which are present in considerable quantities in the gases issuing from the retort when reduction first starts. Additional carbon dioxide may be produced by the reaction $2CO = CO_2 + C$, which is catalyzed by the clay present in the condenser walls. Pure carbon monoxide is an excellent atmosphere in which to distil zinc, provided the walls of the apparatus are free of iron.

CONTRIBUTION FROM THE
PACIFIC EXPERIMENT STATION
U. S. BUREAU OF MINES
BERKELEY, CALIFORNIA
RUSSELL W. MILLAR[4]

RECEIVED JUNE 30, 1928
PUBLISHED OCTOBER 6, 1928

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF DENVER]

A MODIFICATION OF THE SKRAUP SYNTHESIS OF QUINOLINE

BY BYRON E. COHN AND R. G. GUSTAVSON

RECEIVED FEBRUARY 21, 1927 PUBLISHED OCTOBER 6, 1928

The Skraup synthesis of quinoline occupies a position of interest in organic chemistry because it offers a ready method of synthesis of the quinoline group of compounds.

Several modifications have been proposed since the method was inaugurated in 1880. The most important advance has been the enlargement of the yield. The ferrous sulfate modification is outstanding in this phase of the development.[1] The original Skraup method and all of the modifications to date possess one disadvantage in common. The reaction is usually vigorous and at times violent. Clarke and Davis writing in "Organic Syntheses" say, "In the Skraup synthesis of quinoline the principal difficulty has always been the violence with which the reaction generally takes place; it occasionally proceeds relatively smoothly, but in the majority of cases gets beyond control."[1] The occasional violence of the reaction renders the experiment objectionable as a routine laboratory experiment. The authors have succeeded in eliminating this danger by the addition of acetic acid to the reaction mixture, and have studied the effect of variations in the conditions upon the yield of quinoline obtained.

The safety attained by this modification is attested by the fact that the reaction has been carried out in our Laboratories by large classes of students observing no special precaution and the reaction has never become violent.

During the course of the investigation an unsuccessful attempt was made to render the reaction safe by dilution of the sulfuric acid. The method

[4] Associate chemist.

[1] H. T. Clarke and Anne W. Davis, "Organic Syntheses," John Wiley and Sons, New York, **2, 79** (1922).

used to obtain an equivalent dehydrating power of the sulfuric acid can be applied in many types of reactions and is therefore of interest. The method consists of the assumption that the dehydrating power of sulfuric acid is directly proportional to the heat of dilution. A curve very well adapted for the computation of the equivalent amount of the dilute sulfuric acid necessary may be found in a paper by Zeisberg.[2]

Acetic Acid Modification

The acetic acid modification of the original Skraup method is conducted as follows. The following reagents are weighed out and placed in a liter flask in the order given: aniline, 38 g.; nitrobenzene, 24 g.; glycerol, 100 g.; acetic acid (80%), 60 cc.; sulfuric acid (95%), 54 cc.

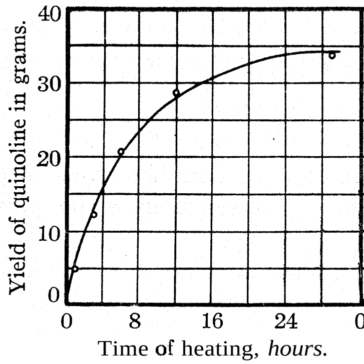
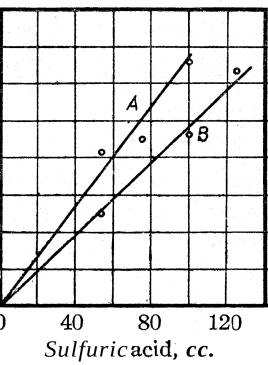


Fig. 1.



A, six *hours; B, three hours.*

Fig. 2.

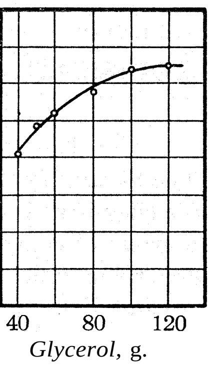


Fig. 3.

The flask is connected with a water reflux condenser and is heated with a Bunsen flame until the boiling point is reached. (In this modification it is not necessary to remove the flame while the reaction is taking place.) The contents of the flask are then kept simmering for a period of sixteen hours. The flame is removed, the contents are diluted with water and steam is passed through the contents of the flask until the distillate is clear, which shows that all of the nitrobenzene has been removed.

The contents of the flask are cooled, made alkaline with a concentrated solution of sodium hydroxide and again distilled with steam. When the distillate is clear, the current of steam is discontinued. The distillate is next dissolved in sulfuric acid, cooled and sodium nitrite solution is added until a drop of the solution causes a starch–potassium iodide spot to turn blue. The material is allowed to stand for about an hour and is then heated to about 100°, being kept at this temperature until thoroughly steamed out. This usually requires about an hour.

The contents of the flask are allowed to cool, are made alkaline with

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[2] Zeisberg, *Chem. Met. Eng.*, 27, 23 (Fig. 4) (1922).

sodium hydroxide and again steam distilled. As in the preceding cases, the steam is passed in until the distillate comes over clear. The distillate is extracted with ether, the ether is evaporated and the resulting quinoline is weighed. Although in the various processes the material is usually further purified by distillation, in our work the results are based on comparisons of the yield at this stage.

Graphs.—The effect of the time of heating upon the yield of quinoline is shown in Fig. 1. The effect of varying the amount of sulfuric acid is shown in Fig. 2. The effect of the quantity of glycerol upon the yield of quinoline is shown in Fig. **3.** The concentration of the acetic acid has no decided effect upon the yield of quinoline.

Theory of Modification

The authors believe and experiments indicate that the violence of the ordinary Skraup reaction is due to the sudden liberation of acrolein resulting from the action of sulfuric acid upon the glycerol. The acetic acid was introduced in an effort to form a glycerol mono or diacetate and thereby remove a large proportion of the glycerol from the reaction sphere. Acetic acid was used because it is quite stable and relatively cheap.

Summary

1. A modification of the Skraup process which may be conducted with safety has been developed.

2. The variation of the yield under different conditions has been studied.

DENVER, COLORADO

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

THE NITRATION OF PIPERONAL

BY JOHN B. EKELEY AND MARGARET S. KLEMME[1]

RECEIVED MAY 1, 1928 PUBLISHED OCTOBER 6, 1928

In a former paper[2] it was reported that commercial o-nitropiperonal yielded two benzylidene derivatives when treated with anthranilic acid in alcohol solution. The one was a yellow crystalline compound melting at 128° and the other yellowish-brown crystals melting at 185'. These two benzylidene products, in turn, reacted with acetic anhydride to form the corresponding nitropiperonylacet-keto-dihydrobenzmetoxazines melting at 206 and 165°, respectively. The conclusion was that Kahlbaum's

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[1] Extract from a thesis by Margaret S. Klemme submitted to the Graduate School of the University of Colorado in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Ekeley, Rogers and Swisher, THIS JOURNAL, 44, 1756 (1922). The *o*-nitropiperonal used was Kahlbaum's product. Material from the same lot was used in these experiments.

o-nitropiperonal contained a small amount of a second isomeric nitropiperonal. Further study of the matter was desirable. To this end the above reactions were repeated and verified. The two benzylidene anthranilic acids melting at **128** and 185°, respectively, were hydrolyzed, the former yielding o-nitropiperonal melting at 98.5° and the latter a compound melting at 143° which showed the reactions of an aldehyde and gave the following analysis: calcd. for $C_8H_5NO_5$: N, **7.18.** Found: N, **7.17.** In addition fractional crystallizations were carried out with a quantity of Kahlbaum's o-nitropiperonal melting as an impure substance at 80°. The fractionations were carried out in ethyl alcohol, with the result that a yellow crystalline product was obtained melting at 143° and another, the major portion, melting at 98.5°. Both were nitropiperonals and yielded the above described benzylidene compounds with anthranilic acid which, in turn, were transformed into the benzmetoxazine derivatives. The one melting at **143°** gave the following analysis: calcd. for $C_8H_5NO_5$: N, 7.18. Found: N, 7.22. The benzmetoxazine derivatives made from it gave the following analysis: calcd. for $C_{15}H_{10}N_2O_6$: N, **8.91.** Found: N, **8.89.**

We are unable to find anything in the literature on the nitration of piperonal since Fittig and Remsen's paper of **1871.** A systematic study of the nitration products of piperonal then seemed advisable and this paper is a report of the results from the nitration of piperonal under twenty-one different experimental conditions. In no case was it possible to isolate from the reaction product a nitropiperonal melting at 143°. We have been unable to obtain from Kahlbaum the method of nitration used in preparing their product, so that we do not know the conditions under which it was formed. Our experiments show that besides o-nitropiperonal, there were formed in varying quantities, according to the nitration method used, nitropiperonylic acid, mononitromethylenecatechol, dinitromethylenecatechol, and under one set of conditions an isomeric mononitromethylenecatechol, hitherto unknown.

Experimental

The nitrations were carried out by adding small portions at a time of powdered piperonal to the nitration mixture at the temperatures indicated in each case. The raw nitration product after removal from the nitration mixture was washed and first treated with potassium hydroxide solution to obtain any acid product. Next it was treated with sodium bisulfite solution to remove aldehydes. The remaining solids were then subjected to distillation with steam. The non-volatile residue was purified, examined qualitatively and identified. In case two products were found, they were separated by fractional crystallization. The yields of the several nitration products were determined by weighing the product. The original filtrate was evaporated to dryness and oxalic acid determined.

I. Fifty g. piperonal, 250 cc. HNO_3 (sp. gr. 1.31) at 23°, stood for two hours when temperature finally rose to 40°. Yields: nitropiperonal, 40 g.; mononitromethylenecatechol,[3] m. p. 144°, 5 g., obtained by Jobst and Hess by nitrating piperonylic acid.

II. Fifty g. piperonal, 250 cc. HNO_3 (sp. gr. 1.31), at 2–4°. Yields: nitropiperonal, 50 g.; mononitromethylenecatechol, 4 g.; oxalic acid, small amount.

III. Fifty g. piperonal, 250 cc. HNO_3 (sp. gr. 1.38), without cooling, temperature rising finally to the boiling point, 91° at Boulder. Yields: nitropiperonal, 35 g.; mononitromethylenecatechol, 5 g.; oxalic acid, 7.7 g.

IV. Fifty g. piperonal, 250 cc. HNO_3 (sp. gr. 1.38), below 45°. Yields: nitropiperonal, 51.7 g.; mononitromethylenecatechol, 10 g.; oxalic acid, 2.6 g.

V. Fifty g. piperonal, 250 cc. HNO_3 (sp. gr. 1.403), at 0–10°. Yields: nitropiperonal, 50 g. Non-aldehyde portion gave mononitromethylenecatechol, 8 g., and a small amount of a compound melting at 100°, and shown by properties and analysis to be dinitromethylenecatechol,[4] obtained by Jobst and Hess by nitrating piperonylic acid.

VI. Fifty g. piperonal, 500 cc. HNO_3 (sp. gr. 1.403), at 0–10°. Yields: nitropiperonal, 49.1 g.; mononitromethylenecatechol, 13.3 g.; a trace of dinitro, a trace of a compound melting at 172° (see IX) and a small amount of oxalic acid.

VII. Fifty g. piperonal, 250 cc. HNO_3 (sp. gr. 1.403), at 0–10° in sunlight. Yields: nitropiperonal, 46.6 g.; mononitromethylenecatechol, 10 g.; a trace of the dinitro; a trace of the compound melting at 172°; oxalic acid 2 g.

VIII. Fifty g. piperonal, 250 cc. HNO_3 (sp. gr. 1.43), below 40°. Yields practically the same as in VII.

IX. Fifty g. piperonal, 250 cc. HNO_3 (sp. gr. 1.43), on ice for a week. Yields: nitropiperonal, trace; nitropiperonylic acid, m. p. 172°, 35 g.; oxalic acid 7.5 g. Nitropiperonylic acid was obtained by Jobst and Hess[5] by the nitration of piperonylic acid.

X. Fifty g. piperonal, 250 cc. fuming HNO_3 at 30–70°. As was to be expected, there was severe oxidation, the yields being nitropiperonal, 25 g.; dinitromethylenecatechol, 4 g.; oxalic acid, 30 g.

XI. Fifty g. piperonal, 250 cc. fuming HNO_3, on ice three days. Yields, nitropiperonal, 16.5 g.; dinitromethylenecatechol, 20 g.; a small amount of the mononitro; oxalic acid, 10 g.

XII. Fifty g. piperonal, 250 cc. fuming HNO_3, at 0°, the piperonal being added very slowly during ten hours. Yields: nitropiperonal, 9 g.; dinitromethylenecatechol, 8 g., oxalic acid, 14 g.; 20 g. of a yellow crystalline compound melting at 70°. This was separated from the dinitromethylenecatechol by fractional crystallization and was shown by its properties and analysis to be an isomer of mononitromethylenecatechol.

Anal. Calcd. for $C_7H_5O_4N$: N, 8.40. Found: N, 8.44.

XIII. Fifty g. piperonal, 250 cc. fuming HNO_3, at -5°. Yields: nitropiperonal, 45 g.; dinitromethylenecatechol 13.3 g.; oxalic acid, 1 g.

XIV. Fifty g. piperonal, 250 cc. HNO_3 (sp. gr. 1.403), 250 cc. H_2SO_4 (sp. gr. 1.82), below 10°. Yields: nitropiperonal, 15 g.; dinitromethylenecatechol, 32.5 g.; a trace of nitropiperonylic acid, a small amount of oxalic acid.

XV. Fifty g. piperonal, 250 cc. HNO_3 (sp. gr. 1.403), 250 cc. H_2SO_4 (sp. gr. 1.82) below 0°. Yields: nitropiperonal, 25 g.; dinitromethylenecatechol, 12 g.; some oxalic acid.

XVI. Fifty g. piperonal, 250 cc. fuming HNO_3, 250 cc. H_2SO_4 (sp. gr. 1.48), at 0". Yields: nitropiperonal, 20 g.; dinitromethylenecatechol, 5.8 g.; oxalic acid, 35 g.

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[3] Fittig and Remsen, *Ann.*, 159, 134 (1871); Jobst and Hess, *Ann.*, 199, 73 (1879); Salway, *J. Chem. Soc.*, 95, 1163 (1909).

[4] Jobst and Hess, *Ann.*, 199, 75 (1879).

[5] Jobst and Hess, *Ann.*, 199, 70 (1879).

XVII. Fifty g. piperonal, 250 cc. fuming HNO_3 into which SO_2 had been led for twelve hours, at 0°.[6] Yields: nitropiperonal, 38.3 g.; dinitromethylenecatechol 20 g.; oxalic acid, 1 g.

XVIII. Fifty g. piperonal, 250 cc. HNO_3 (sp. gr. 1.403), 250 cc. glacial acetic acid[7] at 25°. Yields: nitropiperonal, 40 g.; mononitromethylenecatechol, 10 g.; a trace of the dinitro; oxalic acid, 1 g.

XIX. Fifty g. piperonal, 250 cc. HNO_3 (sp. gr. 1.403), acetic acid, 166 g., acetic anhydride,[8] 166 g. at 25°. Yields: nitropiperonal, 47 g.; mononitromethylenecatechol, 8.3 g.; a trace of the dinitro; some oxalic acid.

XX. Fifty g. piperonal, 250 cc. HNO_3 (sp. gr. 1.403) and $HgNO_3$[9] 11.8 g. at 20°. Yields: nitropiperonal, 50 g.; mononitrocatechol, 13.3 g.; a trace of oxalic acid. No phenolic compounds were formed.

XXI. Fifty g. piperonal, 250 cc. HNO_3 (sp. gr. 1.403), 250 cc. H_2SO_4 (sp. gr. 1.48), $HgNO_3$, 11.8 g., at 0°. Yields: no nitropiperonal; mononitromethylenecatechol, 6.6 g.; dinitro, 26.6 g.; some oxalic acid.

It was noticed that nitropiperonal on exposure to sunlight changes to a brown color. Since the isomeric nitropiperonal isolated from Kahlbaum's product is brownish-yellow, it was thought that it might have been formed from the ordinary form through a light reaction. Ordinary nitropiperonal was, therefore, exposed in thin layers to sunlight and to ultraviolet light, but on recrystallizing the brown product only nitropiperonal, m. p. 98.5°, and a brown tarry residue were obtained.

Summary

1. An isomer of the ordinary nitropiperonal has been isolated and found to melt at 143°. It was found in the commercial Kahlbaum nitropiperonal, m. p. 80°, both by means of derivatives made therefrom and by fractional crystallization of the Kahlbaum product.

2. In an attempt to prepare the isomeric nitropiperonal, piperonal was nitrated under varying conditions of temperature and of nitric acid concentrations with and without sulfuric acid in the presence and absence of catalytic agents and in the presence and absence of sunlight.

3. Besides o-nitropiperonal, mononitro and dinitromethylenecatechol, nitropiperonylic acid and an isomeric mononitromethylenecatechol may be obtained by nitrating piperonal.

4. Increase in temperature in general causes an increase in oxidation products.

5. Beyond a nitric acid of sp. gr. 1.38, increase in acid concentration causes an increase in oxidation products.

6. The presence of nitrosulfonic acid causes a decrease in oxidation and an increase in nitration, the presence of glacial acetic acid causes an

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[6] Varma and Kulkarni, THIS JOURNAL, 47, 143 (1925).

[7] Witt and Utermann, *Ber.*, 39, 3901 (1906); Orton, J. *Chem. Soc.*, 81, 806 (1902).

[8] Orton, *Ber.*, 40, 370 *(1907)*.

[9] Wolffenstein and Boters, *Ber.*, 46, 586 (1913); Davis, Worrall, Drake, Helmkamp and Young, THIS JOURNAL, 43,594 (1931).

increase in the nitration, but the best yield of nitropiperonal was obtained with nitric acid of sp. gr. 1.38 at 45°.

7. No trace of the isomeric nitropiperonal, m. p. 143°, present in Kahlbaum's commercial product, m. p. 80°, was obtained in any of the experiments.

8. That the isomeric nitropiperonal was probably formed as an intermediate product in the experiment using fuming nitric acid at 0° is indicated by the isolation of an isomeric mononitromethylenecatechol from the reaction mixture.

BOULDER, COLORADO

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

EQUILIBRIUM IN THE REACTION $C_2H_6 \rightleftarrows C_2H_4 + H_2$[1]

BY ROBERT N. PEASE[2] AND ELFORD S. DURGAN[3]

RECEIVED MAY 11, 1928 PUBLISHED OCTOBER 6, 1928

Bone and Coward[4] have shown that ethane is rather rapidly decomposed at 675°, and that the primary products of decomposition are ethylene and hydrogen; and it is well known that ethylene and hydrogen combine quantitatively to form ethane in the presence of catalysts from room temperature up to at least 350°.[5] The indications are, therefore, that the reaction $C_2H_6 \rightleftarrows C_2H_4 + H_2$ is reversible somewhere within the temperature region between 350 and 675°, and that equilibrium should be determinable. Indeed, Berthelot[6] has reported that dissociation and formation of ethane both occur at a low red heat. These results have encouraged us to attempt the measurement of equilibrium in this reaction.

Methods and Apparatus

The work of Bone and Coward having proved that prolonged heating of ethane or ethylene gives rise to by-products such as methane, it was necessary to show that the reaction under consideration was the main reaction under the conditions of our experiments. We therefore carried out forward and reverse reactions at each temperature, making a check-up of

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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.

[2] Research Associate, American Petroleum Institute.

[3] Research Assistant, American Petroleum Institute.

[4] Bone and Coward, J. Chem. *Soc.*, 93, **1197 (1908).**

[5] Sabatier and Senderens, ***Ann.*** *chim.* phys., [8] **4, 344** (1905).

[6] Berthelot, **Ann.** *chim.*, [4] 9, 431 **(1886).**

reactants and products, and selecting times for heating such that side reactions constituted only a small fraction of the total. From these measurements the approximate position of equilibrium could be estimated. In order to obtain a more accurate value, mixtures of ethane, ethylene and hydrogen were made up to correspond to the calculated equilibrium, and were heated for the same lengths of time as the gases in the preliminary experiments. These measurements furnished the basis for our final values of the equilibrium constants.

Our method of experimentation was essentially as follows. The desired gas mixture was made up in a buret and delivered to an evacuated silica bulb which was heated electrically. After heating for the desired length of time, the pressure was determined, and a "snap" sample of the gas was transferred by means of a Topler pump to a gas analysis apparatus. From the volume and composition of the gas admitted, the volume of the bulb together with the temperature and pressure, and the analysis of the gas sample, the amount of reaction could be determined.

The silica reaction bulb was connected to a gas buret, a mercury manometer and a Topler pump through suitable stopcocks. The bulb occupied the middle third of a resistance furnace, the ends of which were packed with loose magnesia. The volume of the bulb was **207.5** cc. The temperature of the central portion of the furnace was determined by means of a calibrated two-junction chromel-alumel thermocouple. This central portion contained a sheath of sheet iron to insure uniformity of temperature.

The gas analysis apparatus was of the Bureau of Mines precision type. Ethylene was determined by absorption in dilute bromine water, the bromine subsequently being removed by absorption in a 30% solution of potassium hydroxide to which had been added sodium thiosulfate in order to minimize the evolution of oxygen. Fuming sulfuric acid proved very unsatisfactory because of the simultaneous absorption of ethane. No sharp end-point could be obtained. Oxygen was absorbed in alkaline pyrogallol. Hydrogen was determined by preferential combustion with copper oxide at 350°. The saturated hydrocarbons were determined by preferential combustion with copper oxide at 550° followed by absorption of carbon dioxide in **30%** potassium hydroxide solution.

Hydrogen and ethylene were obtained from tanks of the pure gases. Ethane was prepared in 500cc. lots from ethylene and hydrogen by passage of a 50% mixture of these over a supported nickel catalyst at room temperature. The only purification consisted in freezing out moisture at −79°. The hydrogen contained 1.0% of nitrogen; the ethylene, 1.6% of nitrogen.

Results

Our equilibrium measurements were made at 600, 650 and 700°. Observations were also made at 500 and 550°, but the extreme slowness of the reactions and other factors rendered the measurements unsatisfactory. At 600° and above equilibrium could be approached more rapidly. Methane formation could not be avoided entirely, and at 700° would seem to have reached serious proportions. However, the consistency of our results inclines us to the belief that our final equilibrium values are not far from the truth.

Our final experimental results are presented in Table I. For each experiment we give the composition and pressure of the gas mixture as introduced into the reaction bulb, and the composition and pressure after heating.

TABLE I

EQUILIBRIUM DATA

Heating time, min.	Mixture	Press., atm.	Composition of gas, % C_2H_4	H_2	C_2H_6	CH_4	N_2	$K_{atm} = \frac{[C_2H_4][H_2]}{[C_2H_6]} \times \frac{P}{100}$
				At 600°				
30	Initial	0.6730	...	5.80	92.00	...	2.20	
	Final	.7915	13.55	17.65	65.50	1.55	1.75	(0.0289)
30	Initial	.9770	48.40	50.20	...	...	1.40	
	Final	.6620	17.05	25.95	45.30	10.35	1.30	(0.0647)
30	Initial	.9115	14.35	16.05	67.95	...	1.65	
	Final	.9260	14.55	14.75	62.80	6.15	1.75	0.0316
				At 650°				
6	Initial	0.5555	...	5.80	92.00	...	2.20	
	Final	.7290	20.35	24.40	47.15	6.70	1.35	(0.0768)
8	Initial	1.0040	49.00	49.60	...	...	1.40	
	Final	0.7145	21.40	25.20	35.85	15.25	2.30	(0.1075)
6	Initial	1.0205	19.80	21.70	56.75	...	1.80	
	Final	1.0500	19.20	20.35	50.90	7.90	1.70	0.0806
6	Initial	0.9690	20.85	25.05	52.55	...	1.55	
	Final	.9785	17.30	23.60	47.60	10.65	0.85	0.0839
				At 700°				
5.75	Initial	0.5230	...	6.85	90.70	...	2.45	
	Final	.7345	19.00	26.55	21.15	31.45	1.90	(0.175)
4.5	Initial	1.0500	48.05	50.55	...	...	1.40	
	Final	0.7760	20.95	29.45	15.90	32.35	1.35	(0.301)
5	Initial	0.9975	24.75	30.95	42.40	...	1.90	
	Final	1.0925	15.60	26.10	22.55	34.10	1.65	0.197
5	Initial	0.9640	34.20	35.95	28.10	...	1.70	
	Final	.9735	17.45	26.15	22.65	31.78	1.95	0.196

Three other experiments carried out at 600° with mixtures initially close to equilibrium gave for the equilibrium constant the values 0.0309, 0.0307, 0.0315.

Our data indicate that the equilibrium constants at 600, 650 and 700° are 0.0310, 0.082 and 0.20, respectively. The plot of the corresponding values of log K against I/T gives a straight line. The data are satisfactorily reproduced by the Equation $\Delta F = -RT \ln K = 31{,}244 - 28.88T$.

According to the above equation, the heat of dissociation of one mole of ethane into ethylene and hydrogen at 600–700° is —31,244 cal. From the combustion data of Thomsen and of Berthelot[7] the heat of dissociation of ethane may be calculated to be —31,200 cal. (Thomsen) or —37,100 cal. (Berthelot), the average being —34,200 cal. Although adequate specific heat data are lacking, the indication is that our value at 600–700°

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[7] Thomsen and Berthelot, Landolt-Börnstein, "Tabellen," 1923, p. **1588**.

might be reduced by 1000–3000 cal. at room temperature, making it approximately 28,000–30,000 cal. as compared to the above average of —34,200 cal., which also is for room temperature.

It is difficult to estimate the accuracy of our results. The most serious source of error is indicated by the presence of considerable amounts of methane among the products of some of the experiments. The corresponding side reaction undoubtedly has displaced equilibrium to some extent. However, in view of the facts that approximately the same end-point is reached from either side and that our calculated heat of reaction is not unreasonable, we are inclined to believe that our data are not greatly in error.

Summary

The position of equilibrium in the reaction $C_2H_6 \rightleftarrows C_2H_4 + H_2$ has been measured at 600, 650 and 700°. Equilibrium was approached from both sides. Some uncertainty exists owing to the simultaneous formation of methane, but the indications are that the equilibrium constants at the three temperatures are 0.0310, 0.082 and 0.20, respectively, partial pressures being expressed in atmospheres.

PRINCETON, NEW JERSEY

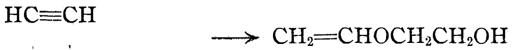
[COMMUNICATION FROM THE DEPARTMENT OF INDUSTRIAL AND CELLULOSE CHEMISTRY, McGILL UNIVERSITY]

THE MECHANISM OF THE ACETAL REACTION. THE EXPLOSIVE REARRANGEMENT OF HYDROXY-ETHYL VINYL ETHER INTO ETHYLIDENE GLYCOL[1]

HAROLD S. HILL[2] AND LLOYD M. PIDGEON

RECEIVED MAY 28, 1928 PUBLISHED OCTOBER 6, 1928

In a previous paper[3] dealing with the formation of cyclic acetals by the action of acetylene on polyhydroxy compounds in the presence of a catalyst, some speculations as to the mechanism of this interesting reaction were brought forward. Taking the reaction between ethylene glycol and acetylene as an example, it was assumed that the first change involves intermolecular addilion of one glycol hydroxyl to the unsaturated acetylene carbons, giving hydroxy-ethyl vinyl ether, (A)



$$\begin{array}{l} HC{\equiv}CH \\ H{-}OCH_2CH_2OH \end{array} \longrightarrow \underset{\textbf{A}}{CH_2{=}CHOCH_2CH_2OH}$$

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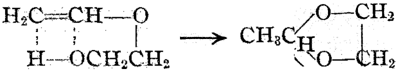
[1] This paper represents one of a series of publications carried out under the joint auspices of the Canadian Pulp and Paper Association, the Pulp and Paper Division of the Forest Products Laboratories of Canada and the Department of Industrial and Cellulose Chemistry, McGill University. The authors wish to express their appreciation of the facilities placed at their disposal by the three cooperating agencies.

[2] Research Fellow, Canadian Pulp and Paper Association.

[3] Hill and Hibbert, THIS JOURNAL, 45, 3128 (1923).

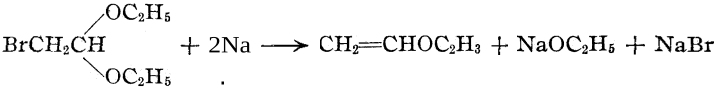
which, undergoing the same general reaction *intra* molecularly, rearranges at once to form ethylidene glycol.



B

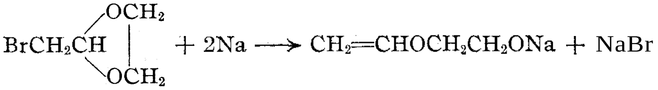
The present communication deals with the synthesis of the intermediate vinyl derivative (A) and shows that its rearrangement into the acetal (B) takes place in a most striking manner.

For the synthesis of hydroxy-ethyl vinyl ether recourse was had to a scheme proposed in an earlier paper.[4] Since Wislicenus[5] had obtained vinyl ethyl ether by the action of metallic sodium on bromo-ethylal, according to the equation



$$\mathrm{BrCH_2CH}\begin{matrix}\diagup\mathrm{OC_2H_5}\\ \\ \diagdown\mathrm{OC_2H_5}\end{matrix} + 2\mathrm{Na} \longrightarrow \mathrm{CH_2{=}CHOC_2H_3} + \mathrm{NaOC_2H_5} + \mathrm{NaBr}.$$

it was considered probable that a similar reaction with bromo-ethylidene glycol would yield the sodium salt of the desired intermediate (A)



$$\mathrm{BrCH_2CH}\begin{matrix}\diagup\mathrm{OCH_2}\\ \vert\\ \diagdown\mathrm{OCH_2}\end{matrix} + 2\mathrm{Na} \longrightarrow \mathrm{CH_2{=}CHOCH_2CH_2ONa} + \mathrm{NaBr}$$

and this is now found to be the case. When metallic sodium is added to a dry ether solution of bromo-ethylidene glycol, a smooth but vigorous reaction takes place accompanied by the gradual accumulation of sodium bromide and the sodium salt of hydroxy-ethyl vinyl ether. The latter compound is obtained by hydrolyzing the sodium salt with water and extraction as described in the experimental part.

Hydroxy-ethyl vinyl ether is a colorless oil, soluble in water, ether and benzene but insoluble in ligroin. It adds bromine readily at the double bond, and the presence of a free hydroxyl group is shown by the evolution of hydrogen on reaction with sodium and by the formation of a monobenzoate.

Rearrangement of Hydroxy-ethyl Vinyl Ether into Ethylidene **Glycol.**—When this vinyl derivative, freshly prepared as above, is brought in contact with a trace of 50% sulfuric acid, an explosive reaction takes place and the unsaturated ether rearranges quantitatively into cyclic ethylidene glycol. The violence and velocity of this transformation are remarkable. Using small amounts, however, and by strong cooling, it may be modified somewhat, although even under these conditions cyclization is complete within a very short time. Any strong acid suffices to effect this rapid change and less dissociated acids cause the same reaction but at a slower rate. In fact, heating hydroxy-ethyl vinyl ether

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[4] Hibbert and Hill, THIS JOURNAL, 45, 740 (1923).

[5] Wislicenus, *Ann.*, **192**, 112 (1878).

alone in the air is sufficient to bring about gradual rearrangement as well as other changes. It is impossible, therefore, to redistil the vinyl derivative after it has been exposed to the air for any length of time. The reason for this may possibly be the formation of traces of acetic acid by slight hydrolysis and oxidation. Distillation is best carried out in the presence of a small amount of carbonate, or traces of sodium hydroxide. The product is quite stable in the presence of alkalies, although long boiling with dilute alkalies causes hydrolysis. The same change takes place with great ease in dilute acids, the products being acetaldehyde and ethylene glycol.

A trace of dry hydrogen bromide added to the vinyl derivative produces the same instantaneous rearrangement that was caused by concentrated sulfuric acid, which, together with the fact that in no case could the presence of free acetaldehyde be detected during or after the change, would seem to preclude the possibility that this transformation involves preliminary hydrolysis to vinyl alcohol, its rearrangement to acetaldehyde and the recombination of the latter product with ethylene glycol to give the cyclic acetal (B).

In this connection, it should be noted that the benzoate of hydroxyethyl vinyl ether, $CH_2{=}CHOCH_2CH_2{-}OCO{-}C_6H_5$, shows no tendency to rearrange or to react in any way in the presence of small amounts of acid, thus indicating a specific role of the hydroxyl group in this interesting transformation.

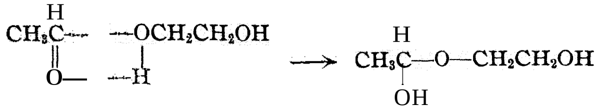
The quantitative nature of the rearrangement is proved not only in a recovery of over 90% of pure ethylidene glycol, but also by the fact that immediately after the reaction there is no trace of remaining unsaturation against bromine in carbon tetrachloride solution.

The identity of the ethylidene glycol formed was established beyond question by its boiling point, refractive index, solubilities, and its quantitative hydrolysis into acetaldehyde and ethylene glycol. It compared in every way with the product obtained from the interaction of acetaldehyde (as paraldehyde) or of acetylene with ethylene glycol.

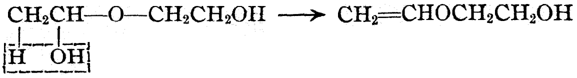
Theoretical Discussion

There would seem to be considerable theoretical significance attached to the above transformation, especially in view of the marked ease with which it takes place. Involving as it does the addition of a hydroxyl group to a *vinyl* double bond, it leads to the suggestion that intermediate unsaturation of this sort may precede many of the reactions of hydroxy compounds. Besides being the mechanism through which ethylene glycol reacts with acetylene, it may also serve as an explanation of acetal formation in general.

Thus, for example, the reaction of ethylene glycol with acetaldehyde may be represented as taking place in three stages: (1) addition of one glycol hydroxyl to the unsaturated C=O group to form a half acetal.[6]

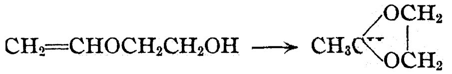


(2) dehydration



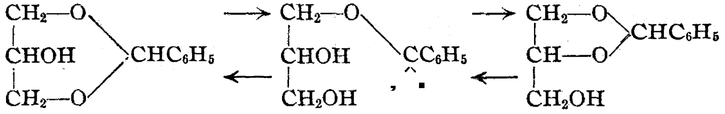
$$CH_2CH{-}O{-}CH_2CH_2OH \longrightarrow CH_2{=}CHOCH_2CH_2OH$$

(3) rearrangement of the vinyl derivative as shown in this paper

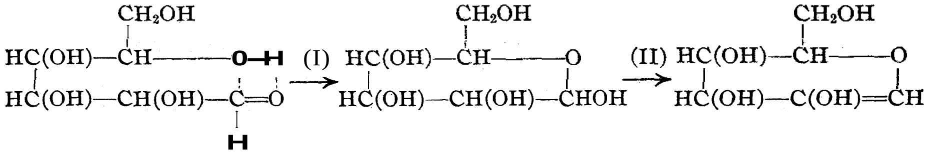


With monohydric alcohols instead of ethylene glycol, the scheme would be the same except that in the last stage the reaction would be intermolecular rather than intra molecular. Substituting formaldehyde or benzaldehyde for acetaldehyde, the dehydration in stage (2) would be from the same carbon. Such an unsaturated carbon compound has never been isolated, but there is much evidence that they occur as intermediates.

For example, it has recently been found[7] that a trace of dry hydrogen chloride causes the interconversion of 1,3-benzylidene glycerol to its 1,2-isomer and *vice versa,* a reaction probably taking place through an unsaturated intermediate



It is of special interest to apply this mechanism to reactions of the sugar and polysaccharide groups, in which the cyclic half acetal configuration is of such common occurrence. Thus, in glucoside formation, starting with the more unstable aldehydic form of glucose, the three identical stages of the acetal reaction above may occur.



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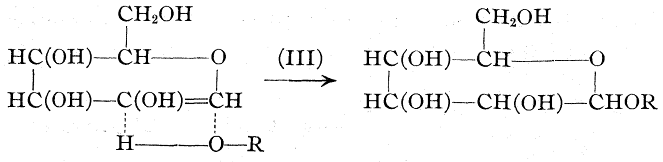
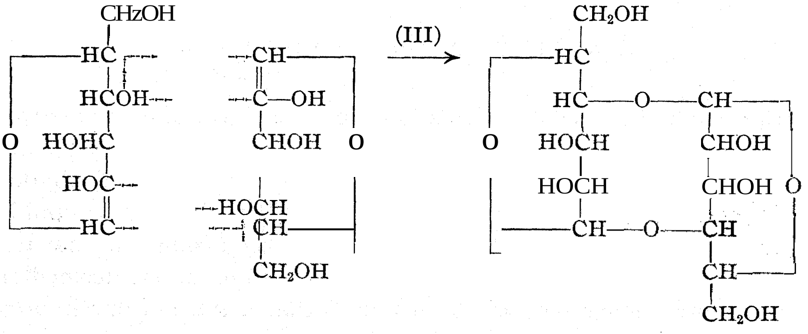
[6] Since this work was completed, Adkins and Broderick, THIS JOURNAL, 50, 499 (1928), have brought forward evidence indicating that the formation of a half acetal, as in Equation 1 is, in fact, the first stage in the acetal reaction. From changes in refractive index it is shown that this initial addition takes place on merely bringing together a pure alcohol and an aldehyde.

[7] Hill, Whelen and Hibbert, THIS JOURNAL, 50, 2238 (1928).



If (R) is another sugar residue, a polysaccharide results, and sugar metabolism in general may well proceed along these lines.

Assuming, for example, cellulose to be based on a unit of a biose anhydride, the latter might be formed from the -ene-1,2-glucose derivative (C) as follows



In like manner it is possible to interpret many other transformations of sugar derivatives.[8]

The fact that such an unsaturated sugar (C) does not appear in the course of these reactions is no more surprising than that the corresponding vinyl derivative is not apparent in the preparation of acetals from acetylene.

Dehydration between adjacent carbons, however, is a very commonly occurring reaction in many classes of hydroxy and polyhydroxy compounds. This fact, coupled with the experimental evidence brought forward above, leads to the conclusion that among these unsaturated vinyl

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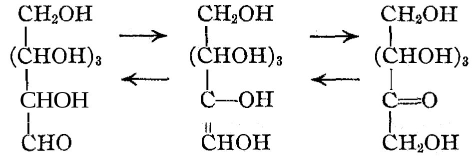
[8] Somewhat different unsaturated intermediates have been proposed as a basis for the explanation of certain transformations of sugar derivatives in alkaline solution. Thus Wohl, *Ber.*, 33, 3095 (1900), postulated a scheme in which the glucose-mannose fructose interconversion takes place through an intermediate "enediol" form



Recent investigations of Evans and his co-workers have yielded much experimental evidence in favor of this mechanism, THIS JOURNAL, 47, 3085, 3098, 3102 (1925); 48, 2665, 2678, 2703 (1926); 50, 486 (1928); see also Wolfrom and Lewis, *ibid.*, 50, 837 (1928).

derivatives there may prove to be the key to the mechanism of many of the reactions of this group, including such important changes as occur in natural metabolism of sugars and polysaccharides.

Experimental Part

Preparation of **Bromo-ethylidene** Ethylene **Glycol.**[9]—One hundred and twenty-five g. of paraldehyde was brominated at –12" as described[4,10] with 315 g. of bromine. After stirring the brominated mixture at –10° for ten hours, a slight excess of bromine was removed by bubbling in sulfur dioxide with stirring. One hundred and thirty-five g. of ethylene glycol was added during two hours through a dropping funnel, keeping the temperature below –10°. The cooling bath was then removed and efficient stirring continued for six hours at room temperature. The mixture was extracted with ether, neutralized with sodium carbonate, washed successively with small amounts of concentrated sodium bisulfite solution, 10% sodium hydroxide, water and dried over solid potassium carbonate After removal of the ether, fractionation under reduced pressure yielded 260 g. of bromo-ethylidene glycol, b. p. 68–71" (15 mm.). The yield is 80% of the theoretical calculated on the basis that all of the bromine was available as bromo-acetaldehyde.

The product obtained by this method shows a tendency to darken on standing. It may then be purified by shaking with 10% sodium hydroxide solution, followed by redistillation.

Bromo-ethylidene glycol may also be prepared by the interaction of ethylene glycol with crystalline dibromoparaldehyde[10] in the presence of 40% sulfuric acid as a catalyst.

One hundred and forty g. of ethylene glycol with 2 cc. of 40% sulfuric acid was added to 185 g. of dibromoparaldehyde (m. p. 57°) in a three-necked flask equipped with a stirrer, mercury seal and reflux condenser. The mixture was heated on the steam-bath with stirring for ten hours, after which it was worked up as in the above experiment. Fractionation gave some low boiling ethylidene glycol, followed by bromo-ethylidene glycol; b. p. 65–66" (12 mm); yield, 77 g. or 40%. The yield is poor but the product is very pure and shows no darkening on standing.

Action of Metallic Sodium on Bromo-ethylidene Glycol. Preparation **of Hydroxy-ethyl** Vinyl Ether.—Seventy-five g. of bromo-ethylidene glycol dissolved in three volumes of anhydrous ether was placed in a 500cc. flask equipped with a motor stirrer, mercury seal and reflux condenser protected against atmospheric moisture and carbon dioxide. Twenty g. of clean metallic sodium was added in small pieces as rapidly as convenient. A brisk reaction took place, causing the ether to boil, but after a time this subsided and gentle heat was applied. Heating and stirring were continued for seven hours. It is well to have vigorous and efficient stirring in order to expose fresh surfaces of the sodium. The ether contained a heavy suspension of the sodium salt of hydroxy-ethyl vinyl ether, together with sodium bromide and some unchanged sodium. The latter was removed by flushing through a wire gauze with ether. The ether sludge so obtained was treated with an amount of water just sufficient to dissolve the solids, the first of this being added cautiously on the chance that bits of sodium might be present. The water layer was separated and extracted several times with ether. The ether extract was washed once with a minimum amount of water and dried over potassium carbonate. After removal of the ether, employing a column, the product was distilled under reduced pressure. Apparently the only product of the reaction was hydroxy

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[9] This product was isolated earlier (ref. 4) but by the above modifications the yield has been doubled.

[10] Stepanow, Ber., 48, 1718 (1925).

ethyl vinyl ether, b. p. 44–45' (10 mm.); 140° (760 mm.); yield 22 g., or 56.4% of the theoretical.

Anal, Subs., 0.2105: CO_2, 0.4176; H_2O, 0.1729. Calcd. for $C_4H_8O_2$: C, 54.54; H, 9.09. Found: C, 54.15, H, 9.00.

The product is a slightly viscous, colorless oil having a faint ethereal odor and n_D^{17} = 1.4564. It is soluble in water, alcohol, ether and benzene but insoluble in ligroin. It is strongly unsaturated against bromine in carbon tetrachloride, and against potassium permanganate, and also shows the reactions characteristic of the hydroxyl group. This vinyl derivative is stable when distilled from a slightly alkaline solution but is very sensitive to acids, dilute acids causing hydrolysis and traces of concentrated acids bringing about intramolecular rearrangement.

Benzoate of Hydroxy-ethyl Vinyl Ether.—Ten grams of the vinyl derivative (freshly prepared) was benzoylated in the usual manner with 10 cc. of benzoyl chloride and 20 cc. of dry pyridine. Pouring the reaction product into water, extracting with ether, washing the ether solution with cold dilute sodium hydroxide followed by water, drying over potassium carbonate and fractionating gave the benzoate of hydroxy-ethyl vinyl ether, b. p. 133° (9 mm.)

Anal. Subs., 0.2219: CO_2, 0.5406; H_2O, 0.1108. Calcd. for $C_{11}H_{12}O_3$: C, 68.75; H, 6.25. Found: C, 68.75; H, 6.56.

The product is a viscous oil, reacting as an unsaturated derivative, but in contrast to the free alcohol above shows no activity in contact with a trace of concentrated acid.

Intramolecular Rearrangement of Hydroxy-ethyl Vinyl Ether into Ethylidene Glycol.—As already described, this reaction takes place under the agency of a trace of concentrated acid. If the vinyl derivative is freshly prepared and pure, the rearrangement is so violent that it can be carried out safely only in test-tube quantities. The following modification was found practicable for the conversion of larger amounts of the unsaturated ether.

Two cc. of hydroxy-ethyl vinyl ether was placed in a flask large enough to hold the final volume of the product to be converted. A fraction of a drop of 40% sulfuric acid was added with cooling. After the rapid reaction had taken place, fresh vinyl derivative was slowly added and, since it was converted progressively, the danger of too violent a reaction was obviated. Cooling was necessary to prevent loss of ethylidene glycol.

The product so formed had all the physical and chemical properties of ethylidene glycol, b. p. 81–82' (760 mm.); n_D^{17} = 1.4035, as compared with n_D^{17} = 1.4565 for the vinyl derivative before rearrangement; n_D^{17} of ethylidene glycol prepared from acetylene and glycol, 1.4034.

Anal. Subs., 0.1404: CO_2, 0.3391; H_2O, 0.1404. Calcd. for $C_4H_8O_2$: C, 54.54; H, 9.09. Found: C, 54.09; H, 9.12.

In a quantitative experiment 4.3 g. of hydroxy-ethyl vinyl ether yielded 3.5 g. of ethylidene glycol, b. p. 81–83° (760 mm.), approximating a 90% recovery.

To confirm further the identity of the ethylidene glycol obtained above, it was quantitatively hydrolyzed to acetaldehyde and glycol; 2.552 g. of the product together with 2 g. of 5% phosphoric acid was placed in a test-tube attached to a small reflux condenser maintained at 40–50°. Gases from the condenser were led through a strongly cooled trap. Boiling the mixture in the tube for one hour yielded 1.535 g. of acetaldehyde in the trap, which corresponds to a recovery of 94% of the theoretical amount to be obtained by the hydrolysis of ethylidene glycol.

Acknowledgment is made of the receipt by one of us (L. M. P.) of a grant from the National Research Council of Canada, during the tenure of which this work was performed.

Summary

1. The synthesis of hydroxy-ethyl vinyl ether is described.

2. It is shown that this vinyl derivative in contact with a trace of concentrated acid undergoes instantaneous rearrangement into ethylidene glycol.

3. The latter change is offered as strong support for a mechanism proposed for the acetal reaction postulating a "vinyl" derivative as an intermediate product.

4. This mechanism is elaborated so as to include similar reactions such as those occurring in glucoside and polysaccharide formation.

MONTREAL, CANADA

[COMMUNICATION FROM THE DEPARTMENT OF INDUSTRIAL AND CELLULOSE CHEMISTRY, McGILL UNIVERSITY]

VINYL DERIVATIVES: THEIR RELATIONSHIP TO SUGARS AND POLYSACCHARIDES[1]

BY HAROLD S. HILL[2]

RECEIVED MAY 28, 1928 PUBLISHED OCTOBER 6, 1928

In a preceding[3] paper dealing with the mechanism of acetal formations, the synthesis of hydroxy-ethyl vinyl ether and its rearrangement into ethylidene glycol are described. The extreme ease and the instantaneous character of the latter change led to the suggestion that unsaturated derivatives of the vinyl type may be the intermediates through which many other reactions of hydroxy compounds take place. From the application of this idea to the transformation of the sugars and polysaccharides, it was concluded that an unsaturated sugar[4] such as (IV) which may be considered as a vinyl derivative occupies a position of importance in a logical scheme picturing the mechanism of such reactions as occur in glucoside and polysaccharide formation.

The present paper describes the synthesis of additional vinyl derivatives, their transformations, and shows that the relationship indicated above is in fact a close one.

It seemed desirable first of all to show that the rearrangement of hydroxy-ethyl vinyl ether into ethylidene glycol

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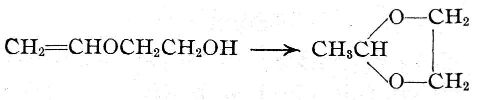
[1] This paper represents one of a series of publications carried out under the joint auspices of the Canadian Pulp and Paper Association, the Pulp and Paper Division of the Forest Products Laboratories of Canada and the Department of Industrial and Cellulose Chemistry, McGill University. The author wishes to express his appreciation of the facilities placed at his disposal by the three coöperating agencies.

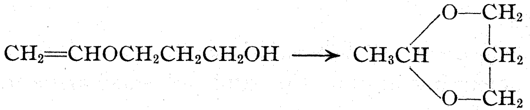
[2] Research Fellow, Canadian Pulp and Paper Association.

[3] Hill and Pidgeon, THIS JOURNAL, 50, 2718 (1928).

[4] This unsaturated sugar is somewhat similar to Fischer's glucal, Ber., 47, 196 (1914) and also to the enolic form of glucose postulated by Wohl, Ber., 33, 3095 (1900), as an intermediate in the glucose-mannose-fructose interconversion.

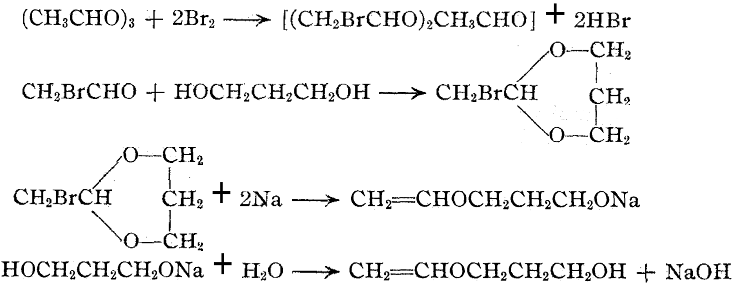


represents a general tendency toward cyclization in derivatives of this type. For this purpose the synthesis of hydroxypropyl vinyl ether (I) was undertaken, since this compound on rearrangement should give as readily the six membered cyclic acetal (II)



I II

Hydroxypropyl vinyl ether (I) was synthesized, starting with paracetaldehyde. This was brominated at a low temperature and the product condensed in *situ* with trimethylene glycol, giving in good yield bromoethylidene trimethylene glycol. The action of sodium on this halogen acetal gave (I) in 85% yield through its sodium salt, the changes being represented as follows



$$(CH_3CHO)_3 + 2Br_2 \longrightarrow [(CH_2BrCHO)_2CH_3CHO] + 2HBr$$

$$CH_2{=}CHOCH_2CH_2CH_2ONa + H_2O \longrightarrow CH_2{=}CHOCH_2CH_2CH_2OH + NaOH$$

Hydroxypropyl vinyl ether resembles closely its lower homolog previously described.[3] It undergoes the same violent, quantitative rearrangement into (II) when brought into contact with a trace of 50% sulfuric acid or dry hydrogen chloride.

It is probable, therefore, that such instantaneous cyclizations represent a general type reaction and may be looked for in all hydroxy-alkyl vinyl ethers where the hydroxyl group is in the β- or γ-position.[5]

The next step was to show that a vinyl derivative will undergo reactions analogous to that of glucoside formation. For this purpose it was necessary to block off the free hydroxyl group of (I) by methylation, giving the methyl ether (III), the latter being conveniently prepared in good yield

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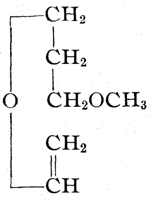
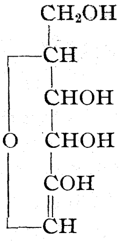
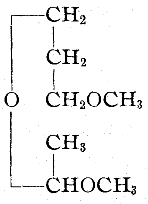
[5] This is presumably an example of the still more general tendency toward cyclization exhibited by many classes of compounds having a hydroxyl in the 3- or 4-position to an unsaturated group, as evidenced by the formation of lactones, cyclic acid anhydration, oxidic forms of sugars and cyclic oxides. The first three involve the addition of a hydroxyl to a C=O, while in the last it is to a C=C group formed by an initial dehydration.

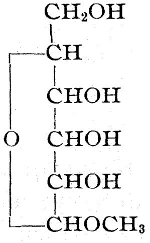
by the action of sodium on bromo-ethylidene trimethylene glycol, as indicated above, and the subsequent in *situ* reaction of the sodium salt of (I) with methyl iodide.

Comparison of this new ether with the postulated anhydro glucose (TV) shows the following relationships


III


IV


V

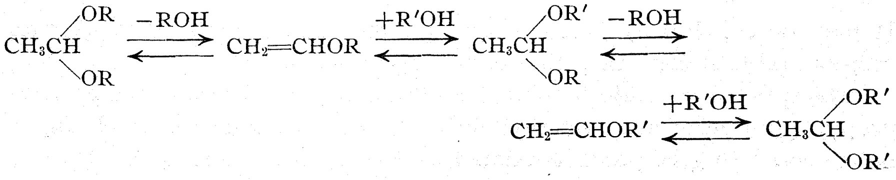

VI

If (IV) is the intermediate in the formation of a-methyl glucoside (VI), then (III) under the same conditions should give the corresponding mixed acetal or "vinylide" (V).

It was found that (III) on being mixed with an equimolecular amount of methyl alcohol and brought in contact with a trace of dry hydrogen chloride, undergoes an instantaneous reaction, the saturation in the molecule disappearing completely. Examination of the products disclosed that an interesting secondary reaction had taken place, for not only was the "vinylide" (V) found, but also a considerable amount of dimethyl acetal, $CH_3CH(OCH_3)_2$. Using an excess of methyl alcohol in the experiment, the latter acetal was formed almost exclusively.

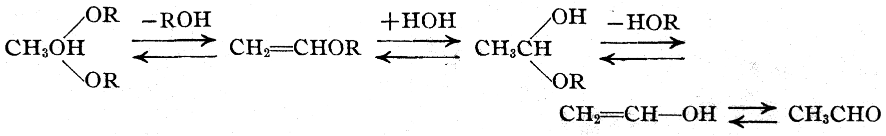
It is considered that these results strongly support the general theory of vinyl derivatives as intermediates, for they indicate the labile character of the alcohol residue in acetals and point toward the existence of an equilibrium, however slight, between the saturated acetal on the one hand and a vinyl derivative on the other.

If other alcohols are present, there may be secondary additions to the vinyl derivative and the equilibrium is continually displaced until the most stable system is attained. It appears that, in general, the lower alcohols tend to displace those higher in a series. This phenomenon is similar to that of *alcoholysis* and the analogous well-known displacements in the acetal series. Presumably the mechanism is in all cases the same, passing as indicated through the intermediate vinyl stage.



$$CH_3CH\begin{smallmatrix}OR\\OR\end{smallmatrix} \xrightleftharpoons{-ROH} CH_2{=}CHOR \xrightleftharpoons{+R'OH} CH_3CH\begin{smallmatrix}OR'\\OR\end{smallmatrix} \xrightleftharpoons{-ROH} CH_2{=}CHOR' \xrightleftharpoons{+R'OH} CH_3CH\begin{smallmatrix}OR'\\OR'\end{smallmatrix}$$

Hydrolysis, then, may be an identical reaction. Water instead of a lower alcohol adds onto the intermediate vinyl ether, shifting the equilibrium continually to the right. Analogous secondary equilibria are then established between the half acetal thus formed and vinyl alcohol and acetaldehyde.



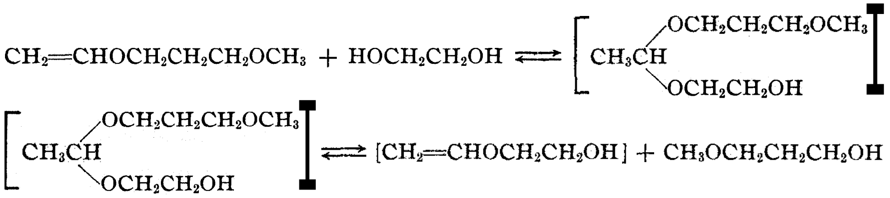
$$CH_3OH\begin{matrix}OR\\OR\end{matrix} \underset{}{\overset{-ROH}{\rightleftharpoons}} CH_2{=}CHOR \overset{+HOH}{\rightleftharpoons} CH_3CH\begin{matrix}OH\\OR\end{matrix} \overset{-HOR}{\rightleftharpoons}$$

$$CH_2{=}CH{-}OH \rightleftharpoons CH_3CHO$$

Hydrolysis of a glucoside or polysaccharide map proceed along the same lines, namely, through the intermediate unsaturated sugar of the type (IV) which, by adding on water, displaces the partial equilibrium and yields a saturated sugar in its cyclic oxide form. The latter may be considered as a cyclic half acetal. That the reaction rests at this stage and does not proceed far toward the free carbonyl derivative, as in the case with acetals, is due to the general tendency for cyclization to take place in preference to intermolecular addition. This is well brought out in the following experiments.

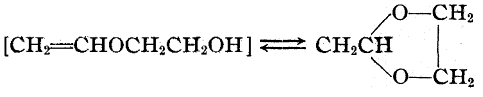
When equimolecular amounts of hydroxypropyl vinyl ether (I) and methyl alcohol are brought in contact with a trace of acid, the main product is ethylidene trimethylene glycol (II) rather than dimethyl acetal or the "vinylide" (V). Here, as in the case of sugars, cyclization is favored.

The reaction of ethylene glycol with methoxypropyl vinyl ether (III) lends further evidence. The products are ethylidene glycol, and monomethyl trimethylene glycol, presumably formed through an intermediate vinyl derivative as follows



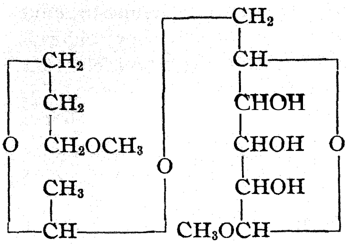
$$CH_2{=}CHOCH_2CH_2CH_2OCH_3 + HOCH_2CH_2OH \rightleftharpoons \left[CH_3CH\begin{matrix}OCH_2CH_2CH_2OCH_3\\OCH_2CH_2OH\end{matrix}\right]$$

$$\left[CH_3CH\begin{matrix}OCH_2CH_2CH_2OCH_3\\OCH_2CH_2OH\end{matrix}\right] \rightleftharpoons [CH_2{=}CHOCH_2CH_2OH] + CH_3OCH_2CH_2CH_2OH$$

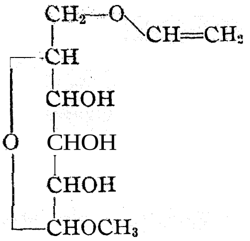


It may be concluded, therefore, that the resulting cyclic form represents a more stable system than that of the mixed acetal.

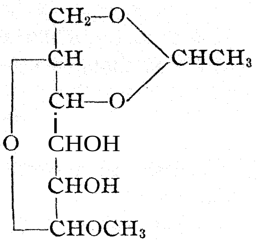
Attempts were made to obtain addition reactions between methoxypropyl vinyl ether and a-methyl glucoside, and also glucose, which might be expected to give products related to disaccharides, such as (VII).



VII



VIII



IX

A great difficulty lay in the mutual insolubility of the vinyl derivative and the sugar. Using a-methyl glucoside, however, a partial reaction took place, the final product being again not the mixed acetal (VII) but rather ethylidene a-methyl glucoside (IX).

As in the preceding scheme, the first stage is logically the formation of (VII), followed by the establishment of an equilibrium with (VIII) and the final rearrangement of this vinyl intermediate into the cyclic acetal (IX). Here also the cylic structure is indicated as being the most stable system.

The extremely rapid and quantitative character of the above reactions (whether they be inter- or intramolecular) of the vinyl derivatives may be taken as evidence that the latter are true intermediates. It also explains their lack of appearance under the conditions occurring in such changes as acetal, glucoside and polysaccharide formation.

Experimental Part

Preparation **of Bromo-ethylidene** Trimethylene Glycol.—One hundred and thirty-two g. of paracetaldehyde was brominated at −12° as previously described with 320 *g.* of bromine. After stirring the brominated mixture at −10° for eight hours, 240 g. of trimethylene glycol was slowly added, keeping the temperature below −10°. Then the temperature was allowed to rise to 0° and the mixture stirred overnight, and later for four hours at 20°. Extraction with ether was facilitated by the addition of ice water. The ether solution was neutralized with potassium carbonate, washed with 20% sodium hydroxide, water and dried over potassium carbonate. Two fractionations yielded 200 g. (55% reckoned on the bromine used) of bromo-ethylidene trimethylene glycol; b. p. 74–75° (10 mm.).

Preparation **of Hydroxy-propyl** Vinyl Ether.—Fifty-four g. of bromo-ethylidene trimethylene glycol was dissolved in 150 cc. of absolute ether in a three-necked flask equipped with *a* reflux condenser and an efficient mechanical stirrer protected from the atmosphere. Fourteen g. of freshly cut sodium was added, cooling the flask enough to keep the reaction from becoming too violent. After stirring overnight, the sludge of accumulated salts was washed with ether through a wire gauze to filter out a small amount of unchanged sodium. Enough water was added to dissolve the salts, the mixture was extracted three times with ether, and the latter solution dried over potassium carbonate. Fractionation yielded 25 g. (85% of the theoretical) of hydroxypropyl vinyl ether; b. p. 64–65' (10 mm.).

Anal. Subs., 0.2003: CO_2, 0.4305; H_2O, 0.1736. Calcd. for $C_5H_{10}O_2$: C, 58.82; H, 9.80. Found: C, 58.61; H, 9.63.

Hydroxypropyl vinyl ether is a colorless oil, strongly unsaturated against bromine in carbon tetrachloride solution, and yielding a monobenzoate with benzoyl chloride in dry pyridine solution. When treated with a few bubbles of dry hydrogen chloride, a violent reaction took place, the unsaturation completely disappearing. Neutralizing with potassium carbonate and distilling gave an almost quantitative yield of ethylidene trimethylene glycol; b, p. 108–110°.

The same transformation catalyzed with 50% sulfuric acid took place with explosive violence.

Reaction of Hydroxypropyl Ether with Methyl Alcohol.—Five and one-tenth g. hydroxypropyl vinyl ether and 1.6 g. of methyl alcohol were treated with a few bubbles of dry hydrogen chloride. After the sharp reaction was over, the products were neutralized with potassium carbonate, filtered and distilled, using a small bead column; 3.5 g. of ethylidene trimethylene glycol was obtained (b. p. 105–110°) as the main product. Using three times the amount of methyl alcohol, the main product was dimethyl acetal (b. p. 63–65°).

Preparation of Methoxypropyl Vinyl Ether.—Ninety g. of bromo-ethylidene trimethylene glycol in 250 cc. of absolute ether was treated with 23 g. of sodium as described above. After stirring overnight, most of the ether was distilled from the reaction flask (care being taken to exclude atmospheric moisture), 80 g. of methyl iodide was added and the mixture refluxed with stirring for sixteen hours. Enough water to dissolve the salts was added cautiously, the mixture extracted twice with ether and the latter solution washed with water and dried over potassium carbonate. Fractionation yielded 40 g. (69%) of methoxypropyl vinyl ether; b. p. 68–78° (152 mm.). Refractionation gave 32 g. of a pure product; b. p. 75–76° (137 mm.).

Anal. Subs., 0.1821: CO_2, 0.4140; H_2O, 0.1687. Calcd. for $C_6H_{12}O_2$: C, 62.07; H, 10.35. Found: C, 62.01; H, 10.28.

Reaction of Methoxypropyl Vinyl Ether with Methyl Alcohol.—Five and five-tenths g. of methoxypropyl vinyl ether was mixed with 1.5 g. of methyl alcohol, cooled and treated with a trace of 40% sulfuric acid. A vigorous reaction took place which was complete in a few seconds. The products were neutralized with potassium carbonate, washed with concd. calcium chloride to remove traces of CH_3OH and $CH_3OCH_2CH_2$, CH_2OH and dried over calcium chloride. Fractionation yielded 1 g. of dimethyl acetal (b. p. 63-65"), 2 g. of intermediate mixture and 3 g. of the mixed acetal $CH_3CH(OCH_3)$-$OCH_2CH_2CH_2OCH_3$ (b. p. 153–155°).

Anal. Subs., 0.2000: CO_2, 0.4142; H_2O, 0.1945. Calcd. for $C_7H_{16}O_3$: C, 56.76; H, 10.81. Found: C, 56.49; H, 10.81.

Reaction of Methoxypropyl Vinyl Ether with Ethylene Glycol. Five and eight-tenths g. of methoxypropyl vinyl ether was mixed with 3.1 g. of ethylene glycol and treated with a few bubbles of dry hydrogen chloride. On shaking a vigorous reaction took place, the unsaturation against bromine in carbon tetrachloride disappearing immediately. The product was neutralized with potassium carbonate and fractionated. The two main products were ethylidene glycol (b. p. 80–83°) and monomethyl trimethylene glycol, b. p. 86–92' (15 mm.). The latter product was further identified by its benzoate prepared in dry pyridine solution.

Anal. (benzoate). Subs., 0.2100: CO_2, 0.5264; H_2O, 0.1269. Calcd. for $C_{11}H_{14}O_3$: C, 68.04; H, 7.22. Found: C, 68.40; H, 6.80.

Reaction of Methoxypropyl Vinyl Ether with a-Methyl Glucoside.—Four g. of methoxypropyl vinyl ether was incorporated with 7.5 g. of finely powdered α-methyl glucoside and the mixture treated with a few bubbles of dry hydrogen chloride. Considerable heat was evolved although much of the glucoside did not go into solution.

After allowing to stand for four hours with occasional shaking, the paste was extracted with ether and the latter solution neutralized with solid potassium carbonate, filtered and evaporated in a vacuum. The residue was a small quantity of colorless sirup which crystallized after remaining in a vacuum for several weeks. After crystals were once obtained the sirups were readily crystallized by "seeding." Recrystallization from a mixture of ether and ligroin gave pure ethylidene α-methyl glucose, m. p. 77°.

Summary

1. The synthesis of hydroxypropyl vinyl ether and its methylated derivative is described.

2. The former compound, in contact with a trace of concentrated acid, is shown to rearrange quantitatively into the cyclic acetal, ethylidene trimethylene glycol.

3. Further evidence is brought forward regarding the mechanism of acetal, glucoside and polysaccharide formation, as well as the mechanism of the hydrolysis of this class of compounds.

4. This evidence supports the hypothesis of vinyl derivatives being the intermediates through which transformations of this nature take place.

MONTREAL, CANADA

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

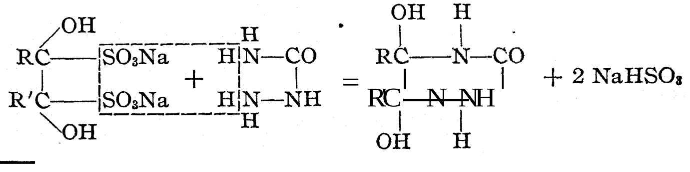
DIHYDROXY- AND DICHLORO-KETO-HEXAHYDROTRIAZINES

BY JOHN B. EKELEY AND ADRIAN A. O'KELLY

RECEIVED JUNE 6, 1928 PUBLISHED OCTOBER 6, 1928

Glyoxal and semicarbazide hydrochloride yield a mono-[1] and a disemicarbazone.[2] Similarly the aliphatic 1,2-diketones yield disemicarbazones,[3] but not the mono-derivative. Aromatic diketones also yield semicarbazones in alkaline solution,[4] but in acid solution the monosemicarbazones condense to triazine derivatives.[3]

If, on the other hand, semicarbazide hydrochloride and the sodium bisulfite addition products of glyoxal, methyl glyoxal or of aliphatic 1, 2-diketones are brought together in molecular proportions in hot water solution, there is a quantitative precipitation of a dihydroxy-keto-hexahydro-α-triazine, the compound being formed by a reaction accompanied by the splitting off of two moles of sodium bisulfite.



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[1] O. Diels, *Ber.*, **35**, 347 (1902).

[2] Harries and Temme, *Ber.*, **40**, 171 (1907).

[3] Posner, *Ber*, **34**, 3977 (1901).

[4] Thiele and Stange, *Ann.*, **283**, 6, 27 (1894); Biltz and Arnd, *Ber.*, 35, 346 (1902).

The triazine derivatives thus obtained are insoluble in organic solvents except hot glacial acetic acid, in which they are slightly soluble and from which in very dilute solutions they may be obtained as minute colorless needles. They do not melt, but begin to decompose at definite temperatures. They are decomposed on boiling with strong acids, but in the cold yield salts. They are stable against hot alkalies. The two hydroxyl groups are replaced by chlorine on treatment with phosphorus trichloride, except in the case of the higher members which are decomposed by this reagent.

Experimental

I. Sodium Bisulfite Addition Products of Aliphatic **1,2-Diketones.**—We find no statement in the literature concerning these. When 1 mole of aliphatic 1,2-diketone is treated with 2 moles of sodium bisulfite in water solution, the diketone goes into solution and the yellow color disappears. By evaporating the solution, the crystalline addition product is obtained. The diketones were prepared from the corresponding monoketones by hydrolysis of the oximes prepared by means of nitrous acid.

TABLE I

SODIUM BISULFITE ADDITION PRODUCTS

Ketone	Decompn. temp., °C.	S, calcd., %	S, found, %
Diacetyl	145–155	21.77	21.21
Propionylacetyl	135–150	20.77	20.62
Butyrylacetyl	130–140	19.87	19.97
Valerylacetyl	100–110	19.04	19.27
Caproylacetyl	95–100	18.82	18.56

2. **Dihydroxy-keto-hexahydro-α-triazines** from Semicarbazide Hydrochloride and Sodium Bisulfite Addition Products of **1,2-Diketones.**—The decomposition temperatures, formulas and analytical data of the triazines prepared are given in Table II.

TABLE II

DIHYDROXY-KETO-HEXAHYDRO-α-TRIAZINE AND HOMOLOGS

Derivative	Decompn. temp., °C.	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
....	265–270	$C_3H_7N_3O_3$	27.06	26.84	5.26	5.43	31.57	31.56
				27.27		5.50		
Methyl	250–255	$C_4H_9N_3O_3$	32.65	32.34	6.21	6.20	28.57	28.40
Dimethyl	240–245	$C_5H_{11}N_3O_3$	37.26	37.04	6.83	6.75	26.08	26.00
Methylethyl	230–235	$C_6H_{13}N_3O_3$	41.14	41.27	7.42	7.38	24.00	24.12
Methylpropyl	240–245	$C_7H_{15}N_3O_3$	44.44	44.49	7.93	7.66	22.22	22.05
				44.60				21.90
Methylbutyl	230–235	$C_8H_{17}N_3O_3$	47.29	47.10	8.37	8.10	20.69	20.51
				47.01		8.37		20.52
Methylamyl	100–105	$C_9H_{19}N_3O_3$	49.77	49.37	8.75	8.97	19.35	19.50
				49.68		9.04		19.60

3. Dichloro-keto-hexahydro-a-triazines from Phosphorus Trichloride and the Compounds in 2.—The decomposition temperatures, formulas and analytical data of these triazines are summarized in Table III.

TABLE III

DICHLORO-KETO-HEXAHYDRO-α-TRIAZINE AND HOMOLOGS

Derivative	Decompn. temp., °C.	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen. % Calcd.	Nitrogen. % Found	Chlorine, % Calcd.	Chlorine, % Found
...	265–270	$C_3H_5N_3OCl_2$	21.18	21.20	2.94	3.21	24.71	25.00	41.15	41.00
Methyl	260–270	$C_4H_7N_3OCl_2$	26.08	26.00	3.80	3.80	22.82	22.83	38.58	38.56
Dimethyl	250–260	$C_5H_9N_3OCl_2$	30.31	30.30	4.54	4.54	21.20	21.32	35.85	35.75
Methylethyl	240–245	$C_6H_{11}N_3OCl_2$	33.50	33.41 33.20	5.19	5.30 5.10	19.81	19.60 19.62	33.65	33.50 33.46
Methylpropyl	230–235	$C_7H_{13}N_3OCl_2$	37.18	37.10	5.75	5.80	18.59	18.40	31.39	31.46

Experiments carried out with isobutyrylacetyl did not yield the expected dihydroxytriazine derivative. A soluble compound was formed whose constitution we have not yet determined.

Summary

1. Semicarbazide hydrochloride reacts with the sodium bisulfite addition products of glyoxal, methylglyoxal and 1,2-aliphatic diketones with the formation of dihydroxy-keto-hexahydro-a-triazines, compounds insoluble in the usual organic solvents except acetic acid, in which they are slightly soluble. They do not melt, but begin to decompose at definite temperatures; soluble in acids; stable against alkalies.

2. The above compounds yield with phosphorus trichloride dichloro-keto-hexahydrotriazines which resemble the original substances in their properties.

3. The sodium bisulfite addition products of a number of 1,2-diketones have been prepared.

BOULDER, COLORADO

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF KANSAS]

THE REDUCTION OF AROMATIC NITRO COMPOUNDS WITH SODIUM ALCOHOLATES

BY C. M. SUTER[1] AND F. B. DAINS

RECEIVED JUNE 18, 1928 PUBLISHED OCTOBER 6, 1928

Nearly 100 years ago (1834) Mitscherlich[2] used a solution of potassium hydroxide in ethyl alcohol as a reducing agent and obtained with nitrobenzene, azoxybenzene and the potassium salt of an organic acid. Since that time investigations in this field have been confined mainly to the action of various aromatic nitro compounds upon solutions of sodium in

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[1] From a dissertation presented by C. M. Suter to the Faculty of the Graduate School of the University of Kansas in partial fulfilment of the requirement for the degree of Doctor of Philosophy.

[2] Mitscherlich, *Ann.*, 12, 311 (1834).

methyl or ethyl alcohol or sodium or potassium hydroxide dissolved in water or the same alcohols.[3] In general azoxybenzene or its derivatives were isolated, together with acids such as carbonic, oxalic, etc., and occasionally the formation of primary amines was noted, while with halogen nitrobenzenes some of the halogen might be displaced, yielding phenols or phenol ethers.

As a result of some observations on the action of sodium butylate on bromonitrobenzene, it was decided to investigate especially the reduction of nitro aromatic compounds with the higher sodium alcoholates in other than alcohol solutions. Benzene was chosen as solvent because it would diminish the ionizing effect of the excess of alcohol and would without question speed up the reaction, as was shown by Brühl[4] in his study of activated sodium methylate in xylene, where he obtained a quantitative yield of azoxybenzene.

Experimental

The general procedure was as follows. Sodium (0.1 mole) was added to the alcohol (2 4 moles) dissolved in benzene (100–450 cc.). The mixture was then refluxed for several hours until the metal had been changed to the alcoholate. To the cooled solution was added the nitro compound (0.05 mole) dissolved in a little benzene if a solid, in small portions so that the reducing agent was always in excess. The reaction usually began in the cold but for completion the mixture was heated on a water-bath for two hours. It was then distilled with steam, which removed the benzene solvent **A,** and other readily volatile substances such as excess alcohol and traces of aldehyde and ketones.

The water distillate, B, was found to contain the amine, unchanged nitro product and benzaldehyde when benzyl alcohol was used. The residue, C, in the flask consisted of non-volatile products and sodium salts.

The different portions were worked up as follows. The benzene solution, **A,** was extracted with water to remove traces of aldehyde or ketone that might be formed and then with dilute sulfuric acid, which dissolved any amine present. The water distillate, B, was acidified with sulfuric acid and separated from any unchanged nitro product. The acid solutions were then made up to a definite volume and the total amine determined by titration with a bromate–bromide solution, using the method of Francis and Hill.[5] It was found that the small amounts of alcohol present in the solution had but little effect on the accuracy of the titration in the cold but did not interfere if the solutions were warm.

The non-volatile reduction products in the flask, C, (mainly azoxybenzenes) which separated from the water solution as solids or oils, were isolated, washed with water, dried and weighed and their identities determined. The water solution in C contained the sodium salts of aliphatic or amino acids, occasionally small amounts of phenolic compounds and sodium halides from halogen nitrobenzenes. In some cases the volatile acids were determined qualitatively in the distillate after acidifying with sulfuric or

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[3] Otto and Voigt, *J. prakt. Chem.*, [1] **36,** 98 (1887); (b) Claus, *Ber.*, 5, 364 (1872); (c) Schmidt and Schultz, *Ann.*, 207, 328 (1881); (d) Leuckart, *Ber.*, 15, 81 (1882); (e) 16, 81 (1883); (f) Meisenheimer, *Ann.*, 355, 255 (1907); (g) Lachman, THIS JOURNAL, 24, 1178 (1902); (h) Smith with Lyons, *ibid.*, 48, 3165 (1926).

[4] Brühl, Ber., 37, 2066 (1904).

[5] Francis and Hill, THIS JOURNAL, 46, 2498 (1924).

phosphoric acid. No effort was made to ascertain the nature of the phenolic compounds and in only a few cases was the amount of halogen removed from the ring determined.

The following tables give a résumé of the results obtained followed by a discussion of the special points. In general halogen nitro compounds

Table I

Table of Results

No.	Na, moles	Alcohol	C_6H_6, cc.	Nitro comp., moles	Amine, %	Azoxy, %	Other products
I	0.3	CH_3	450	0.15 *p*-$C_6H_4CH_3NO_2$	1.3	..	Conds. prods.
II	.1	CH_3	150	.05 *p*-$C_6H_4ClNO_2$	3.5	4.6	HCOOH
III	.1	C_2H_5	C_6H_6	*p*-$C_6H_4CH_3NO_2$	..	..	(Less resins than with CH_3)
IV	.1	C_2H_5	C_6H_6	*p*-$C_6H_4ClNO_2$	Trace	..	
V	.2	*iso*-C_3H_7, 200 cc.	...	.125 $C_6H_5NO_2$	...	Little	...
VI	.1	*iso*-C_3H_7	150	.05 *p*-$C_6H_4ClNO_2$	29	33	(Trace acetone, HCOOH, resins)
VII	.1	*n*-C_4H_9	150	.05 $C_6H_5NO_2$	28.8	Little	
VIII	.1	*n*-C_4H_9	150	.05 *p*-$C_6H_4ClNO_2$	19.6	49.5	...
IX	.1	*n*-C_4H_9	150	.05 *p*-$C_6H_4ClNO_2$	29	40	...
X	.1	*n*-C_4H_9	150	.05 *p*-$C_6H_4ClNO_2$	23	48.5	HCOOH
XI	.1	*n*-C_4H_9	150	.05 *p*-$C_6H_4ClNO_2$	33 8	Pres.	HCOOH
XII	.1	*n*-C_4H_9	150	.05 *p*-$C_6H_4ClNO_2$	27.7	55	HCOOH
XIII	.1	*n*-C_4H_9	150	.05 *p*-$C_6H_4ClNO_2$	32.2	54	...
XIV	.1	*n*-C_4H_9	150	.05 *p*-$C_6H_4ClNO_2$	28.2	42.7	...
XV	.1 NaOH	*n*-C_4H_9, 100 cc.	...	.05 *p*-$C_6H_4ClNO_2$	10	56	...
XVI	.1	*n*-C_4H_9	150	.05 *m*-$C_6H_4ClNO_2$	25	56	...
XVII	.1	*n*-C_4H_9	150	.05 *p*-$C_6H_4BrNO_2$	30 8	48.5	...
XVIII	.1	*n*-C_4H_9	200	.05 *p*-$C_6H_4INO_2$	27.4	43	...
XIX	.1	*iso*-C_4H_9	150	.05 *p*-$C_6H_4ClNO_2$	32.6	37	...
XX	.1	*iso*-C_4H_9	250	.05 *p*-$C_6H_4ClNO_2$	42.5	45	...
XXI	.1	*sec.*-C_4H_9	150	.05 *p*-$C_6H_4ClNO_2$	32.6	14.8	...
XXII	.1	*sec.*-C_4H_9	100	.05 *p*-$C_6H_4BrNO_2$	Pres.	Pres.	HAc, ketone test
XXIII	.1	*iso*-C_5H_{11}	C_6H_6	.05 *p*-$C_6H_4ClNO_2$	25	67 azo, mainly	HCOOH
XXIV	.1	$C_6H_5CH_2$	100	.05 $C_6H_5NO_2$	..	Pres.	C_6H_5COOH
XXV	.1	$C_6H_5CH_2$	100	.05 *m*-$C_6H_4(NO_2)_2$	..	Pres.	C_6H_5COOH
XXVI	.1	$C_6H_5CH_2$	150	.05 *p*-$C_6H_4CH_3NO_2$	..	Little	C_6H_5COOH, C_6H_5CHO
XXVII	.1	$C_6H_5CH_2$	150	.05 2-$C_{10}H_7NO_2$	..	Tar	C_6H_5COOH, C_6H_5CHO
XXVIII	.1	$C_6H_5CH_2$	150	.05 *p*-$C_6H_4ClNO_2$	..	100	C_6H_5COOH
XXIX	.1	$C_6H_5CH_2$	250	.05 *p*-$C_6H_4ClNO_2$	..	100	C_6H_5COOH, 73%; C_6H_5CHO
XXX	.1	$C_6H_5CH_2$	300	.05 *p*-$C_6H_4ClNO_2$	..	95	C_6H_5COOH
XXXI	.1	$C_6H_5CH_2$	100	.05 *m*-$C_6H_4ClNO_2$	..	Pres.	C_6H_5COOH
XXXII	.1	$C_6H_5CH_2$	100	.05 *m*-$C_6H_4ClNO_2$	..	Pres.	C_6H_5COOH
XXXIII	.1	furfural	300	.05 *p*-$C_6H_4ClNO_2$	..	91	...
XXXIV	.1	*n*-C_3H_7	300	.05 *o*-$C_6H_4OCH_3NO_2$	Found	Tar	...

were used as oxidizing agents, both for ease in the separation of the reduction products and to compare the effect of halogen in the ortho, meta and para positions.

Discussion

The results point out distinctive differences between the action of methyl and ethyl alcohols and those from propyl on, while series VI–XXIII brings out clearly the special activity of the higher aliphatic alcohols in that nearly 40% of the reduction products appear as amines and not as azoxy derivatives. In XV, where butyl alcohol alone was used as solvent, the decreased amount of amine (15%) illustrated the definite effect of the benzene solvent. The amines are evidently formed directly and not through intermediate azoxybenzenes, since sodium butylate had no reducing effect on *p*,*p*′-dichloro-azoxybenzene under the same conditions. The reductions with benzyl alcohol (XXIV–XXXII) are noteworthy in that there is practically no amine formation but instead high yields of azoxybenzene and of benzoic acid or the intermediate benzaldehyde, which has been isolated for the first time. This absence of amine may be due to the stability of the benzoic acid, which remains unchanged while the aliphatic acids are oxidized further to acids with less carbon content and even to formic acid and are hence more effective reducing agents. Aliphatic aldehydes and ketones, the first oxidation products, speedily disappear. Only in VII was a trace of acetone and in XXII evidence of a ketone obtained and acetic acid absolutely proved.

o-Halogen Nitrobenzenes with Sodium Alcoholates

These reactions are grouped by themselves in Table II since they offer some interesting differences as compared with the *p*- and m-halogen isomers. While the experimental results have shown the usual formation of amines,[6] it has been found that the azoxybenzenes were replaced almost entirely by a-amino acids, o-halogen $C_6H_4NHCH(R)COOH$, when *n*-propyl or alcohols of the type RCH_2-CH_2OH were used.

Synthesis of Phenylamino Acids

α-*o*-Chloro-anilinopropionic Acid, $ClC_6H_4NHCH(CH_3)COOH$ (XXXVII–XLI).—Sodium (6.9 g.) was dissolved in benzene (250 cc.) and n-propyl alcohol (80 cc.). To this solution was added o-chloronitrobenzene (16 g.) and the mixture refluxed for two hours.

The reaction product contained 40% of o-chloro-aniline but no dichloro-azoxybenzene. From the alkaline solution was isolated on acidifying 12.5 g. of an acid melting at 150° after crystallizing from hot water, in which it is soluble to the extent of 0.44 g. per 100 cc. at the boiling point; at 30°, 0.094 g. per 100 cc.

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[6] Paal and Otten, *Ber.*, 23, 2587 (1890); Miller and Plochl, *Ber.*. 25, 2020 (1892); Bischoff and Hausdorfer, *Ber.*, 25, 2270, 2298 (1892); Bischoff and Mintz, *Ber.*, **25,** 2314, 2326 (1892); Dzierzgowski, *Ber.*, 27, 1983 (1894); Bischoff, *Ber.*, 30, 2303, 2464, 2760, 3169 (1897).

Anal. Calcd. for $C_9H_{10}ClNO_2$: N, **7.06; Cl, 17.73;** mol. wt., **199.5.** Pound: **N, 6.67, 6.86; Cl, 17.6; mol. wt., 230** in acetic acid.

Its identity was further proved by comparison with the acid synthesized as follows. A mixture of o-chloro-aniline **(30** cc.), 2-bromopropionicacid (18 cc.) and water **(60** cc.) was heated over a small flame for thirty minutes until the solution became homogeneous. It was then made alkaline, distilled with steam to remove excess aniline and the amino acid was precipitated with dilute sulfuric acid. It crystallized from hot water in white needles, m. p. 150°.

Anal. Calcd. for $C_9H_{10}ClNO_2$: N, **7.00.** Found: **6.99, 6.97.**

The acid was soluble in alkalies, sodium carbonate, dilute mineral acids and the usual organic solvents, though not in benzene near its freezing point. A drop of copper sulfate added to a water solution of the acid gave a green coloration characteristic of this class of compounds When heated above 165°, it lost carbon dioxide with the formation of monoethyl-o-chlorophenylamine, which was identified by conversion into its phenylurea, m. p. 144°.

N-Ethyl-o-chloro-aniline, *o*-$C_2H_5NHC_6H_4Cl$.—This was prepared from o-chloro-aniline and diethyl sulfate. The oil boiled at 219° (corr.) at **726** mm ; sp. g., 25°/4°, **1.104;** 35°/4°, **1.0911.** The hydrochloride melted at 138–139°.

Anal. Calcd. for $C_8H_{10}ClN$: N, **9.03.** Found: 8.9, 9.1.

a-Ethyl-a-o-chlorophenyl-6-phenylurea made from the amine and phenyl isocyanate crystallized from alcohol in white needles which melted at **144".**

Anal. Calcd. for $C_{15}H_{15}ClN_2O$: N, **10.20.** Found: **10.21, 10.37.**

α-o-Chloro-anilinobutyric Acid, $ClC_6H_4NHC(C_2H_5)COOH$ (XLIV–XLV).—Sodium-n-butylate and o-chloronitrobenzene gave the amine and the amino acid, which was very soluble in organic solvents but less so in water than the lower homolog. It was best purified by crystallization from gasoline; the white rosets melted at 95°.

Anal. Calcd. for $C_{10}H_{12}ClNO_2$: N, **6.55.** Found: **6.30, 6.20.**

Its identity was confirmed by comparison with the same acid prepared from o-chloro-aniline and 2-bromobutyric acid.

Discussion

The results tabulated show that only alcohols with the grouping CH_2-CH_2OH (XXXVI–XLVI, XLIX, I,) thus far have yielded the amino acids. With ethyl alcohol (XXXVI) where it might be expected, the acetic aldehyde has resinified too quickly to condense with the nitrosobenzene. Isobutyl (XLVIII) and cinnamyl (LIII) alcohols with a single hydrogen attached to the second carbon gave none, while benzyl alcohol (LI–LII) showed the same behavior with all three isomers.

TABLE IIA

RESULTS OF EXPERIMENTS

No.	Other amino acids	M. p , °C., from		Nitrogen Calcd., %	Found, %
XLIX	a-o-Chloro-anilino-isovaleric	75,	dil. HAc	6.18	5.99 5.98
XLII	a-o-Bromo-anilinopropionic	162–164,	hot water	5.73	5.67 5.51
XLIV	a-o-Bromo-anilinobutyric	83,	gasoline	5.42	5.21
XLI	α-2,5-Dichloro-anilinopropionic	163,	hot water	5.96	5.77 5.81
L	**a-o-Chloro-anilinophenylacetic**	160,	yellow crystals, alcohol	6.37	6.10 5.27

TABLE IIB

REACTIONS OF 0-HALOGEN SUBSTITUTED NITROBENZENES

No.	Na, moles	Alcohol	C_6H_6, cc.	Nitrobenzene deriv., moles	Amine, %	Azoxy, %	Amino acid, RNHCHRCOOH, %
XXXV	0.3	CH_3	450	0.15 o-Chloro	2.1	81	18.6 Cl from ring
XXXVI	.3	C_2H_5	450	.15 o-Chloro	17.5	Tar	...
XXXVII	.3	*n*-C_3H_7	300	.1 *o*-Chloro	40	..	α-$ClC_6H_4NHCH(CH_3)$-COOH, 60
XXXVIII	.3	*n*-C_3H_7	300	.15 *o*-Chloro	35	..	Same, 47
XXXIX	.1	*n*-C_3H_7	300	.1 o-Chloro	35	..	Same, 50
XL	.1	*n*-C_3H_7	300	.05 *o*-Chloro	43	..	Same, 26
XLI	.1	*n*-C_3H_7	250	.05 2,5-Dichloro	19.4	..	$Cl_2C_6H_3NHCH(CH_3)COOH$, 60
XLII	.3	*n*-C_3H_7	300	.15 o-Bromo	23.8	..	α-*o*-$BrC_6H_4NHCH(CH_3)$-COOH, 41
XLIII	.1	*n*-C_3H_7	250	.05 *o*-Iodo	23.7	Tar	157°, too little for anal.
XLIV	.3	*n*-C_4H_9	300	.15 o-Chloro	24.7	..	α-*o*-$ClC_6H_4NHCH(C_2H_5)$ COOH
XLV	.3	*n*-C_4H_9	450	.15 *o*-Chloro	16.8	..	Same
XLVI	.3	*n*-C_4H_9	300	.15 o-Bromo	14.5	Present	α-*o*-$BrC_6H_4NHCH(C_2H_5)$-COOH, 68 8
XLVII	.1	*iso*-C_4H_9	300	.15 *o*-Chloro	41.5	37	...
XLVIII	.3	*iso*-C_4H_9	300	.15 o-Chloro	42	Impure	...
XLIX	.1	*iso*-C_5H_{11}	300	.05 o-Chloro	24	Little	α-*o*-ClC_6H_4NHCH (*iso*-C_3H_7) COOH
L	.1	$C_6H_5C_2H_4$	250	.05 *o*-Chloro	32	...	α-*o*-$ClC_6H_4NHCH(C_6H_5C_2H_4)$ COOH, 27
LI	.1	$C_6H_5CH_2$	250	.05 *o*-Chloro	..	Present	C_6H_5COOH, 98
LII	.1	$C_6H_5CH_2$	250	.05 *o*-Chloro	Trace	Present	C_6H_5CHO, C_6H_5COOH
LIII	.1	$C_6H_5CH{=}CH$	300	.05 *o*-Chloro	..	Impure	$C_6H_5CH{=}CHCOOH$

While there is no experimental evidence for the real cause of the special reactivity of the *o*-halogen derivatives, it may be associated with the increased negative nature of the nitroso nitrogen due to the neighboring halogen atom and the increased ability of the nitroso nitrogen group to add an aldehyde complex and then rearrange as follows

$$o\text{-}XC_6H_4NO_2 + RCH_2CH_2OH = o\text{-}XC_6H_4NO + RCH_2CHO + NaOH = RCH_2CHOH\,(ONa)$$

$$o\text{-}XC_6H_4NO + RCH_2CHOH(ONa) = o\text{-}XC_6H_4N(OH)CRHCHOH(ONa) \;\; \text{(rearrange)}\; o\text{-}XC_6H_4NHCH(R)COONa + H_2O$$

Where X is chlorine or bromine, the amino acid formation goes smoothly; with the less negative iodine (XLII), the yield is much diminished, while an o-methoxy group (XXXIV) gave only the amine and tar.

Summary

1. A study has been made of the action of sodium alcoholates on (mainly halogen) nitro aromatic compounds in benzene solution.
2. With the exception of *o*-halogen nitro derivatives, propyl, butyl and *iso*-amyl alcohols gave a yield of from 50–90% reduction products, consisting of amine and azoxybenzenes.
3. o-Halogen nitrobenzenes condensed with the methylene grouping of the alcohols RCH_2CH_2OH with the formation of amino acids, o-halogen $C_6H_4NHCH(R)COOH$.

4. Benzyl alcohol reduced the nitro compound to azoxybenzene and was fully oxidized to benzaldehyde and benzoic acid.

5. The aliphatic alcohols were oxidized to acids of less carbon content, among them formic.

LAWRENCE, KANSAS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE STATE UNIVERSITY OF IOWA]

NITROGEN TRICHLORIDE AND UNSATURATED HYDROCARBONS. II

BY GEORGE H. COLEMAN, G. M. MULLINS AND ELIZABETH PICKERING

RECEIVED JUNE 20, 1928 PUBLISHED OCTOBER 6, 1928

The reaction of nitrogen trichloride with the unsaturated hydrocarbons,[1] 1-butene, 2-butene and trimethylethylene has been reported in a previous communication, as has also its reaction with the unsaturated ketones,[2] benzalacetophenone and benzalacetone.

The reaction has now been studied with ethene, propene, methylpropene, 2-pentene and cyclohexene. There is a wide difference in the reaction rates of these hydrocarbons. Ethene reacts most slowly and methylpropene most rapidly. The degree of difference is indicated by the fact that at 20–25° two weeks or longer is required for the completion of the reaction with ethene, while with methylpropene the reaction, even at -45 to $-50°$ is complete within two to three hours. The reaction rates of the other hydrocarbons fall between these two extremes.

The products of the reaction with ethene are nitrogen, ammonium chloride, ethylene chloride and 2-chloro-1-dichloro-amino-ethane. This compound was not isolated but was converted by hydrochloric acid to 1-amino-2-chloro-ethane. On further reduction with sodium amalgam ethylamine was obtained.

With propene, which reacts more rapidly than ethene but more slowly than the others, the products are similar to those obtained with ethene. Of the two possible addition products, $CH_3CHNCl_2CH_2Cl$ and $CH_3CHClCH_2NCl_2$, only the first was definitely shown to be formed. Attempts to prove the presence of the other isomer were not successful.

With methylpropene, although the products were much the same, the reaction differed in some respects from the others. In nearly all of the reactions thus far studied of nitrogen trichloride with unsaturated hydrocarbons, all or at least the greater part of the stable addition product remains in solution in the carbon tetrachloride as the dichloro-amino compound and is obtained as the hydrochloride of the corresponding amine by treatment with hydrochloric acid. In this case, however, most of the

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[1] Coleman and Howells, THIS JOURNAL, 45, 3084 (1923).

[2] (a) Coleman and Craig, *ibid.*, 49, 2593 (1927); (b) 50, 1816 (1928).

amine was precipitated as the hydrochloride along with the ammonium chloride during the reaction. A similar precipitation of the amine hydrochloride occurs with benzalacetone.[2b] This may be due to a greater reactivity toward hydrochloric acid of the dichloro-amino group in these compounds. Again only one addition product $(CH_3)_2CNCl_2CH_2Cl$ was found. The formation of a moderate yield of the amine in this reaction, although the dichloro-amino group is attached to a tertiary carbon atom, may be due to the very low temperature at which the reaction was carried out. Experience with similar compounds in reactions at higher temperatures has indicated that little or none of the amine is usually formed. In general the lower the temperature at which the reaction is carried out the better the yield of the amine.

The reactions with 2-pentene and cyclohexene are quite similar to those already described. Stable addition products are obtained in each case.

Experimental Part

The unsaturated hydrocarbons used were prepared by well-known methods. Ethene was obtained from ethyl alcohol and sulfuric acid. Propene was prepared from isopropyl iodide and alcoholic potassium hydroxide. Ethene and propene were collected and measured over water. Methylpropene was prepared by adding isobutyl iodide slowly to warm alcoholic potassium hydroxide. The gas was passed through a 30cm. water-jacketed fractionating column and subsequently through a concentrated solution of calcium chloride. The amount obtained was determined by titration with bromine in carbon tetrachloride solution. 2-Pentene was prepared from diethyl carbinol and sulfuric acid by the method of Norris and Joubert.[3] Cyclohexene was prepared from cyclohexanol by the method given in "Organic Syntheses."[4] The hydrocarbons were all dried with fused calcium chloride and dissolved in cold carbon tetrachloride.

Nitrogen trichloride was prepared and analyzed as described in earlier

The method of carrying out the reaction was essentially the same as that previously used.[5] The highest yields of addition products were obtained when at least two moles of the hydrocarbon for each mole of nitrogen trichloride were used. With methylpropene, when the reaction was carried out at a low temperature, a little chloroform was added in order to keep the reaction mixture liquid. In every case except with methylpropene the dichloro-amino chloro compound was changed to a chloro-amine by dry hydrogen chloride. With methylpropene, as already mentioned, the chloro-amine hydrochloride was obtained during the initial

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[3] Norris and Joubert, THIS JOURNAL, 49, 886 (1927); "Organic Syntheses," 7, 76 (1927).

[4] Coleman and Johnstone, "Organic Syntheses," 5, 33 (1925).

[5] Ref. 1, p. 3086.

addition reaction. A small amount of chloro-amine hydrochloride was obtained in each instance by final treatment with aqueous hydrochloric acid. Benzoyl derivatives of the chloro-amines were prepared, and usually the Schotten-Baumann method was used. However, in the case of the chloro-amine from methylpropene, the hydrochloride was suspended in benzene, a little concentrated potassium hydroxide solution added and the mixture shaken until all the hydrochloride had reacted. The benzene solution of the amine was separated and dried with solid potassium hydroxide. To this after filtering was added a little less than the calculated amount of benzoyl chloride and the mixture was allowed to stand for one or two hours. It was then filtered and the benzene was evaporated nearly to dryness on the water-bath. The residue solidified on cooling. It was crystallized from petroleum ether (b. p. 40–60°). Table I summarizes the results.

TABLE I

YIELDS OF CHLORO AMINES AND ANALYSES OF THEIR BENZOYL DERIVATIVES

Hydrocarbon	Prep. of amine hydrochloride Temp., °C.	Yield, %	M. p., °C.	Formula of benzoyl derivative	Nitrogen, % Calcd.	Found	Found	Chlorine, % Calcd.	Found	Found
Ethene	20 to 25	13.7	104–105	$C_9H_{10}ONCl$	7.63	7.82	7.70	...	...	...
Propene	−10	19.5	74–75	$C_{10}H_{12}ONCl$	7.09	6 93	7.01	17.97	18 27	18.04
Pentene	0 to 10	10–21	106–107	$C_{12}H_{16}ON_2Cl$[a]	10.35	10.33	10.31	13.10	13.16	13.20
Cyclohexene	−19	23	162–163	$C_{13}H_{16}ONCl$	5.89	5.82	5.91	14.95	15.10	15.11
Methylpropene	−50	12 2	83–84	$C_{11}H_{14}ONCl$	6.62	6.69	6.74	...	...	...

[a] *p*-Nitrobenzoyl derivative. The corresponding benzoyl derivative is an oil.

The chloro-amines obtained from ethene and propene were reduced with sodium amalgam in acid solution to the corresponding amines, ethylamine and isopropylamine. The benzoyl derivatives of these were prepared and identified by mixed melting points with the known compounds. No depression was observed in either case. Attempts to reduce the chloro-amines obtained from methylpropene and 2-pentene were not entirely successful. This was also true of the benzoyl derivative obtained from methylpropene. However, when the benzoyl derivative was tested with alcoholic silver nitrate for the presence of chlorine attached to a tertiary carbon atom, no precipitate was obtained until the solution was warmed. A control test with a known tertiary chloride formed a precipitate immediately. This test indicated that the compound was benzoyl-2-amino-1-chloro-2-methylpropane, since the isomer would contain chlorine attached to a tertiary carbon atom.

Summary

Nitrogen trichloride reacts with ethene, propene, methylpropene, 2-pentene and cyclohexene.

Nitrogen, ammonium chloride, the dichloride of the hydrocarbon and a C-chloro-N-dichloro-amine are formed with each.

IOWA CITY, IOWA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

O,N,N-TRIALKYLHYDROXYLAMINES

BY LAUDER W. JONES AND RANDOLPH T. MAJOR

RECEIVED JUNE 21, 1928 PUBLISHED OCTOBER 6, 1928

A number of trialkyl substituted hydroxylamines of the amine oxide type, R_3NO, have been described, but information concerning the isomeric compounds of the form R_2NOR is very limited. With the exception of Lossen's[1] O,N,N-triethylhydroxylamine, the description of which was so meager as to make the evidence for its existence quite doubtful, and the substituted hydroxylamino alcohols, $R(RO)NCH_2CH_2OH$, described by Jones and Burns[2] and by Jones and Major,[3] no O,N,N-trialkylhydroxylamines have been prepared.

Dunstan and Goulding[4] isolated trimethylamine oxide, $(CH_3)_3NO$, from the products obtained by the action of methyl iodide upon hydroxylamine. To account for the amine oxide, they suggested that O,N,N-trimethylhydroxylamine, $(CH_3)_2NOCH_3$, or its salt, was probably an intermediate product and that, by rearrangement, it passed to the amine oxide.[5]

$$(CH_3)_2NOCH_3 \longrightarrow (CH_3)_3N{=}O$$

Since O,N,N-trimethylhydroxylamine had not been prepared, it was not possible to reach a decision concerning the correctness of this assumption. However, certain other O,N,N-trisubstituted hydroxylamines were found to be comparatively stable compounds[1,2,3,6] which showed no tendency to rearrange to amine oxides. This made the explanation of the reaction proposed by Dunstan and Goulding rather unlikely. It is interesting to note, also, that Meisenheimer and his co-workers have observed that certain amine oxides, when heated in alkaline solution, suffer the reverse change and pass to O,N,N-trisubstituted hydroxylamines.[6b,c]

In the course of these investigations, O,N,N-trimethylhydroxylamine was obtained by the action of methyl iodide upon O,N-dimethylhydroxylamine in ether according to the equation

$$CH_3I + 2CH_3ONH(CH_3) \longrightarrow CH_3ONH_2(CH_3)I + CH_3ON(CH_3)_2$$

The ether solution, separated from the iodide, was treated with phenyl isocyanate to eliminate any O,N-dimethylhydroxylamine as α-phenyl-

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[1] Lossen, Ann., 252,233 (1889).

[2] Jones and Burns, THIS JOURNAL, 47,2972 (1925).

[3] Jones and Major, *ibid.*, 49, 1532 (1927).

[4] Dunstan and Goulding, J. *Chem. Soc.*, 75, 794 (1899).

[5] Dunstan and Goulding, *ibid.*, 75, 1004 (1899).

[6] (a) Behrend and Leuchs, Ann., 257, 225, 237 (1890); (b) Meisenheimer, *Ber.*, 52, 1667 (1919); (c) Meisenheimer, Greeske and Willmersdorf, *Ber.*, 55, 513 (1922); (d) ref. 3, pp. 1535, 1536.

β,β′-methylmethoxyurea. Ether and the trimethyl compound were then distilled from the urea and the O,N,N-trimethylhydroxylamine hydrochloride was precipitated from the ether by hydrogen chloride gas. The free base, liberated from the salt in the usual manner, was a liquid boiling at 30°. It did not reduce ammoniacal silver nitrate. It showed no tendency to rearrange to trimethylamine oxide. Obviously it cannot be regarded as the intermediate in the preparation of trimethylamine oxide as Lossen supposed. Undoubtedly methyl iodide reacts with hydroxylamine in such a fashion that methyl groups become attached to the nitrogen atom until the compound $(CH_3)_3NOHI$ is formed, which is responsible for the amine oxide.

When O,N,N-trimethylhydroxylamine was heated with concentrated hydrochloric acid at 190°, methylamine and formaldehyde were produced. Behrend and Leuchs[7] found that O,N,N-tribenzylhydroxylamine was decomposed by concentrated hydrochloric acid to give dibenzylhydroxylamine and benzyl chloride according to the equation

$$(C_6H_5CH_2)_2NOCH_2C_6H_5 + HCl \longrightarrow (C_6H_5CH_2)_2NOH + ClCH_2C_6H_5$$

If O,N,N-trimethylhydroxylamine decomposed in a similar manner, we should expect dimethylhydroxylamine and methyl chloride as products of the reaction. It is well known that N,N-dialkylhydroxylamines are quite readily decomposed to give aldehydes and alkylamines.[8] Therefore, if one disregards salt formation, the action of hydrochloric acid on O,N,N-trimethylhydroxylamine may be represented schematically as follows

$$\begin{aligned}&(CH_3)_2NOCH_3 + HCl \longrightarrow (CH_3)_2NOH + CH_3Cl\\&(CH_3)_2NOH \longrightarrow CH_3N{=}CH_2 + H_2O\\&CH_3N{=}CH_2 + H_2O \longrightarrow CH_2O + CH_3NH_2\end{aligned}$$

The possibility that the production of formaldehyde depended upon the initial elimination of the methoxy group as formaldehyde according to the equation

$$(CH_3)_2NOCH_3 \longrightarrow (CH_3)_2NH + CH_2O$$

followed by decomposition of dimethylamine by the acid to yield methylamine, was excluded because of the fact that at the temperature of the experiment, namely, 190°, dimethylamine was not decomposed by concentrated hydrochloric acid.

By similar reaction, O,N-diethyl-N-methylhydroxylamine was formed from methyl iodide and O,N-diethylhydroxylamine. Ethyl iodide, however, reacted with O,N-diethylhydroxylamine very slowly; even when the reaction was allowed to continue three times as long, scarcely any addition was observed.

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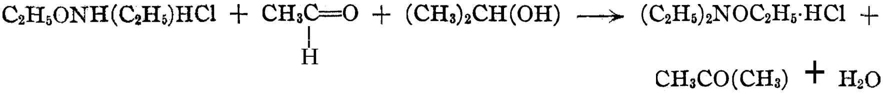
[7] Behrend and Leuchs, *Ann.*, 257, 231 (1890).

[8] (a) Walder, *Ber.*, 219, 1629, 3287 (1886); (b) Behrend and Leuchs, *Ann.*, 257, 233 (1890); (c) Dunstan and Goulding, J. Chem. *Soc.*, 75, 793 (1899); (d) Bewad, J. *prakt. Chem.*, 63, 193 (1901).

An unsuccessful attempt was made to prepare O,N,N-triethylhydroxylamine by the action of acetaldehyde on O,N-diethylhydroxylammonium chloride in the presence of isopropyl alcohol, according to the equation



$$C_2H_5ONH(C_2H_5)HCl + CH_3\underset{H}{\underset{|}{C}}{=}O + (CH_3)_2CH(OH) \longrightarrow (C_2H_5)_2NOC_2H_5\cdot HCl + CH_3CO(CH_3) + H_2O$$

Ethyl piperidine has been made in a similar manner by the action of acetaldehyde on piperidine hydrochloride in the presence of isopropyl alcohol.[9] Since acetone was observed among the products of the reaction, it was thought possible that isopropyl alcohol reduced O,N-diethylhydroxylammonium chloride. This was found to be the case; a mixture of O,N-diethylhydroxylammonium chloride, heated with isopropyl alcohol at 150°, gave acetone, ethylammonium chloride and probably ethyl alcohol according to the equation

$$C_2H_5ONH(C_2H_5)HCl + (CH_3)_2CH(OH) \longrightarrow C_2H_5NH_2\cdot HCl + CH_3CO(CH_3) + C_2H_5OH$$

When trimethylamine oxide is treated with methyl iodide, trimethylmethoxyammonium iodide is formed according to the equation[10]

$$(CH_3)_3N{=}O + CH_3I \longrightarrow [(CH_3)_3NOCH_3]I$$

The question arose whether the same compound would be formed by the action of methyl iodide on O,N,N-trimethylhydroxylamine, as follows

$$(CH_3)_2NOCH_3 + CH_3I \longrightarrow [(CH_3)_3NOCH_3]I$$

This was found to be the case; the compound formed in this way corresponded in every respect to the substance described by Dunstan and Goulding and by Meisenheimer.

Experimental Part

1. O,N,N-Trimethylhydroxylamine, $(CH_3)_2NOCH_3$

Preparation of O,N,N-Trimethylhydroxylammonium Chloride.—Two-tenths mole of O,N-dimethylhydroxylamine, prepared by Major and Fleck's modification of Jones' method,[11] was added to a solution of 0.1 mole of methyl iodide in dry ether. A white solid soon began to form. After the mixture had stood in a closed vessel for four days, the white precipitate was removed by filtration. It melted at 134° and weighed 13 g. It was dissolved in alcohol and shaken with sufficient silver oxide to combine with all of the iodide ion present. The free base was then distilled at room temperature under reduced pressure and collected in dilute hydrochloric acid. The small oily residue left in the distilling flask was probably trimethylmethoxyammonium hydroxide. The hydrochloric acid solution, evaporated to dryness, gave a white, crystalline solid which, after one crystallization from absolute alcohol, melted at 115–116°. A mixture of this compound with pure O,N-dimethylhydroxylammonium chloride, m. p. 115–116°, also melted at 115–116°.

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[9] D. R. P. 291,222; Friedlander, 12, 803 (1914–16).

[10] (a) Dunstan and Goulding, J. *Chem. Soc.*, 75,797 (1899); (b) Meisenheimer, *Ann.*, 397,288 (1913).

[11] (a) Jones, *Am.* Chem. J., 20, 44 (1898); (b) Major and Fleck, THIS JOURNAL, 50,1480 (1928).

A little *dry* potassium carbonate, to combine with any hydrogen iodide, and 0.17 of a mole of phenyl isocyanate were added to the cooled ethereal filtrate from the above mentioned solid (m. p. 134°). The isocyanate removed any O,N-dimethylhydroxylamine by combining with it to give a urea derivative. The mixture was allowed to stand in a closed container at room temperature for fifteen hours. Ether and free O,N,N-trimethylhydroxylamine were then distilled into a receiver surrounded by an ice-bath. Dry hydrogen chloride passed into the ether solution caused a white precipitate which was recrystallized from absolute alcohol; m. p. 123°; yield, 46%.

Anal. Subs., 0.2691: AgCl, 0.3416. Calcd. for $C_3H_{10}ONCl$: Cl, 31.81. Found: 31.66.

Chloroplatinate.—To 0.2 g. of O,N,N-trimethylhydroxylammonium chloride dissolved in absolute alcohol a solution of 0.5 g. of chloroplatinic acid in absolute alcohol was added. Orange-colored crystals precipitated. They were recrystallized from hot absolute alcohol; m. p. 159°, with decomposition.

Anal. Subs., 0.2356: Pt, 0.0819. Calcd. for $C_6H_{20}O_2N_2PtCl_6$: Pt, 34.85. Found: 34.79.

Isolation of the Free Base.—To prepare O,N,N-trimethylhydroxylamine, the hydrochloride was treated with an excess of a concentrated solution of potassium hydroxide. This solution was distilled and the vapors were passed over solid pieces of potassium hydroxide heated to 95° before they were condensed. Pure O,N,N-trimethylhydroxylamine distilled at 30°. The hydrochloride, regenerated from base by passing dry hydrogen chloride into an ether solution of it, melted at 123° and corresponded in every way with the hydrochloride from which the free base had been made. This excluded the possibility of rearrangement. Free O,N,N-trimethylhydroxylamine possessed a fishy odor somewhat like that of other alkyl substituted hydroxylamines. It did not reduce ammoniacal silver nitrate.

Decomposition of O,N,N-Trimethylhydroxylamine by Treatment with Hydrochloric Acid.—A solution of 0.7 g. of O,N,N-trimethylhydroxylamine in 5 cc. of concentrated hydrochloric acid was heated in a sealed tube at 190° for eight hours. Considerable gas, undoubtedly methyl chloride, escaped when the tube was opened. The contents of the tube was dark in color. About half of it was distilled. The distillate had a pronounced odor of formaldehyde and gave a distinct color test for this substance with a solution of guaiacol in concentrated sulfuric acid.[12] The portion that remained in the distilling flask was evaporated to dryness on a water-bath. A rather dark colored solid was obtained, which, after recrystallization twice from absolute ethyl alcohol, was colorless and melted at 231°. A mixture of this compound with methylammonium chloride, m. p. 231°, also melted at 231°.

Action of Hydrochloric Acid on Dimethylamine.—A solution of 1 g. of dimethylammonium chloride, m. p. 171°, in 5 cc. of concentrated hydrochloric acid was heated at 190° for nine hours. The tube was cooled and opened and its contents evaporated to dryness on a water-bath. Unchanged dimethylammonium chloride, melting at 171°, was recovered.

2. O,N-Diethyl-N-methylhydroxylamine, $C_2H_5ON(C_2H_5)CH_3$

One-tenth mole of O,N-diethylhydroxylamine, prepared by the method of Major and Fleck,[11b] was added to a solution of 0.05 mole of methyl iodide in dry ether. The mixture was allowed to stand in a closed container at room temperature for four days. A heavy, pink oil gradually formed. It was separated from the ether solution by decantation. After washing it thoroughly with dry ether, it was made alkaline with

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[12] "Deutsches Arzneibuch," R. v. Decker's Verlag, Berlin, 1926, p. LIV.

potassium hydroxide and the free base recovered in the usual manner. Four g. of the free base, b. p. 78–84°, was recovered. It had the characteristic odor of O,N-diethylhydroxylamine. The major fraction, b. p. 83°, was added to a solution of phenyl isocyanate in benzene. Evaporation of the benzene, after the mixture had stood for a day, left a white solid which melted at 63°, after it had been recrystallized once from ligroin. Pure α-phenyl-β,β'-ethylethoxyurea melts at 63°.[13]

The ether solution, from which the pink oil was separated, was shaken with a little mercury in order to remove a trace of dissolved iodine. A little potassium carbonate and 0.9 of a mole of phenyl isocyanate were then added to remove any O,N-diethylhydroxylamine by the formation of a substituted urea. The mixture was allowed to stand in a closed container at room temperature for two days. Ether and free O,N-diethyl-N-methylhydroxylamine were then distilled and collected in a receiver surrounded by an ice-bath. Dry hydrogen chloride was passed into the ether solution. A heavy oil precipitated. The ether was decanted but since the oil was somewhat soluble in ether, probably due to a partial splitting into hydrogen chloride and O,N-diethyl-N-methylhydroxylamine, it was not washed with pure ether but with a little ether which had been saturated with hydrogen chloride. The oil failed to solidify.

Free O,N-diethyl-N-methylhydroxylamine was obtained from this hydrochloride in the manner described above in the preparation of O,N,N-trimethylhydroxylamine from its hydrochloride. It boiled at 79°. It had an odor somewhat like that of the other alkyl substituted hydroxylamines but slightly more ethereal; yield, 20%. Dry hydrogen chloride precipitated an oily hydrochloride from an ether solution of a portion of the free base.

Chloroplatinate.—A solution of 0.25 g. of O,N-diethyl-N-methylhydroxylamine in absolute alcohol was saturated with dry hydrogen chloride. The calculated amount of a solution of chloroplatinic acid in absolute alcohol was added. Orange needles soon precipitated. The amount of these was increased by adding dry ether. They were recrystallized from hot 95% alcohol; m. p. 158°. The compound was very soluble in water, readily soluble in hot 95% alcohol, but soluble only with difficulty in hot or cold absolute alcohol and insoluble in ether.

Anal. Subs., 0.2055: Pt, 0.0651. Calcd. for $C_{10}H_{28}O_2N_2PtCl_6$: Pt, 31.68. Found: 31.68.

3. Action of Isopropyl Alcohol on O,N-Diethylhydroxylammonium Chloride

To a solution of 0.56 g. of O,N-diethylhydroxylammonium chloride in 1 cc. of water was added 1 cc. of acetone-free isopropyl alcohol. This mixture was heated at 150° for two hours. When the tube was cooled and opened, a brownish solution was found. A portion of this solution was distilled and the distillate tested for acetone with vanillin according to the method of Kolthoff.[14] It gave a very pronounced test for acetone.

The rest of the solution was evaporated to dryness on the water-bath. The dark, solid residue was recrystallized several times by dissolving it in absolute alcohol and reprecipitating it by the addition of dry ether; m. p. 98°. A mixture of this hydrochloride with ethylammonium chloride (m. p. 98°) also melted at 98°.

4. Trimethylmethoxyammonium Iodide, $[(CH_3)_3NOCH_3]I$

To 1 g. of O,N,N-trimethylhydroxylamine was added an equivalent molecular portion of methyl iodide. The mixture became turbid at once and in four hours had

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[13] Jones and Major, THIS JOURNAL, 49, 1538 (1927).

[14] Kolthoff, *Pharm. Weekblad*, **55**, 1021 (1918); *C. A.*, 12, 2180 (1918).

changed entirely to a solid, white, crystalline mass. This was recrystallized from dry methanol. It did not have a definite melting point but, as described by Meisenheimer for the trimethylmethoxyammonium iodide prepared from trimethylamine oxide and methyl iodide, gradually darkened and decomposed at about 162°.[10b] It formed narrow, plate-like crystals which were readily soluble in water, less so in alcohol and insoluble in ether.

Anal. Subs., **0.2271:** AgI, **0.2451.** Calcd. for $C_4H_{12}ONI$: I, 58.48. Found: **58.34.**

Decomposition of Trimethylmethoxyammonium Hydroxide by Heat.—When a solution of trimethylmethoxyammonium hydroxide, obtained from the iodide made by the action of trimethylamine oxide on methyl iodide, was heated, formaldehyde was formed.[15] In order to find out whether or not the same change would take place with the trimethylmethoxyammonium hydroxide obtained from O,N,N-trimethylhydroxylamine and methyl iodide, **1** g. of trimethylmethoxyammonium iodide was made alkaline with a concentrated solution of sodium hydroxide. The volatile portions of this solution were distilled into an aqueous solution of *p*-nitrophenylhydrazine hydrochloride. An orange-colored precipitate formed which was recrystallized from dilute alcohol; m. p. **181°**. Formaldehyde p-nitrophenylhydrazone melts at 181–182°.[16] The odor of formaldehyde was also very marked when trimethylmethoxyammonium iodide was warmed with sodium hydroxide.

Summary

1. O,N,N-trimethylhydroxylamine and O,N-diethyl-N-methylhydroxylamine have been prepared by the action of methyl iodide on O,N-dimethylhydroxylamine and O,N-diethylhydroxylamine, respectively.

2. It has been shown that O,N,N-trimethylhydroxylamine is a comparatively stable compound which shows no tendency to rearrange to trimethylamine oxide. The probable course of the action of methyl iodide on hydroxylamine has been outlined in harmony with this fact.

3. The decomposition of O,N,N-trimethylhydroxylamine when heated with hydrochloric acid has been studied and the probable course of the reaction discussed.

4. The action of isopropyl alcohol on O,N-diethylhydroxylammonium chloride has been investigated.

5. It has been found that the trimethylmethoxyammonium iodide obtained by the action of methyl iodide on O,N,N-trimethylhydroxylamine is the same as that obtained by the action of methyl iodide on trimethylamine oxide.

PRINCETON, NEW JERSEY

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[15] Ref. 10 **b,** p. **292.**

[16] Bamberger, **Ber., 32, 1807 (1899).**

[CONTRIBUTION FROM THE WILLIAM H. CHANDLER CHEMISTRY LABORATORY, LEHIGH UNIVERSITY]

MONONITRO- AND DINITROTHIOPHENES

BY V. S. BABASINIAN

RECEIVED JUNE 22, 1928 PUBLISHED OCTOBER 6, 1928

I. Mononitrothiophene

The introduction of a nitro group into the thiophene nucleus has been a problem fraught with difficulties. Victor Meyer and his co-workers[1] made "countless futile attempts" to nitrate this compound by the usual method. They finally succeeded in accomplishing this[2] by drawing a vigorous stream of air charged with thiophene through red fuming nitric acid. The product was a mixture of mononitro- and dinitrothiophenes and an oily residue. The two nitro compounds could only be extracted and separated by repeated fractional distillation and the yield was admittedly unsatisfactory. The nitration of ethylthiophene by this method failed to produce the mononitro derivative;[3] diethylthiophene yielded a product of unknown composition;[4] while the nitration of thioxene resulted in the formation of a resin.[5] Despite these limitations, for thirty years this remained the only known method for the nitration of thiophene and its homologs.

Following the study of diacetyl-ortho-nitric acid,[6] benzoyl nitrate,[7] and acetyl nitrate,[8] as nitrating agents, Steinkopf and Kirchoff[9] proposed an improved method for the nitration of thiophene. The compound was dissolved in acetic anhydride and treated with a solution of fuming nitric acid in the same solvent, the temperature during nitration being maintained between 0 and 5°. Upon treating the product with ice water, an unstable dark oil and a brown precipitate were formed, from which mononitrothiophene was obtained by distillation with steam. Although it must be admitted that this is a decided improvement over the earlier method, the success of the experiment depends upon painstaking manipulation at a low nitration temperature, and the oily product has been found to undergo rapid decomposition.

A Modified Method of Nitration

The method of nitration proposed in this paper has been given a thorough trial. The process is carried out, almost exclusively, at the room tem-

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[1] **Meyer, "Die Thiophengruppe," Braunschweig,** 1888, **p.** 95.

[2] **Meyer and Stadler,** *Ber*., 17,2648 (1884).

[3] **Bonz,** *Ber.,* 18, 552 (1885).

[4] **Muhlert,** *Ber.,* 19, 635 (1886).

[5] Messinger, *Ber.,* 18, 1639 (1885).

[6] **Pictet and Genequand,** *Ber.,* 35, 2526 (1902)

[7] **Francis,** *Ber.,* 39, 3801 (1906).

[8] **(a) Pictet and Khotinsky,** *Ber.,* 40,1163 (1907); (b) *Compt. rend.,* 144,210 (1907).

[9] *(a)* **Steinkopf and Kirchoff, Ann.,** 403, 17, 27 (1914); (b) **Steinkopf and Lützkendorf, German patent,** 255,394.

perature. The reaction yields a product which is stable under all conditions and the weight of the purified substance is from 80 to 85% of that required by theory. Moreover, the method has been repeatedly employed, with equal success, for the nitration of a derivative of thiophene.

Although solutions containing diacetyl-ortho-nitric acid, or acetyl nitrate, have often been employed with marked success for the nitration of aromatic hydrocarbons or their derivatives,[10] attempts to nitrate thiophene in this Laboratory with these reagents have clearly shown that in order to insure a satisfactory yield it is necessary to observe certain rigid conditions. Pictet and Genequand[11] and, later, Pictet and Khotinsky[12] had made the observation that these reagents may acetylate, oxidize or nitrate, the course of the reaction depending upon circumstances.

With thiophene there is no indication that acetylation occurs when acetic acid or anhydride solutions of these nitrating agents are employed. That oxidation takes place, with the incident rupture of the thiophene ring, cannot be doubted. It has also been demonstrated that in the formation of mononitrothiophene with these solutions, temperature is an important factor. At lower temperatures the reaction, if it takes place at all, is almost exclusively one of nitration; while at elevated temperatures oxidation sets in almost invariably, the course of the reaction being indicated by the evolution of heat and the liberation of nitrogen peroxide. Moreover, at higher temperatures the liberated nitrogen peroxide attacks the thiophene vapor in the nitrating flask, converting it into a tarry product, which has been shown to contain traces of dinitrothiophene by the application of the Meyer-Stadler test.[13] Schaarschmidt's studies[14] show that the nitration of thiophene with nitrogen peroxide yields products which are not easy to purify,

No less than twenty-five nitrations have been carried out in this Laboratory with solutions of nitric acid and thiophene in acetic acid or acetic anhydride. The method that has reduced the side reactions to a minimum is given in outline.

Procedure

(1) Eighty-four g. of thiophene is dissolved in 340 cc. of acetic anhydride and (2) eighty g. of nitric acid (sp. gr. 1.52) is dissolved in 600 cc. of glacial acetic acid.

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[10] (a) Van Romberg, *Rec. trav. chim.*, *7*, 226 (1888); (b) Kunze, *Ber.*, 21, 3331 (1888); (c) Hirsch, *Ber.*, 22, 335 (1889); (d) Komppa, *Chem. Zentr.*, 1898, ii, 1169; (e) Orton, *J. Chem. Soc.*, 81, 806 (1902); (f) Witt and Utermann, *Ber.*, 39, 3901 (1906); (g) Arnall, *J. Chem. Soc.*, 125, 811 (1924); (h) Menke, *Rec. trav. chim.*, *44*, 141 (1925); *C. A.*, 19, 2191 (1925); (i) *ibid.*, 44, 269 (1925); *C. A.*, 19, 2480 (1925); (j) Bacharach, THIS JOURNAL, 49, 1522 (1927); (k) other examples: Houben, "Die Methoden der organischen Chemie," 2nd ed., Vol. 4, pp. 146–150.

[11] Ref. 6, p. 2526.

[12] Ref. 8a, p. 1163.

[13] Meyer and Stadler, *Ber.*, 17, 2780 *(1884).*

[14] Schaarschmidt and so-workers, *Ber.*, **58B**, *499* (1925)

Each solution is divided into two equal parts. One-half of solution **(2)** is introduced into a large three-necked, round flask, provided with a thermometer, a motor stirrer and a dropping funnel. The flask is cooled to 10°. With moderate stirring one-half of the thiophene solution is introduced, drop by drop, and at such a rate as to prevent the heating of the reaction mixture above the room temperature. A rapid rise of temperature will occur during the addition of the first fraction of the thiophene solution. The temperature is controlled by dipping the nitrating flask into a bath of cold tap water. The use of ice water is not necessary, as cooling with ice will retard the reaction. On the other hand, care should be taken to avoid superheating the reaction mixture. After the addition of the first half of thiophene, the temperature of the reaction mixture is reduced to 10° and the remainder of nitric acid is rapidly introduced into the flask. Nitration is continued by the gradual addition of thiophene. Throughout the nitration the solution should show a permanent light brown color. The appearance of a pink or dark red color indicates oxidation.[15] The product is allowed to remain at the room temperature for two hours. It is then treated with an equal volume of ice water with rapid shaking. Mononitrothiophene will begin to separate out in faint yellow crystals. More crystals will form if the mixture is allowed to remain in the ice chest for at least twenty-four hours. It is filtered cold through a Büchner funnel, washed thoroughly with ice water, pressed and dried in a brown desiccator,[16] charged with sulfuric acid and granules of caustic soda.

The filtrate and the washings contain in solution a quantity of mononitrothiophene. This is recovered by distillation with steam. The acid distillate will consist of white crystals and a solution of the compound. The solid is removed by filtration and washed. The filtrate is extracted with ether, neutralized with a weak solution of sodium carbonate, dried with calcium chloride and subjected to distillation.

If the nitration was carried out in accordance with this outline, the product will be crystalline and faint yellow in color. The color is due to traces of dinitrothiophene and other impurities. Mononitrothiophene has been crystallized by earlier workers from ether, alcohol, benzene and other solvents. As a rule these solvents fail to yield a snow-white product. It has been found in this work that petroleum ether (b. p. 20–40°) possesses decided advantages in that by prolonged boiling it extracts mononitrothiophene but does not readily dissolve the impurities. With petroleum ether snow-white crystals of the compound have been obtained in needles 5 to 8 inches in length.

The method of nitration outlined in this paper has been employed repeatedly by the author. In every instance the yield of the purified product was found to be over 80% of the theoretical quantity.

Discussion

Experiments conducted under varying conditions of concentration and temperature lead to the following generalizations.

1. Glacial acetic acid alone does not induce nitration to any extent at the ordinary temperature. At higher temperatures partial oxidation takes place, a tar is produced and a quantity of unattacked thiophene is recovered.

2. In moderate quantities acetic anhydride alone will induce nitration when the reaction is carried out at 0°. Even at this low temperature ni-

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[15] The tarry product formed as a result of oxidation dissolves in the reaction mixture, imparting to it a pink or a dark red color.

[16] Earlier investigators have noted that the compound is extremely sensitive toward light, ref. 2, p. 2649.

tration is accompanied by oxidation with the formation of an unstable by-product.

3. Under the most favorable conditions the yield is satisfactory and the product free from contamination when thiophene is added to nitric acid. The reverse process does not complete the reaction; if the reaction mixture be heated to complete nitration, the unchanged thiophene is oxidized, heat is evolved and nitrogen peroxide liberated.

II. Dinitrothiophene

The entry of a negative substituent into the thiophene nucleus protects the compound from the oxidizing action of nitric acid, permitting nitration by the ordinary method. By the direct addition of the negatively substituted derivative to fuming nitric acid at low temperatures, nitro compounds have been obtained from b-thiophenic acid,[17] acetothienone,[18] ethyl acetothienone,[19] methyl acetothienone,[20] and from a number of polysubstituted derivatives.[21]

That mononitrothiophene has not been heretofore employed for the large-scale production of the dinitro compound has undoubtedly been due to the difficulty of preparing the former. The only method described in the literature for the preparation of dinitrothiophene is that of Meyer and Stadler.[22] It should be added that although the yield by this process was highly unsatisfactory, the compound had been subjected to a thorough investigation.[23]

The Preparation of Dinitrothiophene

The nitrating mixture proposed for the conversion of thiophene into the mononitro derivative does not react with the latter to produce dinitrothiophene. **A** reaction carried out with this mixture resulted in the recovery of the nitrothiophene employed. On the other hand, mononitrothiophene is readily nitrated with a mixture of nitric and sulfuric acids to form dinitrothiophene. Although derivatives of thiophene are known to react with sulfuric acid with the greatest ease, sulfonic acids have not been detected in this process of nitration.

Procedure

Thirty-five g. of nitric acid (sp. gr. 1.4) was dissolved in 55 g. of sulfuric acid (sp. gr. 1.82) and the ice-cooled solution was treated with 20 g. of mononitrothiophene in

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[17] Nahnsen, ***Ber.***. 17, 2196 (1884).

[18] Peter, ***Ber.***, 17, 2646 (1884)

[19] Schleicher, ***Ber.***, 18, 3022 (1885).

[20] Demuth, ***Ber.***, 18, 3025 (1885).

[21] (a) Peter, ***Ber.***, 18, 541 (1885); (b) Rosenberg, *Ber.*, 19, 652 (1886).

[22] Ref. 2, p. 2648.

[23] (a) Meyer and Stadler, ***Ber.***. 17, 2778 (1884); (b) Stadler, ***Ber.***, 18, 530 ***(188.5);*** (c) Meyer, ***Ber.***, 18, 1328 (1885); (d) Rosenberg, ***Ber.***, 18, 1778 (1885); (e) Gattermann and co-workers, ***Ber.***, 18,3012 (1885).

gram portions. The first 5 g. of the solid formed an almost colorless solution. Additional quantities produced cloudiness, imparting to the liquid a faint yellow color. When the reaction mixture was brought to room temperature, it separated into two transparent layers—a reddish-yellow upper layer and a faint yellow lower layer. It was heated in a water-bath with continued shaking, the temperature being gradually increased in the course of half an hour from **30** to **85°**. The reaction product, consisting of an upper yellow layer and a lower light brown layer, was cooled in an ice-bath for one hour. The white crystals of dinitrothiophene were filtered with suction, digested in ice water and dried. Upon treatment with ice, the filtrate formed an additional quantity of the compound in fine needles. The product was crystallized from ordinary alcohol; yield, over 80% of the theoretical quantity; melting point, 52°.

Anal. Calcd. for $C_4H_2S(NO_2)_2$: S, **18.68.** Found: **18.94.** Mol. wt. Subs., **0.1959:** benzene, **21.76; AT, 0.256".** Calcd.: **174.** Found: **185.**

Isomeric Dinitrothiophenes

In their studies of dinitrothiophene, Meyer and his co-workers[24] had found that the compound melting at **52°** yields upon distillation with steam an isomer melting at 78°. After searching investigation they concluded that the two isomers were identical in structure. They made the further assertion that by repeated fractional distillation with steam ordinary dinitrothiophene (m. p. 52°) is completely transformed into the isomer melting at 78°.[25, 23a,b]

It should be stated that these investigators had based the latter assertion on experiments carried out with only small quantities of the lower melting modification.

An extended study of the behavior of ordinary dinitrothiophene fails to show that the compound melting at 52° can be completely transformed into the isomer melting at 78°.

1. When dinitrothiophene is subjected to prolonged distillation with steam, a dark residue remains in the distillation flask, which was presumably taken by earlier workers as a decomposition product. When an alcoholic solution of this residue is purified with animal charcoal, it yields dinitrothiophene possessing a sharp melting point of 54°. The product is not very volatile with steam and could not be converted into the higher melting modification after repeated distillation with steam.

2. In a study of the vapor pressure curve for dinitrothiophene,[26] a trace of the compound was found to condense in the cooler regions of the isoteniscope at temperatures above 140°. This fraction melted at **76–78",** while the bulk of the compound in the apparatus gave, after crystallization from alcohol, a melting point of 52–54°. If ordinary dinitrothiophene was transformed in the isoteniscope into its isomer at temperatures above 140°, it was natural to assume that prolonged heating would induce fur-

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[24] Ref. **2,** p. **2649.**

[25] Ref. **1,** p. **98.**

[26] Results to be published.

ther transformation, converting the lower melting compound into the other modification. The compound melting at 52–54' was therefore transferred into a long combustion tube, closed at the lower end. The tube was submerged in a bath of toluidine and heated at 180°. In a few hours a solid melting at 72–78° condensed in the cooler regions of the tube. Continued heating, for almost one week, failed to produce additional quantities of the higher melting isomer. The residue in the tube when freed from traces of tarry impurities showed a sharp melting point of 54".

3. Specimens of the two isomers were spread in thin layers in two quartz test-tubes and exposed for one hour, at a distance of ten inches, to the action of ultraviolet irradiation, a Cooper-Hewitt Quartz Uviarc being used for the experiment. The ordinary modification had melted completely at the end of the hour and the isomer had changed into a semi-solid. The two tubes were exposed for another hour at a distance of fifteen inches. A slight decomposition had taken place in each tube. The materials were dissolved in alcohol, treated with animal charcoal and crystallized. No change in melting point was observed in either compound.

Evidently ordinary dinitrothiophene contains a weighable quantity of the isomer melting at 78°, but there is no conclusive evidence of transition from one isomer into the other.

Summary

Solutions containing acetyl nitrate and di-acetyl-ortho-nitric acid will nitrate thiophene and may simultaneously oxidize it, the course of the reaction depending upon concentration and temperature.

When conditions are under proper control, nitration will take place almost exclusively, even at the room temperature, with a satisfactory yield of mononitrothiophene.

With a mixture of nitric and sulfuric acids mononitrothiophene is readily converted into dinitrothiophene.

Studies of the behavior of dinitrothiophene do not confirm the assertion that the ordinarily prepared compound is transformed into a higher melting isomer.

BETHLEHEM, PENNSYLVANIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE STATE UNIVERSITY OF IOWA]

NITROGEN TRICHLORIDE AND UNSATURATED HYDROCARBONS. III. NITROGEN TRICHLORIDE AND DIPHENYLKETENE

BY GEORGE H. COLEMAN AND ARTHUR W. CAMPBELL[1]

RECEIVED JUNE 28, 1928 PUBLISHED OCTOBER 6, 1928

Many aliphatic unsaturated hydrocarbons[2] of the olefin series react with nitrogen trichloride to form, among other products, C-chloro-N-dichloro-amines. This is also true for some of the unsaturated ketones.[3]

In the present work this reaction was studied with derivatives of ethene in which one or more of the hydrogen atoms of this compound had been replaced by phenyl groups. Diphenylketene was also used since the ketenes undergo addition reactions very readily with ammonia and the amines. It was also thought that the evolution of a large amount of nitrogen which characterizes most addition reactions of nitrogen trichloride might not occur with a highly reactive compound like diphenylketene.

Phenylethene and 1,2-diphenylethene react fairly rapidly with nitrogen trichloride in carbon tetrachloride solution to form nitrogen, the dichloride of the hydrocarbon, a small amount of ammonium chloride and a C-chloro-N-dichloro-amine. These compounds are easily reduced with hydrochloric acid to the corresponding C-chloro-amines, both of which have been previously prepared by other methods.[4] With phenylethene two products are possible. Only one, however, 1-amino-2-chloro-1-phenylethene, was isolated. The reaction rates as well as the products do not differ very greatly from those of the corresponding methyl derivatives, propene and 2-butene.

1,1-Diphenylethene and 1,1-diphenyl-1-propene have reaction rates which are of the same general order as the first two hydrocarbons of this series. Neither of them, however, forms a stable addition product with nitrogen trichloride under the experimental conditions used. Triphenylethene reacts quite slowly, and in this respect differs very decidedly from the corresponding trimethyl derivative, the reaction rate of which is perhaps as rapid as any which has thus far been studied. No amine was isolated. Apparently tetraphenylethene does not react until the mixture is warmed slightly. The slow evolution of nitrogen which then occurs

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[1] This paper is an abstract of the thesis submitted by Arthur W. Campbell in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the State University of Iowa.

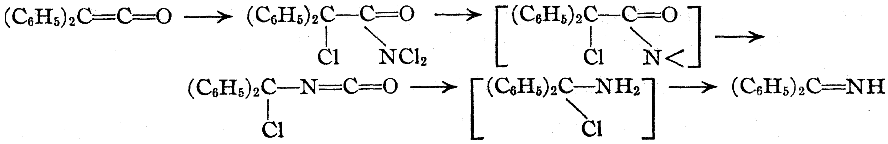
[2] Coleman and Howells, THIS JOURNAL, 45, 3084 (1923); Coleman, Mullins and Pickering, 50, 2739 (1928).

[3] (a) Coleman and Craig, *ibid.*, 49, 2593 (1927); (b) 50, 1816 (1928).

[4] (a) Gabriel and Colman, Ber., 47, 1866 (1914); (b) Darapsky and Spannagel, J. *prakt. Chem.*, 92, 279 (1915).

may be due to reaction with the phenyl groups. Nitrogen trichloride is known to react with benzene and its derivatives.[5] No amine was obtained.

Diphenylketene reacts rapidly with nitrogen trichloride. Practically no nitrogen is evolved and the characteristic odor of nitrogen trichloride disappears if an excess of the ketene is used. On the basis of the addition reactions of nitrogen trichloride with the unsaturated hydrocarbons and the unsaturated ketones, and the well-known reactions of the ketenes, it seems probable that the addition product formed is diphenylchloroaceto-N-dichloro-amide. When the reaction mixture is warmed for a short time with a solution of sodium hydroxide and the non-aqueous layer separated, dried and hydrogen chloride passed into it, benzophenone-imide hydrochloride is precipitated. The reaction possibly involves the following steps



$$(C_6H_5)_2C{=}C{=}O \longrightarrow (C_6H_5)_2\underset{\displaystyle Cl}{\underset{|}{C}}{-}\overset{\displaystyle C{=}O}{}\!\!\searrow NCl_2 \longrightarrow \left[(C_6H_5)_2\underset{\displaystyle Cl}{\underset{|}{C}}{-}C{=}O \searrow N{<}\right] \longrightarrow$$

$$(C_6H_5)_2\underset{\displaystyle Cl}{\underset{|}{C}}{-}N{=}C{=}O \longrightarrow \left[(C_6H_5)_2C{-}NH_2 \searrow Cl\right] \longrightarrow (C_6H_5)_2C{=}NH$$

Experimental Part

The Reaction with Phenylethene (Styrene)

1-Amino-2-chloro-1-phenylethane.—The nitrogen trichloride was prepared and analyzed as described in earlier papers.[3b] The phenylethene was dissolved in carbon tetrachloride. The apparatus was protected from the light and arranged for collecting and measuring the nitrogen evolved. The nitrogen trichloride solution was added slowly through a separatory funnel in the course of one to two hours. During the addition the reaction flask was cooled to −10° or lower and gently shaken. The reaction was fairly rapid and was complete soon after the last of the trichloride had been added. The precipitate of ammonium chloride formed during the reaction was filtered off and dry hydrogen chloride passed into the carbon tetrachloride solution. The amine hydrochloride which precipitated was filtered, dried and weighed.

The amounts used in a typical run were as follows: 71 mg. moles of nitrogen trichloride in 250 g. of carbon tetrachloride, 200 mg. moles of phenylethene in 400 g. of carbon tetrachloride. In this run there were formed 46.4 mg. atm. of nitrogen, 3.2 mg. moles of ammonium chloride and 19.6 mg. moles of the amine, which is 27.6% of the theoretical yield calculated from the nitrogen trichloride.

Benzoyl-1-amino-2-chloro-1-phenylethane.—The benzoyl derivative was prepared from the amine hydrochloride by the Schotten-Baumann method. The product after recrystallization from petroleum ether melted at 133–134° (uncorr.).

Anal. Subs., 0.1553: 5.53 cc. of 0.1076 *N* HCl. Calcd. for $C_{15}H_{14}ONCl$: N, 5.59. Found: 5.36. Subs. 0.1980: 7.70 cc. of 0.0996 *N* $AgNO_3$. Calcd. for $C_{15}H_{14}ONCl$: Cl, 13.66. Found: 13.72.

This compound has been prepared by Gabriel and Colman,[4a] who record a melting point of 137°. The isomeric compound, benzoyl-2-amino-

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[5] Coleman and Noyes, THIS JOURNAL, 43, 2211 (1921).

1-chloro-1-phenylethane, prepared by Wolfheim[6] has a melting point of 124".

The Reaction with 1,2-Diphenylethene (Stilbene)

1-Amino-2-chloro-1,2-diphenylethane.—The 1,2-diphenylethene was prepared from benzylmagnesium chloride and benzaldehyde by the method described by Hell.[7] The reaction with nitrogen trichloride was carried out at −14°. The procedure was similar to that with phenylethene. The time of addition was one hour. Nitrogen was evolved for a short time after all of the trichloride had been added. A heavy precipitate of the dichloride of the hydrocarbon and a little ammonium chloride formed during the reaction. This was filtered off and the ammonium chloride separated by solution in water in which the dichloride is insoluble. The amine hydrochloride was obtained as before by treatment with hydrogen chloride. In one run there were obtained from 91.8 mg. moles of nitrogen trichloride, 16.8 mg. moles of the amine, 70.5 mg. atm. of nitrogen and 2.8 mg. moles of ammonium chloride.

Benzoyl-1-amino-2-chloro-1,2-diphenylethane.—The benzoyl derivative was prepared from the hydrochloride of the amine by the Schotten-Baumann method. After recrystallization from alcohol it melted at 192–193° (uncorr.). The compound has been prepared by Darapsky and Spannagel,[4b] who report a melting point of 195°.

The Reaction with 1,1-Diphenylethene

1,1-Diphenylethene was prepared by the method of Allen and Converse.[8] The reaction with nitrogen trichloride was carried out as described for phenylethene. No amine hydrochloride was obtained. In one run there was obtained from 90 mg. moles of nitrogen trichloride, 85 mg. moles of nitrogen and 4.6 mg. moles of ammonium chloride. The reaction rate was much the same as that of 1,2-diphenylethene.

The Reaction with 1,1-Diphenyl-1-propene

The hydrocarbon was prepared from benzophenone and ethylmagnesium iodide by the method of Klages.[9] The reaction was carried out as described for phenylethene. The reaction rate did not differ noticeably from that of the two hydrocarbons just described. Practically all of the nitrogen of the nitrogen trichloride was given off as a gas. No amine was formed.

The Reaction with Triphenylethene

The hydrocarbon was prepared from benzophenone and benzylmagnesium chloride by the method of Hell and Wiegandt.[10] The reaction rate of this compound was much slower than the others thus far described. Ten hours or longer were required for the completion of the reaction. Again practically all of the nitrogen appeared as gas. No amine was formed.

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[6] Wolfheim, *Ber.*, 47, 1440 (1914).

[7] Hell, *Ber.*, 37, 453 (1904).

[8] "Organic Syntheses," John Wiley and Sons, Inc., New York, 1926, Vol. VI, p. 32.

[9] Klages, *Ber.*, 35, 2646 (1902).

[10] Hell and Wiegandt, *Ber.*, 37, 1431 (1904).

The Reaction with Tetraphenylethene

The hydrocarbon was prepared from diphenylmethane and dichlorodiphenylmethane by the method of Norris, Thomas and Brown.[11]

At −10° there was apparently no reaction with nitrogen trichloride. When the mixture was warmed to 30°, a slow evolution of nitrogen began and continued for thirty-five to forty hours. A little ammonium chloride formed during the reaction but no amine was obtained.

Diphenylketene **and Nitrogen Trichloride.**—A solution of diphenylketene was prepared from diphenylchloro-acetyl chloride and zinc by the method described by Staudinger.[12]

In carrying out the reaction with nitrogen trichloride, the apparatus was arranged for collecting any gas which might be liberated. The nitrogen trichloride solution was added to the ketene solution through a separatory funnel in the course of an hour. A slight excess of the ketene was always used. During the addition the ketene solution was kept at −10° and gently shaken. Little or no gas was evolved. The solution was allowed to remain at this temperature for some time after the trichloride had been added. A residue which proved to be largely zinc chloride formed at the bottom of the flask. The solution was poured off and warmed for thirty to forty minutes at about 40° with 6 *N* sodium hydroxide solution. The non-aqueous layer was separated, dried and hydrogen chloride passed into it. A heavy precipitate of benzophenone-imide hydrochloride was formed. This was filtered off. About an equal quantity of benzophenone was obtained from the filtrate by evaporation.

The best yield of benzophenone-imide hydrochloride obtained was 35% calculated from the nitrogen trichloride. A part of this was purified by dissolving in water, adding a slight excess of cold sodium hydroxide solution and extracting with carbon tetrachloride, drying and reprecipitating with hydrogen chloride. This was analyzed for nitrogen by the Kjeldahl method.

Anal. Subs. 0.2037, 0.2006: 7.88, 7.78 cc. of 0.1205 N HCl. Calcd for $C_{13}H_{12}NCl$: N, 6.44. Found: 6.55.6.56.

A portion of the hydrochloride was heated for a short time with water. The oily product was extracted with ether and the ether evaporated. Benzophenone crystallized on cooling. It was identified by the preparation of the phenylhydrazone.

Summary

1. Nitrogen trichloride reacts with phenylethene and 1,2-diphenylethene to form among other products, C-chloro-N-dichloro-amines. With 1,1-diphenylethene, 1,1-diphenyl-1-propene, triphenylethene and tetraphenylethene no amines are formed under the experimental conditions used.

2. Nitrogen trichloride reacts with diphenylketene. The addition product when warmed with sodium hydroxide solution forms benzophenone imide.

IOWA CITY, IOWA

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[11] Norris, Thomas and Brown, ***Ber.***, 43, 2958 (1910).

[12] Staudinger, *Ann.*, 356, 73 (1907).

[CONTRIBUTION FROM THE DEPARTMENT OF RESEARCH IN PURE CHEMISTRY, MELLON INSTITUTE OF INDUSTRIAL RESEARCH, UNIVERSITY OF PITTSBURGH]

THE PREPARATION OF ETHYL PHENYLMALONATE AND OF 5-PHENYL-BETA-HYDROXYETHYLBARBITURIC ACID[1]

BY WILLIAM L. NELSON AND LEONARD H. CRETCHER

RECEIVED JULY 7, 1928 PUBLISHED OCTOBER 6, 1928

In continuation of the study of the effect of the introduction of a hydroxyl group on the toxicity and therapeutic action of medicinal substances, which has been under way for some time in this Laboratory,[2] it was desired to prepare a number of barbituric acids substituted in the 5-position with phenyl and hydroxyalkyl groups.

In spite of the valuable hypnotic properties of 5-ethylphenylbarbituric acid ("Luminal") but few aryl substituted barbituric acids have been prepared. This is probably largely due to the fact that barbituric acids of this type are difficult to synthesize.

The method which has been generally applied to the synthesis of 5-phenylbarbituric acids has been as follows. Esters of phenylacetic acid have been condensed with esters of oxalic acid to produce an ester of phenyloxalylacetic acid and the latter compound decomposed by heat with loss of carbon monoxide and formation of an ester of phenylmalonic acid.[3] The latter compounds, on condensation with urea, give the desired product.

For the synthesis of Luminal a further method of preparation of the intermediate methyl ethylphenylmalonate has recently been described by Rising and Zee.[4] The procedure recommended involves the following steps: ethylation of phenylacetonitrile; condensation of the sodium salt of phenylbutyronitrile with methyl chloroformate to form methyl ethylphenylcyano-acetate; treatment of the latter substance with a methyl alcohol solution of hydrogen chloride to form the desired ester.

Inasmuch as it is our purpose to prepare a number of derivatives of phenylbarbituric acid, it appeared to us highly desirable to have a method as satisfactory as possible for the preparation of ethyl phenylmalonate, an intermediate useful for the preparation of all of them. For this reason considerable time was devoted to a study of the synthesis of this compound.

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[1] This investigation was conducted in cooperation with the National Research Council Sub-committee on Hypnotics, 1926.

[2] (a) Cretcher and Pittenger, THIS JOURNAL, 46, 1504 (1924); (b) 47,2560 (1925); (c) Cretcher, Koch and Pittenger, *ibid.*, 47, 3083 (1925).

[3] (a) W. Wislicenus, Ber., 27,1091 (1894); (b) Rising and Stieglitz, THIS JOURNAL, 40,723 (1918).

[4] Rising and Zee, THIS JOURNAL, 49, 541 (1927). Another paper by these authors has just appeared [THIS JOURNAL, 50, 1208 (1928)] wherein they describe an improvement of their method which produces an over-all yield of 43.1% of methyl ethylphenylmalonate from phenylacetonitrile.

It was first attempted to prepare ethyl phenylmalonate by condensation of ethyl phenylacetate with ethyl carbonate. The directness of the method is the important advantage which this process would have over that in common use. The condensation was attempted, under varying conditions, in alcohol, ether and benzene, and with both sodium and sodamide. Condensation was effected only with sodium and only in ether and benzene. At best (in benzene) it was not possible to obtain a yield greater than 20%, due to the condensation of ethyl phenylacetate with itself. This is in accord with the observations of Volhard[5] and of Scheibler and Mahboub.[6]

Our attention was then directed to phenylacetonitrile as a suitable intermediate for our purpose. The sodium salt, prepared with sodium in ether, was condensed with ethyl chloroformate. The yield of ethyl phenylcyano-acetate was only 50%.

We next studied the condensation of phenylacetonitrile with ethyl carbonate. The method of Hessler[7]—sodium as condensing agent, in ether—was repeated with results closely checking those of Hessler, who obtained a yield of 55% of ethyl phenylcyano-acetate. Sodium ethylate in alcohol gave 55% and sodamide in benzene gave 30%. By far the best results were obtained with sodamide in ether, according to the method of Bodroux[8] for the condensation of benzyl cyanide with esters. For maximum yield (70%) it is necessary to follow closely the conditions given in the Experimental Part of this paper.

Inasmuch as phenylmalonic esters are not alkylated in good yield, it was thought that it might be an advantage to alkylate phenylacetonitrile before attempting the condensation to introduce the second carboxyl group, In no case, however, did we succeed in condensing a substituted benzyl cyanide with ethyl carbonate.

The conversion of phenylcyano-acetate to ethyl phenylmalonate was effected most advantageously with hydrogen chloride and alcohol according to the method of Wislicenus.[9] It is essential that the alcoholic solution of the nitrile be thoroughly saturated with hydrogen chloride, as analysis showed in one case where saturation was not complete, a nitrogen content indicating 10% of unchanged nitrile, which is practically impossible to separate from the ester owing to the fact that their boiling points are only about three degrees apart.

The ethylation of ethyl phenylmalonate was accomplished most advantageously in alcohol solution with ethyl iodide or bromide or by heating the dry sodium salt of the ester with ethyl bromide in a sealed tube at

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[5] Volhard, *Ann.*, **296**, 1 (1897).

[6] Scheibler and Mahboub, *Ber.*, 60, **564** (1927).

[7] Hessler, *Am. Chem. J.*, **32**, 119 (1904).

[8] **Bodroux**, *Compt. rend.*, **151**, **234**, **1358** (1910)

[9] Wislicenus, *Ann.*, **296**, **361** (1896).

110° without a solvent. Ethylation in alcoholic solution is attended by decomposition of the ethyl phenylmalonate and production of ethyl phenylacetate.[10] It was observed that in case an excess of sodium is used decomposition may be practically complete.

Since our primary interest was not in the discovery of an improved process for making Luminal, we have not occupied ourselves to any extent with the preparation of this substance. A few experiments were conducted on condensing ethyl phenylethylmalonate with urea. The yields averaged between 30–40% and were of the same order as reported by Rising and Stieglitz from the condensation of the methyl ester with urea.[3b]

For the preparation of 5-β-hydroxyethylphenylbarbituric acid according to the method devised in this Laboratory for preparing β-hydroxyethyl compounds,[2c,11] it was necessary to prepare ethyl phenyl-β-vinyloxyethylmalonate as an intermediate. Its synthesis from ethyl phenylmalonate and β-chloro-ethylvinyl ether offered some difficulty in contrast to the ease with which ethyl vinyloxyethylmalonate is prepared from ethyl malonate.[12]

Attempts to condense the sodium salt of the ester with the chloro compound in alcohol, ether, benzene, toluene and xylene were unsuccessful. It was only upon heating the components in a sealed tube in absence of a solvent that we were able to obtain the desired product in appreciable amount.

Experimental Part

Ethyl Phenylcyano-acetate.—Three hundred grams of anhydrous ether and 42 g. of pulverized sodamide were placed in a dry two-liter three-necked, round-bottomed flask. A mercury sealed stirrer passed through the middle neck and a dropping funnel and tall reflux condenser were fitted to the side necks. During constant stirring, 117 g. of freshly distilled phenylacetonitrile was added drop by drop. A vigorous reaction ensued with evolution of ammonia. After all of the nitrile had been added, the reaction mixture was boiled in a water-bath for one-half hour. After cooling to room temperature, 150 g. of freshly distilled ethyl carbonate was added drop by drop. Replacement of the ether lost by evaporation is frequently necessary. After all of the carbonate had been added, the flask was warmed another half hour; then it was cooled in an ice-bath and treated with dilute hydrochloric acid until the aqueous layer was acid to litmus. The product was filtered and the ethereal layer separated and dried over calcium chloride.

After removal of the ether and fractionally distilling *in vacuo*, 133 g. of the desired ester was obtained, boiling (7 mm.) at 140–148° (nearly all at 145°). This is a yield of 70.3%.

A portion was further purified by redistillation. It was a colorless liquid and boiled at 165° at 19 mm.; $d_4^{20} = 1.091$.

Ethyl Phenylmalonate.—A rapid stream of dry hydrogen chloride was passed into a solution of 45 g. of ethyl phenylcyano-acetate, 65 g. of 95% alcohol and 2 g. of water. The flask was connected with a condenser and the hydrogen chloride added to saturation

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[10] Wislicenus, *Ber.*, 28, 815 (1895).

[11] Cretcher, Koch and Pittenger, THIS JOURNAL, 47, 1173 (1925).

[12] Ref. 11, p. 1176.

of the hot solution. The reaction mixture was then cooled in an ice-bath and the cold solution saturated with hydrogen chloride. The flask was allowed to stand overnight at room temperature and on the following morning was heated one hour on a steam-bath. After cooling, sufficient water was added to dissolve the precipitated ammonium chloride; the ester was extracted with ether, washed with water and dried over calcium chloride. After removal of the ether the residual liquid was distilled. A yield of 44 g. (78.3%) of ethyl phenylmalonate was obtained at 163–166° at a pressure of 18 mm.

A portion was further purified. It was a colorless liquid and boiled at 168° (19 mm.); $d_4^{20} = 1.095$. Wislicenus[13] reported the boiling point to be 170–172° at 14 mm. He did not determine the density.

Ethyl **Phenylethylmalonate**.—This ester was produced most satisfactorily by the reaction of ethyl iodide or bromide with the sodium salt of ethyl phenylmalonate in boiling absolute alcohol. With ethyl iodide the yield was 61.1%. This ester boils at 170° (19 mm.); $d_4^{20} = 1.071$. The boiling point given in U. S. Patent 1,036,624 is 166° at 12 mm.

5-Phenylethylbarbituric Acid **(Luminal)**.—Luminal was prepared as follows: 0.69 g. of sodium was dissolved in 11 g. of absolute alcohol in a glass tube and 0.9 g. of powdered urea added to the solution; 2.64 g. of ethyl phenylethylmalonate was then added. The tube was sealed and heated in an oil-bath at 115° for three hours. The tube was then cooled, opened and the contents filtered. Alcohol was removed from the filtrate by distillation *in vacuo*. The residue was dissolved in water and the unaltered ester removed by extraction with ether. The aqueous layer was acidified with a slight excess of dilute hydrochloric acid. A pure white crystalline substance was precipitated. After filtering and drying, the crude product melted at 171°. Upon recrystallization from water the melting point was 173–174°. The yield was 35% of the theoretical.

Ethyl **Phenylvinyloxyethylmalonate**.—After many unsuccessful attempts to prepare this ester in good yield, the following procedure was adopted: 2.3 g. of sodium was pulverized in boiling xylene. The containing tube was cooled, the xylene decanted and the sodium washed quickly with several portions of anhydrous ether. Forty g. of dry ether was added and then 23.6 g. of ethyl phenylmalonate in small portions. There was a very vigorous reaction. A calcium chloride tube was attached to the condenser and the reaction mixture allowed to stand overnight. The ether was then removed by boiling, finally under vacuum. Thirty g. of β-chloro-ethylvinyl ether was added, the tube sealed and heated at 140–145° for fourteen hours. After cooling the tube was opened, water added to dissolve the salt and the ester extracted with ether. After removal of the ether, 15.5 g. of product was obtained, boiling mostly at 189–190° at 10 mm. This is a yield of 52%.

The compound was further purified by redistillation for analytical purposes. Ethyl phenylvinyloxyethylmalonate boils at 196–197°, 17 mm. $d_4^{20} = 1.098$. It decomposes on standing in sunlight, the odor of acetaldehyde being quite strong after several weeks.

Anal. Calcd. for $C_{17}H_{22}O_5$: C, 66.63; H, 7.24. Found: C, 66.43; H, 7.42.

5-(Phenyl-β-hydroxyethyl)-barbituric Acid **(Hydroxy-Luminal)**.—The condensation of ethyl phenylvinyloxyethylmalonate and urea to form 5-phenylvinyloxyethylbarbituric acid was accomplished under exactly the conditions described for the preparation of Luminal. The vinyloxy compound was not isolated in pure form but converted directly into the hydroxy-Luminal by hydrolysis with acid.[2c] For purification the substance was crystallized from water. The yield of pure hydroxy-Luminal, melting at 200°, was only about 10% of the theoretical.

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[13] Wislicenus, *Ber.*, 27, 1093 (1894).

Anal. Calcd. for $C_{12}H_{12}O_4N_2$: N, **11.30.** Found: N, **11.21.**

5-(Phenyl-β-hydroxyethyl)-2-thiobarbituric Acid.—This compound was prepared by condensation of ethyl phenylvinyloxyethylmalonate with thiourea. The procedure was the same as that given directly above, m. p. 167°. The yield was 15%.

Anal. Calcd. for $C_{12}H_{12}O_3N_2S$: N, **10.6.** Found: N, **10.9.**

Phenylvinyloxyethylacetonitrile $C_6H_5CH(CH_2CH_2OCH{=}CH_2)CN$.—This nitrile was prepared by reaction of phenylacetonitrile and β-chloro-ethylvinyl ether, according to the general method devised by Bodroux and Taboury.[14] The yield was 50%. The pure compound boils at 147° (8 mm.); $d_4^{20} = 1.029$.

Anal. Calcd. for $C_{12}H_{13}ON$: N, **7.48.** Found: **N, 7.33.**

Summary

1. A convenient method for the preparation of ethyl phenylmalonate has been described.
2. A new barbituric acid closely related to Luminal, 5-phenyl-β-hydroxyethyl-2,4,6-trioxypyrimidine, has been synthesized.

PITTSBURGH, PENNSYLVANIA

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

THE REACTION BETWEEN THE BINARY SYSTEM, MAGNESIUM + MAGNESIUM IODIDE, AND AROMATIC ACIDS AND ACID DERIVATIVES

BY M. GOMBERG AND W. E. BACHMANN

RECEIVED JULY 9, 1928 PUBLISHED OCTOBER 6, 1928

The interaction of magnesium + magnesium iodide and aromatic ketones results in addition of MgI to the C=O group.[1] A similar reaction occurs with 1,2-diketones,[2] with thio-ketones[3] and apparently with quinones.[4] The MgI, the probable formation of which has been postulated, may thus be regarded as functioning like a monovalent element, as sodium. This comparison holds in reactions that are to be discussed in this communication on acids and in communications to follow, on various classes of compounds containing double and triple bonds.

Reaction of Acids with Magnesium + Magnesium Iodide.—This reaction takes place in two steps: (a) displacement of the acid hydrogen by MgI and (b) reduction of the resulting salt.

The displacement of hydrogen is best explained by the fact that there is an equilibrium reaction between MgI_2 and the organic acid. Only a small amount of HI results by virtue of this reaction; nevertheless, in the

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[14] Bodroux and Taboury, Bull. *soc. chim.*, [7] 4, 666 (1910).

[1] Gomberg and Bachmann, THIS JOURNAL, **49**, 236 (1927).

[2] Gomberg and Bachmann, *ibid.*, **49**, 2584 (1927).

[3] Schönberg and Schütz, *Ber.*, 60, 2351 (1927).

[4] Fieser, THIS JOURNAL, **50**, 464 (1928).

presence of metallic magnesium, which reacts with the HI, the reaction proceeds quantitatively according to the following formulation

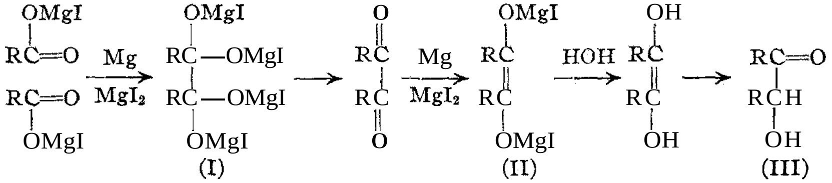
$$2RCOOH + Mg + MgI_2 \longrightarrow 2\ RCOOMgI + H_2 \tag{1}$$

In the course of the reaction the iodomagnesium salt[5] suffers a partial decomposition into the magnesium salt and magnesium iodide, an equilibrium apparently being established between the components of the system

$$2RCOOMgI \rightleftharpoons (RCOO)_2Mg + MgI_2 \tag{2}$$

Since magnesium iodide is thus being regenerated, it follows that a small amount of halide may suffice for a large amount of acid.

With the evolution of hydrogen from the acid at an end, reduction of the salt ensues. Since the hydrogen escapes as such, it is obvious that the reduction is not occasioned by the hydrogen but by the binary system. The reduction proceeds, presumably, along the following course



(3)

Addition of water to the reduction mixture hydrolyzes the iodomagnesium compound of the stilbene-diol (11), and the corresponding benzoin (III) is produced. The yields of benzoins obtained varied, however, with the conditions of experiment and with the nature of the individual acid, and ranged from **30** to 75%. We have reason to assume that the glycolate (II) is practically the sole product of the reduction, and that the low yields of benzoin are due to some subsequent decomposition of the glycolate. Occasionally more than just a small amount of the corresponding benzil is produced, an indication that in such cases some of the product (I) has escaped further reduction to product (II).

Reaction of Esters.—Alkyl esters of aromatic acids are saponified by magnesium iodide in ether solution[6]

$$RCOOCH_2R' + MgI_2 \rightleftharpoons RCOOMgI + ICH_2R' \tag{4}$$

We found that this reaction proceeds in a solution refluxed on the steam-bath. Consequently, in the reaction of the ester with our binary system, saponification takes place first, and this is followed by reduction of the resulting iodomagnesium salt to the precursor (II) of benzoin. At the

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[5] Whether the iodomagnesium salt has the constitution assigned to it or whether it be of the type $(RCOO)_2MgMgI_2$ [Ivanov, *Compt.* rend, 185, *505* (1927)], does not affect our discussion. However, like Grignard and others [Grignard, *Compt. rend.*, 185, *507* (1927); Meisenheimer, *Ber.*, 61, 708 (1928); Meisenheimer and Schlichenmaier, *Ber.*, 61, 720 (1928)], we are of the opinion that the monomolecular formula best represents the structure of the salt.

[6] Zal'kind, J. *Russ. Phys.-Chem. Soc.*, 46, 692 (1914).

same time the alkyl halide, which has resulted from saponification, reacts with the magnesium and there may thus be formed a hydrocarbon, $R'CH_2$-CH_2R', and also the Grignard reagent, $R'CH_2MgI$; the latter may in its turn react with unsaponified ester and with the salt. It may be mentioned that benzoin has been observed also as one of the products of the action of sodium on esters.

Aryl esters, as phenyl benzoate, are split in a manner different from that in the case of alkyl esters

$$\text{RCOOAr} + \text{MgI}_2 \rightleftharpoons \text{RCOI} + \text{IMgOAr}\ (\text{Ar} = \text{Aryl}) \qquad (5)$$

Since no iodomagnesium salt has been formed, no benzoin results on subsequent treatment with the binary system. The acyl iodide, we find, does not yield the stilbene glycolate on reduction, nor does it give rise to benzil when treated with metallic magnesium.[7]

Reaction of Peroxides.—Acyl peroxides react vigorously with magnesium iodide alone

$$\text{RCOO—OOCR} + 2\text{MgI}_2 = 2\text{RCOOMgI} + \text{I}_2 \qquad (6)$$

Likewise, bromine is set free from magnesium bromide. In the presence of magnesium, the halogen is converted into magnesium halide and the organic salt is then reduced to the stilbene-diol compound.

Experimental

Displacement of Hydrogen from the Acids.—Metallic magnesium reacts very slowly with the organic acids dissolved in anhydrous ether or benzene, or in a mixture of both, in the concentrations employed in our experiments (about 5%). Even on prolonged boiling with solutions of acids of twice that concentration only a small quantity of hydrogen is evolved. If, however, to the mixture a small amount of iodine or of magnesium iodide (3 to 10%) is added, the reaction sets in at once—vigorously at the start but soon subsiding. The metal before long becomes coated with the insoluble magnesium salt and the reaction stops entirely. On the other hand, if magnesium iodide is present in amount sufficient to furnish the halomagnesium salt (Equation 1), then the reaction goes to completion in a short time. After many preliminary experiments the following method was adopted as the most suitable for determining the quantity of hydrogen evolved.

A solution of 0.01 mole of magnesium iodide was prepared in 60 cc. of a mixture of ether and benzene (1:2) and a weighed amount of magnesium powder (usually 0.6 g.) was added. The reaction flask was attached by means of a ground-glass connection to a small condenser, from the top of which a capillary tube led to a gas buret filled with water. Between the condenser and buret was a calcium chloride tube. The acid (0.02 mole), in the form of pellets, was supported on a glass basket,[8] which was set above the level of the liquid and so arranged that when the solution was boiling the condensate dripped down upon the acid and brought it down into the solution only gradually. A steady stream of hydrogen was evolved into the buret and the reaction was at an end in fifteen to twenty minutes. In the following table are given representative values obtained with several acids.

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[7] Compare Staudinger and Anthes, *Ber.*, 46, 1417 (1913); Tistchenko, *Bull. soc. chim.*, [4] 37, 623 (1925); Karrer and co-workers, *Helv. Chim. Acta*, 11, 233 (1928).

[8] Gomberg, This Journal, 45, 401 (1923).

TABLE I

HYDROGEN DISPLACED IN REACTION $RCOOH + Mg + MgI_2$

Add	Mg diss., % of calcd.	H % of calcd.	Acid	Mg diss., % of calcd.	H % of calcd.
Benzoic	**108**	**89**	Phenylacetic[a]	**103**	**117**
p-Toluic	**102**	**81**	Diphenylacetic	**94**	97
α-Naphthoic	**100**	**86**	Stearic	**90**	**87**
β-Naphthoic	**104**	**93**			

[a] We have repeated this experiment several times, using most carefully purified acid, and have always obtained the high yield of hydrogen. We wonder whether this may not be due to replaceability of the hydrogen in the alkyl group, similar to what Kohler, Stone and Fuson, THIS JOURNAL, 49, **3181** (1927), have found to be the case with many compounds toward the Grignard reagent.

The formation of hydrogen in our reaction depends primarily upon liberation of hydrogen iodide, which then reacts with the metallic magnesium $RCOOH + MgI_2 \rightleftharpoons RCOOMgI + HI$; $Mg + 2HI \longrightarrow MgI_2 + H_2$. The presence of the equilibrium was demonstrated by the following experiment. **A** mixture of benzoic acid and magnesium iodide, without metallic magnesium present, was refluxed for twenty-four hours; under these conditions the HI, which otherwise would have reacted with magnesium, was now continually being removed through its reaction with the ethyl ether, tending to form ethyl iodide.[9] From **12.2** g. of acid and **32** g. of MgI_2, **12.3** g. of ethyl iodide was obtained. Even in the presence of metallic magnesium this reaction took place to some extent. This reaction, and loss of some HI carried away by escaping hydrogen, accounts for the low yields of hydrogen obtained (Table I).

That hydrogen iodide, under the conditions of our experiments, does react with magnesium in the presence of ether with evolution of hydrogen was definitely established.[10] Dry hydrogen iodide was passed into benzene and it was found that this solution did not react with magnesium. However, addition of an equal volume of ether to this mixture induced *immediate* reaction with extremely lively evolution of hydrogen The quantity of gas corresponded to 96% of the magnesium that had been dissolved. We found also that hydrogen bromide and magnesium react in a mixture of ether and benzene with evolution of hydrogen. Though HCl alone in ether-benzene did not react, the addition of $MgBr_2$ brought about a reaction. On several occasions we analyzed the seemingly homogeneous crystalline deposit that had separated and found it to be not far from the composition $BrMgCl$, or $MgCl_2 \cdot MgBr_2$.

If the reaction mixtures from the organic acids are hydrolyzed soon after all of the hydrogen has been evolved, practically all of the acid can be recovered unchanged from the aqueous solution of its salts. In the case of benzoic acid traces of hexahydrobenzoic acid were unmistakably recognized. Prior to hydrolysis the iodomagnesium salts separated from the solution usually as insoluble, oily etherate compounds; in rare cases crystallization set in. We isolated and analyzed these solid products and found that they consist of mixtures of the halomagnesium and the normal magnesium salts of the acids. In one instance, with benzoic acid, the crystalline compound was almost entirely the pure salt $RCOOMgI$.

Magnesium bromide was found to give insoluble addition products with organic acids, $2RCOOH \cdot MgBr_2 \cdot 2C_4H_{10}O$. As a rule the corresponding magnesium iodide

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[9] Silva, *Ber.*, **8,904 (1875);** Cottrell and Rogers, *Am. Chem. J.*, **21,** 64 **(1899).**

[10] Zelinsky, *J. Russ. Phys.-Chem. Soc.*, *35,* **404 (1903);** see, however, Hess and Rheinboldt, *Ber.*, 54, **2043 (1921).**

compounds were soluble under similar conditions. With toluic acid, however, a crystalline compound of the composition $2RCOOH \cdot MgI_2 \cdot 2C_4H_{10}O$ was formed.

Reduction of Acids

The amount of magnesium iodide employed for reduction usually corresponded to that required by the formulation (3). Frequently much less was used in virtue of the ability of the iodomagnesium glycolate to lose MgI_2.[11]

Reduction of Benzoic Acid.—A mixture of magnesium + magnesium iodide was prepared from 95 g. (0.75 atom) of iodine and 20 g. of magnesium powder in 100 cc. of ether and 200 cc. of benzene. To this colorless mixture 30.5 g. (0.25 mole) of benzoic acid was added in portions. When the lively evolution of gas had ceased, the mixture, protected from air by means of a mercury trap, was heated on the steam-bath. After five days of heating the dark, reddish-brown solution was filtered from the undissolved magnesium and treated with water. Dilute acid was added to dissolve the copious precipitate of magnesium hydroxide that had been produced. The organic solution was extracted with dilute sodium carbonate solution, which removed unchanged benzoic acid. Evaporation of the solvents left a solid contaminated with some oily by-products, and these were removed by digestion of the crude product with ether. The residue consisted of practically pure benzoin, and weighed 12.0 g., which represents a yield of 30%. From the ether extract a small amount of benzoin and benzil were isolated. In another experiment the yield of benzoin was 43%. One reason for the reaction being incomplete appears to be the precipitation of an insoluble material upon the magnesium, probably an etherate of $(MgI)_2O$. The reaction was also carried out at room temperature. A mixture prepared exactly as above, after having been shaken for eighteen days, yielded on hydrolysis 34% of benzoin and 4% of benzil. The remainder was mostly unchanged benzoic acid, with hardly any oily by-products such as occur when the reaction has been carried out by the aid of heat.

Prior to hydrolysis the reduction product is the iodomagnesium salt of stilbene-diol. Its reactions were compared with those of the same glycolate but made directly from benzil, and were found to be identical: treated with iodine, it gave benzil: with benzoyl chloride, the stilbene-diol dibenzoate, m. p. 156°, was formed.

For further verification of our inference that benzoin comes from the reduction of the salt $C_6H_5COOMgI$, we have prepared that salt by two standard methods: $RCOOH + CH_3MgI \longrightarrow RCOOMgI \longleftarrow CO_2 + IMgR$. In each case the reaction mixture was heated with metallic magnesium and the final results were 46% and 20% yields of benzoin, respectively. In some instances one may find it desirable, from the preparative point of view, to make a benzoin from the aryl halide without isolation of the intermediately formed acid. We have done so with benzoin and α-naphthoin from phenyl bromide and naphthyl bromide, respectively.

Reduction of *p*-Toluic Acid.—Taken for experiment: 13.6 g. (0.1 mole) of p-toluie acid, 38 g. (0.3 atom) of iodine and 10 g. of magnesium powder in 150 cc. of benzene–ether (2:1). In a short time the evolution of gas was at an end and the mixture was gently refluxed on the steam-bath for three days. The dark, reddish-brown solution was filtered and decomposed with water. A large amount of toluic acid was extracted from the solution by sodium carbonate. The reduction product was found to consist for the most part of dimethyl benzil rather than the benzoin. Consequently the entire crude product was oxidized to the benzil by heating it for several hours with 8 g. of copper sulfate, 8 g. of pyridine and 4 g. of water. After purification the *p,p'*-dimethyl benzil

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[11] Gomberg and Bachmann, THIS JOURNAL, 49, 2588 (1927).

weighed 3.59 g. (30% yield). The substance melted at 102–104°, and it was found to be identical in all respects with the dimethyl benzil obtained from *p*-tolualdehyde through the benzoin condensation.

Reduction of **α-Naphthoic** Acid.—To the binary system prepared from 15 g. (0.1 atom) of iodine and 10 g. of magnesium powder in 120 cc. of 1:1 ether–benzene, 17.2 g. (0.1 mole) of α-naphthoic acid was added in portions of several grams at a time. After hydrogen had ceased coming off, the mixture was heated. In a few minutes the solution became green in color, then greenish-brown and finally dark reddish-brown. After seven hours the heating was discontinued and the mixture was hydrolyzed. The naphthoic acid that was recovered by extraction with sodium carbonate was contaminated with a gummy product which was found to be very soluble in cold benzene and could thus be removed, leaving 3.05 g. of naphthoic acid. Evaporation of the ether–benzene solution left a residue consisting of a mixture of naphthoin, naphthil and some oil. For a determination of the extent of reduction which the acid had suffered, the crude product was oxidized by means of copper sulfate and pyridine to naphthil. The oxidation product was recrystallized from benzene and obtained in the form of pale yellow needles; m. p. 189–190°; weight, 4.85 g., which is equal to 31% of that possible. Our a-naphthil was found to be identical with the product obtained by oxidation of a-naphthoin which had been prepared from the naphthaldehyde. Although the conditions of reduction of the acid were varied over a wide range, the yield of α-naphthoin or naphthil invariably ran between 30 and 35%.

Reduction of **β-Naphthoic** Acid.—Taken for reaction: 17 g. of iodine, 12 g. of magnesium, 200 cc. of ether–benzene, 17.2 g. of β-naphthoic acid. A few minutes after evolution of hydrogen had ceased, the mixture became light green, then dark green and finally dark reddish-brown in color. After eleven hours the solution was filtered and decomposed with water. The amount of unchanged naphthoic acid was 8% and the reduced product consisted of naphthoin mixed with a considerable quantity of naphthil. The mixture was oxidized by means of copper sulfate and there was thus obtained 11 g. of pure recrystallized β-naphthil, which represents a yield of 70%. Several smaller runs gave yields as high as 75%. From hot benzene the β-naphthil crystallizes in cream-colored needles; m. p. 157–158".

Anal. Calcd. for $C_{22}H_{14}O_2$: C, 85.18; H, 4.55%. Found: C, 84.90; H, 4.84. Mol. wt. Calcd.: 310. Found: 323.

The amount of metallic magnesium dissolved in the come of the reduction process and the magnesium hydroxide produced on hydrolysis of the reduction mixture were determined and they were found to correspond to that required by formulation (3).

Reduction of ***p*-Phenylbenzoic** Acid.—A mixture of 4.0 g. of p-phenylbenzoic acid, 4.0 g. of magnesium iodide and 5 g. of magnesium powder in 60 cc. of benzene–ether (2:1) was heated for five days. In the course of the reaction the solution became green and then reddish-brown in color. After hydrolysis a small amount of unchanged acid was recovered and from the reduction product, after treatment with copper sulfate, 1.7 g. (46%) of *p,p'*-diphenyl benzil was obtained. It was recrystallized from a mixture of alcohol and benzene and was obtained in the form of yellow needles, m. p. 139–140°. It was identical with *p,p'*-diphenyl benzil which had been synthesized through the benzoin condensation from *p*-phenylbenzaldehyde.

Reaction of Esters with Mg + MgI_2

Saponification of Benzyl Benzoate by Magnesium Iodide.—Fifty-three grams (0.5 mole) of benzyl benzoate was added to a solution of 70 g. of magnesium iodide in 300 cc. of ether–benzene (1:2), and the resulting solution was heated on the steam-bath for one week. The red solution was then poured into water. In the aqueous solution was found 30.32 g. (99%) of benzoic acid in the form of water-soluble salts. The ether–benzene solution was dried over anhydrous sodium sulfate and then concentrated to a small volume. On being cooled the solution deposited a large amount of benzyl iodide. By recrystallization from alcohol, 20 g. of pure benzyl iodide was obtained.

Reduction of Benzyl Benzoate.—Taken for experiment: 25.6 g. (0.2 atom) of iodine, 10 g. of magnesium and 21.2 g. (0.1 mole) of the ester, in 120 cc. of the mixed solvents. After a day the greenish color initially formed changed to brown and later to reddish-brown. After being heated for a week the solution was filtered and hydrolyzed. From the ether–benzene solution was obtained a mixture of bibenzyl and benzoin, and they were separated from each other by dissolving the former in petroleum ether. After purification the bibenzyl weighed 6.2 g (70%) and the benzoin amounted to 4.8 g. (45%).

Methyl Benzoate.—Thirty-four grams of this ester was heated with the proper amount of magnesium + magnesium iodide, and yielded 2.2 g. of benzoin. Here the yield of benzoin is necessarily small because the methyl iodide that is produced on saponification forms readily with the magnesium a Grignard reagent, which in turn is able to react with the ester or salt.

Phenyl Benzoate.—No benzoin was obtained on heating 10 g. of phenyl benzoate with the reducing mixture. The main products were phenol, 4.2 g. (90%) and a resinous mass which was found to be soluble in the usual organic solvents, but no crystalline products were obtained for identification. We find that benzoyl iodide treated with the binary system gives resins of a similar nature.

Reaction between Benzoyl Peroxide and Mg + MgI$_2$.—A solution of 4.88 g. (0.2 mole) of benzoyl peroxide in 50 cc. of benzene was slowly added to a solution of magnesium iodide in ether–benzene. The very first drop of the peroxide solution liberated iodine, and as more solution was added the mixture became dark red and a heavy oil of the etherate of iodomagnesium benzoate separated. After twenty hours the mixture was poured into water. From the aqueous solution, on acidification, 4.90 g. (100%) of benzoic acid was obtained. Titration by standard thiosulfate solution showed the presence of 5.0 g. (99%) of iodine. In the same manner benzoyl peroxide liberated bromine from magnesium bromide.

For reduction, 30.3 g. of benzoyl peroxide was cautiously added to a mixture of magnesium and magnesium iodide prepared from 65 g. of iodine and 10 g. of magnesium in 300 cc. of ether–benzene. Each addition of peroxide was accompanied by hissing and crackling noises, and by liberation of iodine. Most of this iodine reacted at once with the magnesium. The grayish mixture was heated for four days. Hydrolysis then gave 12 g. of benzoin, which represents a yield of 45%.

Summary

Organic acids in solution in ether and benzene react vigorously with the binary system Mg + MgI$_2$, hydrogen is evolved and the acid is converted completely into the salt RCOOMgI. This salt then undergoes reduction and, at least in the case of aromatic acids, the reduction product is R(IMgO)C=C(OMgI)R, which when hydrolyzed gives rise to the corresponding benzoin in yields of 30 to 75%. The reducing effect of the binary system is ascribed to the intermediate formation of the compound MgI.

Alkyl esters of aromatic esters and acyl peroxides are reduced by the binary system in a similar manner. Aryl esters are affected differently.

The reduction of acids or of esters by this binary system offers a con-

venient method for obtaining benzoins. This method should prove particularly useful in those instances when the aldehyde requisite for the usual benzoin condensation is not readily accessible.

ANN ARBOR, MICHIGAN

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY,
MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 33]

THE RELATIVE RATES OF BROMINATION OF THE OLEFINS[1]

BY HAROLD S. DAVIS[2]

RECEIVED JULY 10, 1928 PUBLISHED OCTOBER 6, 1928

This paper deals mainly with experimental work on the rates of reaction of the lower olefins with bromine, particularly in carbon tetrachloride solution.

1. The Dark Reaction of Ethylene with Bromine in Dry Carbon Tetrachloride Solution Is Very Slow.—Contrary to general belief,[3] it was found that ethylene brominates in carbon tetrachloride at a rate measurable with time and that if the solutions are dried and kept away from bright light, the reaction requires hours and even days for completion.

2. The Rate of the Dark Reaction of Ethylene with Bromine in Carbon Tetrachloride Varies Greatly with the Quantity of Moisture in the Solution.—Solutions of bromine in carbon tetrachloride were dried in the following ways: (*a*) by refluxing for four hours with phosphorus pentoxide and distilling into a dry receiver protected from moisture in the air by phosphorus pentoxide. In some cases the solution was first shaken for several days with phosphorus pentoxide before refluxing and distilling. (b) By shaking for different periods of time with phosphorus pentoxide and settling Evaporation tests on the clear supernatant liquid showed that it contained less than one part of phosphorus pentoxide in one hundred thousand by weight.

When dry ethylene was added to these solutions the reaction went quite

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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 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.

[2] Director and Research Associate, Project No. 19.

[3] Thus Plotnikov, "Lehrbuch der Photochemie," 1920, pp. 245–255, states that ethylene and bromine unite to form the dibromide at ordinary temperatures instantaneously and completely and the reaction only slackens to one measurable with time at −100°. Working at this temperature in petroleum ether solution, he found the reaction to be of the second order. On the other hand, Stewart and Edlund, THIS JOURNAL, 45, 1014 (1923), found ethylene and bromine to be practically unreactive in the gaseous state.

slowly in the absence of light. Numerous experiments showed the reactions to be of the second order and in solutions 0.05 M for both bromine and ethylene, the lowest value obtained for the reaction coefficient,[4] K, at 25° was 0.006.

An indication of the quantitative relationships between the rate and the water content was obtained in the following experiment which showed the rate of reaction of ethylene with bromine in dry carbon tetrachloride to increase over five times on the addition of 5% by volume of carbon tetrachloride saturated with water.

TABLE I

EXPERIMENT SHOWING THE EFFECT OF WATER ON THE RATE OF DARK BROMINATION OF ETHYLENE IN DRY CARBON TETRACHLORIDE

Conditions: The bromine–carbon tetrachloride solution was distilled from phosphorus pentoxide, and ethylene dried by the pentoxide was added thereto. The course of the reaction was followed by the withdrawal of samples and titration for their bromine content. At the end of the fourth hour, 5% by volume of carbon tetrachloride saturated with water was added. (Water content of resulting solution 0.0005 *M*).[a] Temperature, 25°. *a* (ethylene) = *b* (bromine) = 0.057 M.

t, hours	0	1	2	3	4	5
% reacted	0	5	8	10	12	20
K		0.0167	0.0095	0.0063	0.0065	0.035

[a] C. W. Clifford, *J. Ind. Eng. Chem.*, 13, 632 (1921), gives the following values for the solubility of water in carbon tetrachloride expressed as grams per 100 g. of solution: at 24.0°, 0.010; at 28.5°, 0.013.

Preliminary experiments on the rates in solutions saturated with water at 25° gave much higher values for *K*(0.4 to 4.0).

It might have been expected, from analogy with the effect of water on the photochemical reaction of hydrogen and chlorine,[5] that changes in the water content would affect the rate only when the merest traces were present. This does not, however, appear to be the case. Careful quantitative measurements on the problem will be of considerable value.

It seemed unlikely that water was the only substance which would change the rate of this reaction and tests were made on the effects of two others known to be present in the solutions, namely, oxygen and hydrogen bromide.

The effect of oxygen on the reaction did not appear to be great. That it had no accelerating influence was shown by the fact that the rate could be made very slow in solutions which had been in intimate contact with air. Nor was any increase in the rate noticed when in one experiment a volume of air equal to that of the dissolved ethylene was forced into the reaction tube. That oxygen does not hinder the reaction is indicated by the fact that the rate was still slow in dry solutions from which most of

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[4] $K = 1/[t(a - b)] \ln[(a - x)/(b - x)]\, b/a$, where t = time in minutes, a = initial molar concn. of ethylene, b = initial molar concn. of bromine, and x = molar quantity of each combined in time *t*.

[5] Coehn and Jung, *Z. physik. Chem.*, 110, 719 (1924).

the air had been expelled by boiling for a few moments under reduced pressure. The following experiment shows that hydrogen bromide does not affect the rate.

TABLE II

EXPERIMENT SHOWING THAT HYDROGEN BROMIDE HAS LITTLE OR NO EFFECT ON THE RATE OF BROMINATION OF ETHYLENE IN CARBON TETRACHLORIDE

a (ethylene), 0.071 M; b (bromine), 0.056 M Dry HBr forced into tube equiv. if dissolved to 0.0517 M soln.

Bromine reacted, %	K	Bromine reacted, %	K
28	0.43	64	0.55
42	0.33	74	0.44

The small increase in K can probably be attributed to traces of moisture added with the hydrogen bromide and not to the latter.[6]

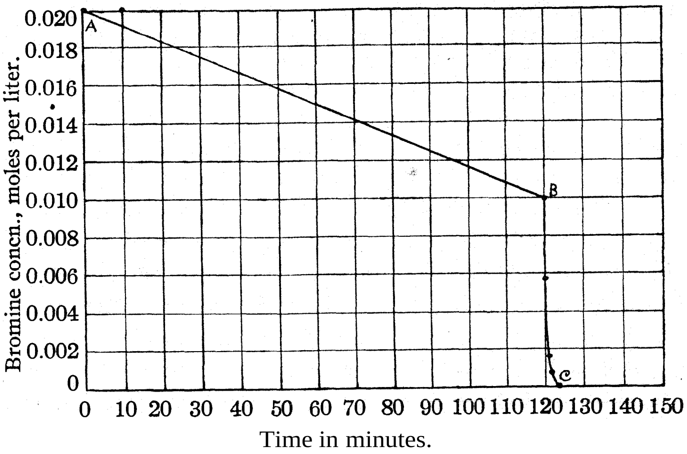

Fig. 1.—Curve showing the effect of sunlight on the rate of bromine addition to ethylene in carbon tetrachloride solution at room temperature. Ethylene concn., 0.06 M; bromine, 0.02 M. Curve A to B—rate of reaction in a 50cc. Nessler tube with light mainly excluded by a brass jacket, $K = 0.07$. Curve B to C—rate of reaction when the tube was removed from its jacket and exposed to bright sunlight, $K = 44$.

3. Bright Light Enormously Increases the Rate of Bromination of Ethylene in Carbon Tetrachloride.—This is illustrated by Fig. 1, which shows the effect of bright sunlight in speeding up the reaction. However, the rates were found to be little affected by illumination sufficient to permit color comparison measurements on the solutions in Nessler tubes, as described later.

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[6] However, Williams and James, J. *Chem. Soc.*, 1928 343, have shown that hydrogen bromide is a very effective catalyst in the addition reaction between ethylenic acids and bromine, Water and hydrogen chloride produce similar effects but not of the same degree.

4. The Rate of the Dark Bromination of Ethylene in Dry Carbon Tetrachloride Increases Progressively as the Temperature is Lowered from 25 to 0°.—In the following experiments the rates at 25 and 0° were found on the same mixture at different stages of the reaction by simply changing the temperature. This procedure was necessary because as already pointed out the rates in separate experiments with dry solutions vary greatly even at the same temperature due to differences in the residual moisture content.

TABLE III

THE RELATIVE SPEEDS OF THE DARK BROMINATIONS OF ETHYLENE IN DRY CARBON TETRACHLORIDE AT 25 AND 0°

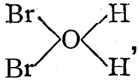
No.	Method of drying Br_2-CCl_4 soln.	Method of measurement	*K* 25°	0°	Ratios of K 25°	0°
1	Distn. from P_2O_5	Titration	0.008	0.4	1	50
2	Distn. from P_2O_5	Color comparison	.4	8	1	20
3	Shaking with P_2O_5	Color comparison	.013	1.4	1	110
4	Shaking with P_2O_5	Color comparison	.012	1.5	1	130

The reaction actually proceeds faster at 0° than at 25°. Measurements at intermediate temperatures have shown that there is no sudden change in the rate. It increases progressively as the temperature is lowered.

These are really very striking experiments. A solution of ethylene and bromine in dry carbon tetrachloride loses its color very slowly in the dark or even in ordinary daylight; but if placed in ice, or better in ice and salt, the color fades away rapidly even though the solution is kept absolutely in the dark. Reheating to 25° does not regenerate the color On the other hand, if the solution is heated up to 25° before decolorization is complete, then the rate falls off to what it was originally at that temperature, but can be speeded up again by lowering the temperature, etc.

That the decreasing of the color really measures the course of the reaction is shown by the following facts. 1. Similar results were obtained when the course of reaction was followed by titration of the bromine (Expt. I, Table III). 2. The color of a bromine–carbon tetrachloride solution changes little, if any, on cooling from 25 to 0°. 3. The quantity of bromine used up was found to be equimolecular to the ethylene, the latter being determined by the volume of ethylene added and the former by the volume of the bromine-carbon tetrachloride solution and its fall in concentration as determined by titration.

The bromine unites to the double bond in the ethylene and there is little substitution as measured by the hydrogen bromide evolved. Thus the products from Expt. 1, Table III (including the gases) were washed with about an equal volume of water which was then filtered and the bromide ion precipitated by silver nitrate). Nephelometric comparisons with similar clouds produced in known solutions of potassium bromide showed that less than 1% of the bromine which had entered into the reaction was to be found as hydrogen bromide.

5. It Is Suggested that the Dark Bromination of Ethylene in Carbon Tetrachloride Proceeds Mainly through a Bromine Hydrate and that the Concentration of this Hydrate Increases as the Temperature Is Lowered from 25 to 0°.—The fact that the dark bromination of ethylene in dry carbon tetrachloride goes very slowly indicates the bromine molecule as such to be relatively inactive toward this olefin. Since traces of water speed up the reaction, it seems reasonable to assume that this is accomplished through a union between the bromine and the water, for ethylene shows little tendency to add the latter, while hydrates of bromine are known to exist. Further, the union of bromine with water, which we may picture thus , so weakens the bond between the bromine atoms that in dilute aqueous solution the complex separates largely into hydrobromic and hypobromous acids.

In support of the hypothesis that the concentration of the hydrate increases as the temperature is lowered, the following facts may be cited. *(a)* The critical temperature of decomposition for the hydrate of bromine in open vessels is 6.8°.[7] (b) I found that the color of an 0.057 N aqueous bromine solution decreased about 40% on cooling from 25 to 3°. On reheating to 25" the color returned to its original value. (c) The "Budde Effect" in bromine vapor is probably due to a photo-active bromine hydrate of composition Br_2H_2O[8] and this effect increases as the temperature is lowered, indicating that the equilibrium $Br_2 + H_2O$ Br_2H_2O shifts to the right.[9]

This phenomenal increase in the rate of bromination of ethylene in dry carbon tetrachloride with decrease in temperature is of considerable interest.[10] It shows how minute traces of intermediate compounds may affect the temperature coefficient of a reaction. It is conceivable that in other cases they might cause an abnormal increase in the reaction rate with rise of temperature.

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[7] Mellor, "Treatise on Inorganic and Theoretical Chemistry," Longmans and Co., New York, **1922**, Vol. II, p. 71.

[8] Lewis and Rideal, *J.* Chem. *Soc.*, **1926**, **583.**

[9] Lewis and Rideal, *ibid.*, **1926**, 596.

[10] Bodenstein, "Photochemical Reactions in Liquids and Gases," The Faraday Society, **1925**, p. **533**, with great perspicacity has thus expressed himself regarding the "purely chemical dark reactions" which very often follow primary photochemical changes—"It need not appear strange that the velocity should decrease with a rise of temperature for the velocity of a reaction which 'uselessly' consumes the intermediate products **may** easily increase far more rapidly with the temperature than that of the reaction leading to the desired ultimate product."

The reactions I have described are, however, not initiated by visible light, since they take place in complete darkness.

6. The **Olefins Brominate** (Dark Reaction) at Very Different Rates in **Dry** Carbon Tetrachloride.—It has been shown that rates of dark bromination of ethylene in carbon tetrachloride can vary (one hundredfold, at least) with changes in the minute moisture content of the solution. It was further found that the rates of bromination of propene and several higher olefins are also greatly dependent upon the dryness of the solutions. Quantitative data on the relation between the rates and the moisture content for the separate olefines have not yet been obtained.[11]

Qualitatively it was found that, just as for ethylene, the bromination of propene goes considerably faster at 0° than at 25". On the other hand, temperature changes seem to have little effect on the rates of bromination of trimethylethene or di-isobutene in dry carbon tetrachloride. Note the following values for di-isobutene: at 25°, K = 23; at 3°, K = 21.

To be consistent with the hypothesis given above for ethylene, it must be considered that the main reaction here is not through a hydrate of bromine but either with the bromine itself or with an intermediate compound between the bromine and the solvent, or between the bromine and some impurity. The di-isobutene was only moderately pure and air was always present. Further, in the bromination of both trimethylethene and di-isobutene, large quantities of hydrogen bromide are given off. Although such foreign substances do not appreciably affect the rate of bromination of ethylene, they may influence that of a higher olefin.

Accordingly, it is not possible to give figures which will represent the relative rates of bromination of the olefins in carbon tetrachloride because the ratios change with the temperature and probably, as my results indicate, with the moisture content. Nevertheless, the data show tremendous differences in the rates at which the olefins are brominated. Thus on intensive drying the bromination of ethylene required days, that of propene, hours, but that of trimethylethene could not be extended beyond a few minutes. The lowest values obtained so far for the different olefins are as follows.

7. **Light** Increases the Rates of Bromination of the **Olefins** but Decreases the Relative Differences between Them.—In the following experiments the rates of dark bromination of the olefins in dry carbon

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[11] Reliable data on this subject may help to clear up the discordances found by other investigators of the rates of bromination of unsaturated compounds in carbon tetrachloride and other solvents. Thus Sudborough and Thomas, *J. Chem. Soc.*, 97, 715, 2450 (1910), found great variations (even 12-fold) in the reaction coefficient for the bromination of olefinic acids in this solvent, although their materials were purified with great care. They state that, "The only reason for this that we can offer is that a trace of some impurity has a considerable effect on the velocity of the reaction," and they also showed that the rate of bromination of crotonic acid is dependent on the dryness of the carbon tetrachloride. See also Herz and Mylius, *Ber.*, 39, 3817 (1906); Hofmann and Kirmreuther, Ber., 42, 4481 (1909).

tetrachloride were first found by the color comparison method and then before the reaction was complete the vessel A, Fig. 2, was exposed to radiation from a 200-watt, 120-volt, clear "Higrade" tungsten lamp suspended end on with the filament 20 cm. from the reaction tube. The reaction rate was again followed by color comparison.

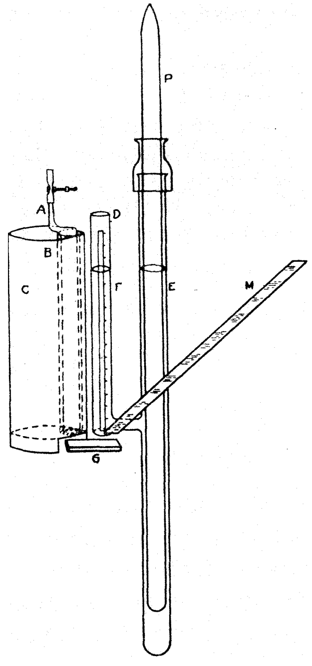

Fig. 2.—Diagram of apparatus used in the color comparison method. A—Reaction chamber' a 50-cc. tube with clear glass ends. B—Brass tube open at both ends and soldered through bottom of bath C. D—Nessler tube containing color standard. F—Scale lettered backwards. M—Mirror for reading scale from above. E—Auxiliary tube with plunger P for rapidly raising or lowering the liquid level in D. G—White surface to reflect light through reaction tube.

The following explanation is suggested for the striking fact that light greatly decreases the relative differences in the bromination rates of the olefins. Assume that an olefin molecule and a molecule of the brominating agent must together have a minimum of activity before interaction can take place. A highly active molecule of either can react with a relatively inactive one of the other. When now a large number of brominating molecules are highly activated by the absorption of light quanta, interaction is extended to olefin molecules which escaped in the dark because of the lowness of their activity. Further, since degrees of activity must be distributed among molecules somewhat like speeds according to the kinetic theory of matter, it is evident that the proportional number of additional molecules thus caught over unit time in the reaction net will be greatest for the olefin having the smallest number reacting in the dark. Thus in Table V, ethylene gave the least increase but the greatest proportional increase (200) for K under the influence of light.

From similar reasoning, water or other catalysts which increase the activity of the brominating agent should decrease the relative differences in the rates of reaction; and if an agent is found which increases the rates and also the relative differences in the rates of reaction of the olefins, we may feel sure that it is operating in some way through the olefin molecules and not through the other reactants.

8. Studies on the Reactions of Olefins with Halogens May Clear Up Many of the Questions Unanswered by Researches on the Photochemical Reactions of Halogens with Hydrogen.—There are many analogies between the reactions of halogens with hydrogen and with olefins. The following peculiarities of the latter type offer addi-

TABLE IV

LOWEST VALUES OBTAINED AT 25° FOR THE DARK BROMINATION RATES OF VARIOUS OLEFINS IN CARBON TETRACHLORIDE DRIED BY PHOSPHORUS PENTOXIDE. THE RELATIVE VALUES ARE ONLY QUALITATIVE

Olefin	K	Olefin	K
Ethylene	0.006[a]	2 Butene Isobutene	60.0
Propene	0.2	Trimethylethene	250.0
1-Butene	2.0	Di-isobutene	20.0

[a] The fact that the ethylene brominates at the slowest rate does not agree with the statement of Plotnikov, "Lehrbuch der Photochemie," 1920, 245, that ethylene reacts with bromine, the fastest of all the olefinic compounds. Suida and Wesley, Z. anal. *Chem.*, 64, 147 (1924), state that ethylene reacts the slowest of the olefins to bromine water but do not give the basis for this conclusion.

TABLE V

A COMPARISON OF THE LIGHT AND DARK BROMINATIONS OF OLEFINS IN DRY CARBON TETRACHLORIDE

Olefin	K, Dark reaction		K, Total light reaction	
	Values	Ratios	Values	Ratios
Ethylene	0.01	1	2	1
Propene	0.2	20	2.5	1.3
Di-isobutene	20.0	2000	40.0	20.0

tional opportunities for learning about the mechanisms involved.[12] *(a)* The reactions are not only photosensitive but proceed in the dark. *(b)* The nature of the unsaturated hydrocarbons can be modified by the radicals attached thereto and it is therefore much easier with olefins than with hydrogen to find what influence the substance being halogenated has on the reaction. (c) The effect of the solvent can be studied. Preliminary experiments showed that the rate of bromination of ethylene is much higher in acetic acid than in carbon tetrachloride, the lowest value obtained for K in the former solvent being 15 compared to 0.006 in the latter when both had been distilled from phosphorus pentoxide.

9. The Methods Used for Following the Course of the Brominations Were (A) Color Comparison with a Standard Bromine Solution, (B) Titration of the Bromine. Care Must Be Taken in the Preservation of the Dried Bromine–Carbon Tetrachloride Solutions.—A. In the color comparison method, the bromine concentration was measured by the height of a standard bromine solution necessary to give the same color intensity. The following measurements will show the degree of accuracy in these measurements.

Actual height of solution..................	100	67.4	60.6	29.6	26.2
Height estimated from color comparison....	100	66.8	54.8	29.9	23.7

The method has the disadvantage that some light must always be sent through the solution during the measurements but the low illumination

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[12] Plotnikov, ref. 3, has stressed the importance of research in this field.

required seems to have little effect on the reaction. It has the great advantages that no samples need be withdrawn from the sealed up reaction vessel and that as many measurements as desired can be made quickly.

Except for preliminary experiments, the reactions were carried out in closed tubes of the type shown in A, Fig. 2, which permitted clear vision through the glass surfaces at the top and bottom. Fifty cc. of the solution of bromine in carbon tetrachloride was placed in the tube through the side neck and then the olefin was added. If a liquid, it was measured from a pipet. If a gas, it was drawn into the partially evacuated chamber from a mercury buret.

There was a vapor space of about 15 cc. in the reaction tubes, but from solubility experiments[13] it was calculated that 93% of the ethylene and 99% of the propene were dissolved by the carbon tetrachloride. Accordingly, no correction was made for the undissolved part.

B. Titration.—In order to follow by titration the course of the bromination of an olefin in carbon tetrachloride, measured samples were removed at definite intervals and shaken with a little water saturated with potassium iodide. The precipitated iodine was then titrated. The bromine reacts with the iodide before the water can appreciably speed up the bromination of the olefin. The titration should be carried out at once as the brominated olefin products can slowly liberate iodine from potassium iodide.[14]

Some of the difficulties encountered in making these measurements account for the discrepancies shown in the results. At 25° carbon tetrachloride dissolves about 0.012% of water by weight, corresponding to a 0.01 *M* solution. Yet, apparently, it is the variations in this minute content which cause the differences in the dark bromination of ethylene in this solvent at 25°.

It is hard to dry carbon tetrachloride thoroughly but when once dry it does not readily take up moisture again. If a drop of water is added without shaking to a solution of equimolecular quantities of bromine and ethylene in dry carbon tetrachloride, the color may persist for a long time, although in solutions saturated with water it will disappear in a few minutes.

Naturally, moisture diffuses but slowly into dry carbon tetrachloride and when its solutions of bromine and ethylene are shaken with water, the greater part of the reaction takes place in the water phase. If potassium iodide is present in the latter, then apparently the bromine as it diffuses from the carbon tetrachloride into the water reacts much faster with the

[13] Carbon tetrachloride was saturated with the gaseous olefin by bubbling and the concentration of the solution determined by bromine titration. The following values were found for the solubility, X, expressed as the concn. of the dissolved olefin divided by the concentration of the gaseous olefin at equilibrium: ethylene at 25°, $X = 4.3$; ethylene at 0°, $X = 5.1$; propene at 25°, $X = 32$ (approx.).

[14] See Sudborough and Thomas, *J. Chem. Soc.*, 97, 717 (1910).

iodide than with the olefin. These facts are illustrated by the following measurements.

	Method of treatment of the bromine–carbon tetrachloride solution (10 cc. samples)	Concn. of bromine as shown by titration of the iodine
1.	Original solution shaken with potassium iodide solution	0.0558 M
	Solutions containing ethylene	
2.	After two minutes the sample was poured into potassium iodide solution and shaken	.0538 *M*
3.	Sample was poured into water, shaken and allowed to stand for ten minutes. Then potassium iodide solution was added	.0165 M
4.	One drop of water was added and the sample allowed to stand for ten minutes. Then it was poured into potassium iodide solution and shaken.	.0433 M

It is now evident that concordant results for the bromination of olefins in carbon tetrachloride cannot be expected unless the solutions have very accurately the same moisture content, and a large number of my results have had to be rejected on this account. Great care must be taken to preserve the dried solutions from atmospheric moisture. All samples removed must be replaced by dried air since there may be enough water vapor in air at 25° to form a solution over 10% saturated in an equal volume of carbon tetrachloride. As already shown, this may increase the bromination rate many times. Finally, bromine-carbon tetrachloride solutions decompose cork and rubber connections and must be preserved in all glass containers.

Materials.—Commercial refined ethylene was used. It dissolved at a slow, steady rate in 86% sulfuric acid (about 0.13% per pass into an Orsat pipet). This showed the absence of propene and higher olefins which are readily absorbed by this acid. Before use it was passed through two bubblers of concentrated sulfuric acid.

Propene was prepared by dehydrating C. P. isopropanol. The alcohol was kept well cooled and well stirred while an equal weight of phosphorus pentoxide was slowly added. On heating the product, propene was smoothly evolved. It was washed with dilute alkali and with water.

Isobutene was made by heating tertiary butanol (m. p. 15° and miscible without any cloud in water) with about one-third its weight of hydrated oxalic acid. The reaction proceeded smoothly at 87–100°, giving an almost quantitative yield of olefin.

1-Butene was prepared by warming normal butyl iodide (Eastman Kodak Co.) with saturated alcoholic potash containing about three times the quantity of hydroxide theoretically necessary. The product was washed well with water, liquefied and distilled. Coffin and Maass[15] have shown that this method yields a very pure product. It is, however, rather expensive.

Impure 1-butene was made by dehydrating normal butanol, b. p. 117.4–117.9°, at 340–360° over an active alumina catalyst which had never been heated above 400°; 80% of the alcohol passed was dehydrated and over 90% of this appeared as olefins. It has been reported that this method yields a mixture of 1-butene and 2-butene in

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[15] Coffin and Maass, THIS JOURNAL, 50, 1429 (1928).

the approximate proportions of 70 to 30.[16] I found that about 5% of the alcohol appeared as normal butyl ether.

When this olefin mixture was dried by rapid passage through phosphorus pentoxide and brominated in dry carbon tetrachloride, its bromination curve showed a very sharp break. About 35% (presumably 2-butene) reacted very rapidly and the remaining 65% slowly. This would indicate that the mixture contained about 35% of 2-butene and 65% of 1-butene.

The mixture was washed with 50% sulfuric acid and with 10% caustic potash, liquefied and distilled from sodium. A column was used provided with an evacuated and silvered jacket and with a still-head cooled by chilled air to −12°. The fraction boiling at −5.5 to −4.8°, which was 70% of the total, was collected and stored in a steel cylinder. Its dry bromination curve indicated that it contained 13% of 2-butene and 87% of 1-butene.

The main interest of these experiments lies in the possibilities they show of making pure I-butene by acid treatment and fractionation of the butene mixture obtained by dehydrating normal butanol over alumina.

2-Butene was prepared by dehydrating 2-butanol manufactured from petroleum gases. Harries[17] states that dehydration with phosphorus pentoxide gives a very pure product but obtained a yield of only 64%. It was found that excellent yields, over 90%, of olefin could be reached by heating the alcohol with about 1.5 times its volume of 86% phosphoric acid at 95 to 120°. The product was liquefied and distilled from calcium chloride in the column already described. The fraction boiling from 1.5–1.7° was collected. Its bromination curve showed that 84% brominated rapidly (2-butene) and the remaining 16% slowly.

A mixture of the product with 50% by volume of propene gave a bromination curve in dry carbon tetrachloride which indicated that approximately 50% of the material, evidently propene, had brominated at a much slower rate than the residue.

These preliminary results with mixtures of the butenes and propene show clearly the possibility of measuring the relative rates of bromination for two olefins under identical conditions by tests on known mixtures of the pure substances.

The trimethylethene obtained through the kindness of Dr. R. Reuter had been made by dehydrating tertiary amyl alcohol with 46% sulfuric acid; b. p. 38.4–38.5°.

The di-isobutene was prepared by distilling tertiary butanol with 50% sulfuric acid and fractionating the product; b. p. 101–103°.

The bromine before use was distilled from potassium bromide.

Carbon tetrachloride guaranteed to be free from sulfur compounds was used to make up the bromine solutions, which were then dried as already described.

Summary

1. The dark reaction of ethylene with bromine in dry carbon tetrachloride solution is very slow.

2. The rate of the dark reaction of ethylene with bromine in carbon tetrachloride varies greatly with the quantity of moisture in the solution.

3. Bright light enormously increases the rate of bromination of ethylene in carbon tetrachloride.

4. The rate of the dark bromination of ethylene in dry carbon tetrachloride increases progressively as the temperature is lowered from 25 to 0°.

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[16] Lépingle, Bull. *soc. china.*, [4] 39, 741, 864 (1926); Bull. *Amer. Petroleum Institute*, **8,** No. 54, 8 (1927).

[17] Harries, *Ann.*, **383,** 181 (1911).

5. It is suggested that the dark bromination of ethylene in carbon tetrachloride proceeds mainly through a bromine hydrate and that the concentration of this hydrate increases as the temperature is lowered from 25 to 0°.

6. The olefins brominate at very different rates in carbon tetrachloride.

7. Light increases the rates of bromination of the olefins but decreases the relative differences between them.

8. Studies in the reactions of olefins with halogens may clear up many of the questions unanswered by researches on the photochemical reactions of halogens with hydrogen.

9. The methods used for following the courses of the bromination were (A) color comparison with a standard bromine solution, (B) titration of the bromine.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 35]

THE RELATIVE RATES OF ABSORPTION OF THE GASEOUS BUTENES INTO SULFURIC ACID[1]

BY HAROLD S. DAVIS[2]

RECEIVED JULY 10, 1928 PUBLISHED OCTOBER 6, 1928

In 1909 Michael and Brunel[3] published data on the proportions of the butenes which were absorbed by sulfuric acid in Hempel pipets after definite periods of shaking. From inspection of the results they gave certain approximate figures for the relative rates of absorption of the three isomers.

Calculations from the data of Michael and Brunel show that in each experiment the rate of solution of the butene was approximately proportional to the quantity undissolved. The following table gives the values of K calculated for the separate experiments where $K = 1/t \ln 1/(1-x)$, t = minutes the pipet was shaken, and x = fraction of olefin dissolved at time t.

The following conclusions can be drawn regarding the rates of solution of olefin gases when shaken with sulfuric acid in Hempel pipets.

1. A pure butene was absorbed at a rate approximately proportioned to the gas undissolved (see Experiments 1, 2, 5, 6 and 7. The high initial rate of solution in 5 may perhaps be attributed to traces of *iso*butene).

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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 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.

[2] Director and Research Associate, Project No. 19.

[3] Michael and Brunel, *Am. Chem. J.*, 41, 118 (1909).

TABLE I

ABSORPTION OF THE BUTENES INTO SULFURIC ACID IN HEMPEL PIPETS

1. Pure isobutene, 58.6% sulfuric acid, 21–22°

t	X[a]	$K \times 10^{-3}$
0	0	..
20	0.59	45
40	.88	53
60	.97	58
120	.98	33
	Av. =	47

2. Pure isobutene, 58.6% sulfuric acid, 28–29°

t	X	$K \times 10^{-3}$
0	0	..
10	0.69	117
20	.89	110
40	.97	87
	Av. =	105

3. Mixture, 51.8% of isobutene + 48.2% of 2-butene, 58.6% sulfuric acid, 21–22°

t	X[b]	$K \times 10^{-3}$
0	..	..
20	0.40	26
60	.82	29
100	.92	25
	Av. =	27

4. Mixture, 57.5% of isobutene + 42.5% of 2-butene, 58.6% sulfuric acid, 28–29°

t	X[b]	$K \times 10^{-3}$
0		..
15	0.45	40
30	.65	35
45	.87	45
60	95	50
	Av. =	43

5. Pure 2-butene, 58.6% sulfuric acid, 28–29°

t	X	$K \times 10^{-3}$
0	..	..
10	0.012	(1.3)
20	.017	0.85
40	.020	.50
150	.048	.33
175	.083	.49
	Av. =	.54

6. Pure 2-butene, 76% sulfuric acid, 29–30°

t	X	$K \times 10^{-3}$
0	..	..
20	0.18	10
40	.33	10
60	.44	9.7
80	.55	10
	Av. =	10

7. Pure 1-butene, 76% sulfuric acid, 29–30°

t	X	$K \times 10^{-3}$
0	..	..
20	0.09	4.8
40	.17	4.7
60	.27	5.3
80	.35	5.4
	Av. =	5.0

[a] Recalculated, taking the proportion soluble in strong sulfuric acid as 100%.

[b] The 2-butene dissolved so much more slowly than the isobutene that it was counted merely as a diluent of the latter.

It is true that the values for K are only approximately constant in any one experiment. Nevertheless, the averages of these values become quite significant for the different gases.

It should be emphasized that Michael and Brunel did not carry out these experiments with a view to calculating absorption coefficients and it is a tribute to the accuracy of the data that this can be done with results so satisfactory as those given above.

2. When diluted with non-reacting gas, isobutene was absorbed at a rate proportional to the isobutene undissolved. The magnitude of the rate was, however, cut down in approximate proportion to the dilution (see Expts. 3 and 4).

This accords with the results from certain experiments of mine on the rates of absorption of olefins by sulfuric acid in rotating tubes at constant volume. The rate of solution was very closely proportional to the partial pressure of the olefin even when admixed with varying quantities of air.

The rates of absorption of the butenes into sulfuric acid may therefore be fairly well compared by their absorption coefficients, K, Table II, from which effects of changes in the gaseous volume, partial pressure of the olefin and time of shaking have been largely eliminated.

TABLE II

ABSORPTION COEPFICIENTS K FOR THE THREE BUTENES INTO SULFURIC ACID IN HEMPEL PIPETS

No.	Olefin	Concn. of H_2SO_4, %	Temp.. °C.	Absorption coefficient, K[a]
1	Isobutene (pure)	58.6	21–22	47×10^{-3}
2	Isobutene (pure)	58.6	28–29	105×10^{-3}
3	Isobutene (57.5%)	58.6	21–22	46×10^{-3}
4	Isobutene (51.8%)	58.6	28–29	75×10^{-3}
5	2-Butene (pure)	58.6	28–29	0.54×10^{-3}
6	2-Butene (pure)	76	29–30	10.0×10^{-3}
7	1-Butene (pure)	76	29–30	5.0×10^{-3}

[a] Calculated for the pure gas at atmospheric pressure.

TABLE III

RELATIVE RATES OF ABSORPTION OF THE BUTENES

From Table II			Relative rates of absorption into sulfuric acid[a]	
$\frac{K_2(\text{2-butene})}{K_1(\text{1-butene})}$	at 29–30°	2	1-butene	1
$\frac{K_3(\textit{iso}\text{butene})}{K_2(\text{2-butene})}$	at 28–29°	140–195	2-butene	2
			isobutene	280–390

[a] This last comparison will not hold broadly if the relative rates depend upon the concentration of the acid or the temperature. The effects of these two conditions on the absorption of olefins into sulfuric acid are now being investigated experimentally.

Summary

Calculations on the relative rates of absorption of the three butenes into sulfuric acid have been made from the experimental data of Michael and Brunel.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

CERTAIN NEW OXIDATION REACTIONS OF ALDEHYDES

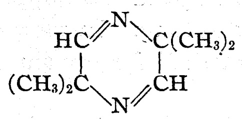
BY JAMES B. CONANT AND JOHN G. ASTON

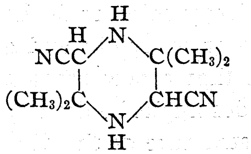
RECEIVED JULY 12, 1928 PUBLISHED OCTOBER 6, 1928

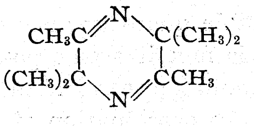
As a continuation of the quantitative study of the irreversible oxidation of organic compounds,[1] we have investigated the oxidation of aldehydes by reversible oxidizing reagents of known potential. In this work we employed the following oxidizing agents in dilute solution at SO°: potassium ferricyanide, potassium tungsticyanide, potassium molybdicyanide, potassium dichromate and ceric sulfate. The last two were used in molar sulfuric acid solution and the others in alkaline buffer solutions. The quantitative results showed that the reduction of these reagents by aliphatic aldehydes proceeded rapidly at certain acidities and that the results could be formulated in terms of "apparent oxidation potentials" as in previous papers from this Laboratory. An examination of the products of the reaction showed surprising complications, however. Instead of the expected oxidation to the corresponding acid, other reactions were apparently predominant in both the alkaline and the acid solutions. We have established that these reactions are the result of an oxidation in the a-position, which we have been able to study in some detail in the case of isobutyraldehyde. The difficulty of isolating products from dilute solutions containing inorganic reagents has prevented our obtaining equally satisfactory evidence with the other aldehydes. Therefore, this paper is concerned primarily with the behavior of isobutyraldehyde. The results of our quantitative study will be reported later.

The Formation of Dihydropyrazine and Piperazine Derivatives by the Action of Ferricyanide

Isobutyraldehyde is oxidized by potassium ferricyanide at 80°, if the solution is made slightly alkaline by the slow addition of potassium hydroxide. In dilute solution (about 0.14 *M* with respect to aldehyde) the chief product is 2,2,5,5-tetramethyldihydropyrazine (I); the yield is about 27%. No *iso*butyric acid is produced. In more concentrated solutions (about 0.28 *M*) 2,2,5,5-tetramethyl-3,6-dicyanopiperazine (II) is also formed. The combined yield of the piperazine and dihydropyrazine derivatives amounted to about 60% of the aldehyde employed, but the iso-


I


II


III

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[1] Conant and Pratt, THIS JOURNAL, 48, 3178, 3220 (1926).

lation of the dihydropyrazine from the more concentrated runs is unsatisfactory since it is contaminated with some oily material.

In this strange reaction the nitrogen atoms of the heterocyclic compounds have been gained at the expense of the ferricyanide ion, since ferric hydroxide and formic acid are also formed. The maximum yield of the two compounds from 0.14 mole of aldehyde corresponds to a gain of 0.126 g. atom of nitrogen. This would be made available by the complete decomposition of 0.021 mole of ferricyanide (about 10% of the equivalent amount of the oxidizing agent). The amount of ferric hydroxide actually obtained corresponded to the decomposition of 0.0130 mole of ferricyanide or 65% of this amount. The major part of the ferricyanide ion was reduced to ferrocyanide, which was isolated from the reaction mixture as crystalline potassium ferrocyanide. An electrometric titration of the reaction mixture also showed that at least 65% of the oxidizing agent was reduced to ferrocyanide.

Further insight into the mechanism of the reaction was obtained by studying the action of potassium ferricyanide in alkaline solution at 80° on methyl isopropyl ketone. The product of the oxidation in this case is the known hexamethyldihydropyrazine (III);[2] the yield was about 25%. The constitution of the tetramethyldihydropyrazine (I) follows from the analysis, molecular weight and the transformation by reduction into a piperazine derivative which yielded a di-nitroso compound. The action of hydrocyanic acid on the dihydropyrazine yielded the dicyanopiperazine (II), whose structure was thus established.

The fact that methyl isopropyl ketone yields a dihydropyrazine when oxidized with alkaline ferricyanide throws much light on the mechanism of the reaction with isobutyraldehyde. The α-oxidation of the ketone is the normal course of the oxidation and it seems quite certain that the α-amino ketone, $CH_3COCNH_2(CH_3)_2$, is an intermediate product. This substance is known to undergo condensation to hexamethyldihydropyrazine in alkaline solution.[2] As a by-product of this condensation another volatile basic material (probably a pyrrole derivative) is formed. We have also found a small amount of other volatile basic material in our reaction mixture. Further evidence of the existence of an intermediate product is afforded by the fact that the formation of hexamethyldihydropyrazine proceeds slowly after oxidation is complete. Thus, a reaction mixture from which no more dihydropyrazine could be distilled yielded an appreciable quantity after standing overnight and again distilling. In view of this fact it seems possible that a new preparative method for certain α-amino ketones and aldehydes might be developed.

An examination of the structure of the dihydropyrazine resulting from *iso*butyraldehyde as well as the analogy with the reaction of methyl *iso*-

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[2] Gabriel, **Ber., 44, 65 (1911).**

propyl ketone shows that the fundamental mechanism is the oxidation of the a-carbon atom. It is the possibility of this reaction and not the presence of the aldehydic group which is responsible for the peculiar course of the reaction between isobutyraldehyde and ferricyanide. The mechanism by which the nitrogen is introduced into the organic molecule is obscure. It might involve the formation of the a-hydroxy aldehyde (or ketone) but this possibility appears to be eliminated by the fact that α-hydroxy-isobutyraldehyde yields no dihydropyrazine when heated with a mixture of ferri- and ferrocyanides in alkaline solution. Since the work reported below demonstrates that the a-oxidation of aldehydes in dilute solution is a regular reaction of these substances, we believe that the first step in the process is an oxidation (dehydrogenation) involving the elimination of the a-hydrogen atom. The first product is probably a highly reactive substance which combines with the complex cyanide forming the a-amino aldehyde (or ketone).

The dicyanopiperazine (11) is probably formed by the interaction of the dihydropyrazine and the hydrocyanic acid set free by the decomposition of a portion of the complex ion.

The oxidation of acetaldehyde by alkaline potassium ferricyanide at 80° yields no acetic acid, no volatile basic products and only a trace of ferric hydroxide. The reduction of the ferricyanide to ferrocyanide was evident both from the electrometric measurements and by the isolation of large amounts of potassium ferrocyanide. After concentration and precipitation of the inorganic salt by alcohol, a gummy material was left. It corresponded, however, to only 10% of the aldehyde employed. No satisfactory evidence as to its nature has yet been obtained and beyond the significant fact that no acetic acid is formed in the reaction, we are not able to make any statements in regard to the course of the reaction between fenicyanidc and acetaldehyde. The reaction of ferricyanide with other aliphatic aldehydes has not yet been investigated.

The a-Oxidation of Aldehydes in Acid Solution

In order to determine whether or not a-oxidation of aldehydes is a general reaction, we examined the action of a number of oxidizing agents in acid solution. Again, our most satisfactory results were obtained with isobutyraldehyde, though the facts given below prove beyond doubt that a-oxidation also takes place to some extent under certain conditions with *n*-butyraldehyde and acetaldehyde.

Potassium dichromate oxidizes a dilute solution of *iso*butyraldehyde in molar sulfuric acid at 80°, with the formation of acetone, carbon dioxide and *iso*butyric acid. In a solution 0.14 M with respect to both aldehyde and reagent the yield of acetone was **37%.** In more concentrated solutions (0.28 *M* to 0.56 *M*) less carbon dioxide (29 to 35%) and more *iso*butyric acid was obtained. The formation of acetone and carbon dioxide must be the result of the oxidation of isobutyraldehyde in the a-position. Isobutyric acid under the same conditions is not oxidized by dichromate but both a-hydroxy-isobutyric aldehyde and acid yield acetone.

The oxidation of *n*-butyraldehyde by dichromate in molar sulfuric acid at 80° yields considerable amounts of carbon dioxide. This must be the result of oxidation of the carbon chain, presumably in the a-position. The reaction was studied by determining both the evolution of carbon dioxide and the number of equivalents of oxidizing agent required for complete oxidation. In a 0.07 M solution the amount of a-oxidation was 25% as determined by the carbon dioxide; 3.6 hydrogen equivalents of dichromate were consumed per mole of aldehyde. The number of equivalents increased to 4.1 in a 0.035 M solution and 4.4 in a 0.018 M solution. The oxidation to *n*-butyric acid corresponds to two equivalents, to carbon dioxide and propionic acid to eight equivalents. Thus, on the basis of the amount of oxidizing agent used up, the process of moxidation comprised about 40% in the very dilute solutions. The amount of carbon dioxide did not increase above 25% but this is undoubtedly due to the difficulty of driving off and determining very small amounts of carbon dioxide in the more dilute solutions.

Ceric sulfate in molar sulfuric acid at 80° is rapidly reduced by *iso*butyraldehyde and in this case it was possible to obtain evidence of the formation of a-hydroxy-isobutyraldehyde in addition to acetone. Unfortunately the isolation of the hydroxy aldehyde from very dilute solutions is difficult and it was not possible to obtain the pure substance or a definite derivative. However, we developed a procedure for estimating the amount of this aldehyde in a dilute water solution which also contained acetone and isobutyraldehyde. The details of the procedure are given in the experimental portion of this paper. The method was carefully tested with known solutions of the three compounds. It depends on the different degree of volatility with steam of the three and on a rather specific reaction of the hydroxy aldehyde. This compound does not give the usual iodoform test but does give iodoform if the solution is warmed with an excess of sodium hydroxide.

Only about 20% of isobutyric acid was formed in the ceric sulfate oxidations. In addition to the a-hydroxy aldehyde, the acetone and the acid, one other product was shown to be present in small amounts. This was a crystalline solid melting at 166–169' and volatile with steam. Only about 0.01 g. per gram of aldehyde was obtained. The elucidation of its structure awaits further work.

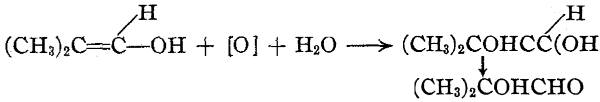
A few experiments were performed with potassium permanganate. A 0.5 *M* solution of this reagent was very slowly dropped into a 0.1 M solution of isobutyraldehyde in molar sulfuric acid at 80–90°. Distillation of the reaction mixture yielded a distillate which contained acetone and gave the characteristic tests for a-hydroxy-isobutyraldehyde. The amount of isobutyric acid was estimated by the Du Claux method; it amounted to only 40% of the theoretical quantity. Isobutyric acid itself is not attacked by permanganate under the same conditions.

Acetaldehyde is oxidized in the a-position, yielding carbon dioxide, if potassium permanganate in molar sulfuric acid in *very* dilute solution is employed. The temperature was 80–90°. One hundred cc. each of *0.25 M* solution of the reagent and *0.25 M* solution of the aldehyde were slowly dropped into *200* cc. of molar sulfuric acid which was rapidly stirred. If no excess of permanganate is allowed to accumulate, the amount of carbon dioxide evolved may correspond to as much as 20% a-oxidation. The yield of acetic acid (determined by the Du Claux method) drops accordingly. If the aldehyde and permanganate are mixed at once, the formation of acetic acid is practically quantitative.[3]

Cobaltic sulfate in 8 N sulfuric acid at 0° oxidizes isobutyraldehyde. The presence of both acetone and hydroxy aldehyde was shown by tests performed with the distillate; isobutyric acid is also formed; no estimation of the relative amounts of products was found possible. Palladium black and chloranil (tetrachloroquinone) slowly oxidize isobutyraldehyde and the presence of a-hydroxy aldehyde in the product was shown by tests performed on the distillate.

Mechanism of the Reaction

The most obvious explanation of our somewhat unexpected results would be that the enolic form of the aldehyde was oxidized by the addition of two hydroxyl groups.



$$\begin{array}{rcl} (CH_3)_2C{=}\overset{H}{C}{-}OH + [O] + H_2O & \longrightarrow & (CH_3)_2COHC\overset{H}{C}(OH)_2 \\ & & \downarrow \\ & & (CH_3)_2COHCHO \end{array}$$

Such an explanation seems to us improbable, however, for several reasons. In the first place, it gives no clue to the striking effect of dilution which so materially increases the amount of a-oxidation with acid oxidizing agents. In the second place, such reagents as ceric sulfate, cobaltic sulfate, palladium and chloranil and ferricyanide do not usually add oxygen to an ethylene linkage as demanded by this mechanism. A third argument against the above mechanism is the fact that the amount of enol present in a strongly acid solution must be very small and yet our results show that a-oxidation proceeds in molar sulfuric acid. The oxidation of the enolic form of acetaldehyde has been carefully studied by Evans and Adkins.[3,4] Using a solution 0.1 M in respect to both potassium permanganate and acetaldehyde, they found that at 25" or at 75° only acetic acid was formed if no alkali were added. With increasing amounts of potassium hydroxide the yield of acetic acid diminished and carbon dioxide and oxalic acid were formed. Obviously these investigators were studying the real oxidation of the enolic form of acetaldehyde. Such an

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[3] Compare Evans and Adkins, THIS JOURNAL, 41, *1385 (1919).*

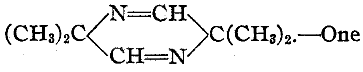
[4] See *also* Denis, ***Am. Chem.*** **J.,** *38, 569 (1917).*

oxidation is an α-oxidation but would appear to be different from the α-oxidation we have studied by using very dilute solutions of permanganate and aldehyde in sulfuric acid.

If the oxidation of the enolic form according to the equation written above is eliminated, it is necessary to construct some other hypothesis. Since the quantitative results are important in this connection, we will postpone a further consideration of the mechanism until the next paper.

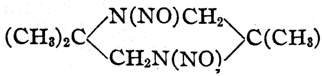
We are indebted to Mr. Carl O. Tongberg for his assistance during part of the experimental work.

Experimental Part

2,2,5,5-Tetramethyldihydropyrazine, .—One hundred and fifteen grams of potassium ferricyanide (0.35 mole) was dissolved in one liter of water in a flask fitted with a mechanical stirrer, a reflux condenser and dropping funnel. The flask and contents were heated in a bath at 80° and 10.0 g. of redistilled *iso*butyraldehyde (0.14 mole) were run in; 320 cc. of 1.0 N sodium hvdroxide was then dropped in over forty-five minutes with stirring. After all of the sodium hydroxide had been introduced, the mixture was allowed to stand for fifteen minutes at 80°, filtered from a red sediment of iron oxide (which weighed 1.11 g. after ignition) and then distilled slowly under ordinary pressure until 1000 cc. of distillate had been collected. The 1000 cc. of distillate was then distilled through a long spiral column until the refractive index of the distillate fell to that of water. The distillate was then continuously extracted for six hours, using 50 to 100 cc. of ether. After drying the ether was distilled from the extract until no more ether passed over. On cooling the residue crystallized. Most of the remaining ether was removed by applying suction to the flask for two or three minutes after cooling. The crystals after drying between filter paper melted at 76–81°. The yield was 2.62 g. (27.5% of the theoretical). The compound was purified by sublimation in vacuum and by drying over dehydrite. It melted at 83–84' and distilled at 160° without decomposition. It is very soluble in water, forming a weakly basic solution which turns methyl orange but not phenolphthalein. A dilute solution gives a yellow precipitate with bromine water and a white precipitate on adding an equal volume of saturated mercuric chloride solution. The application of the bromine test to a fresh reaction mixture showed that the dihydropyrazine was present immediately after the oxidation was complete.

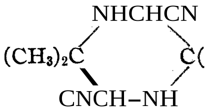
No detectable amount of dihydropyrazine was formed when α-hydroxy-*iso*butyraldehyde was substituted for isobutyraldehyde.

Anal. Calcd. for $C_8H_{14}N_2$: C, 69.6; H, 10.1; N, 20.3. Found: C, 69.5; 69.2; H, 10.4, 10.2; N (Kjeldahl), 20.2. *Equiv.* Weight by titration with standard HCl (methyl orange end-point), calcd., 69.0. Found: 68.2. *Mol. wt.* in benzene (freezing point): Sample, 0.1240; benzene, 17.37 g.; At = 0.257°, 0.263°. Calcd. for $C_8H_{14}N_2$: 138. Found: 141, 136.

Dinitroso-2,2,5,5-tetramethylpiperazine, .—The tetramethyldihydropyrazine was reduced to the corresponding piperazine by means of sodium and alcohol. The piperazine was distilled with steam from the diluted reaction mixture and the distillate treated with hydrochloric acid and potassium nitrite. The dinitroso compound separated as a white crystalline precipitate; 3 g. of the dihydropyrazine yielded 1.8 g. of crude product, m. p. 208–210°. It was recrystallized from 5% acetic acid and melted at the same point.

Anal. Calcd. for $C_8H_{16}N_4O_2$: C, 48.0; H, 8.11; N, 28.0. Found: C, 47.9; H, 5.1; N, 28.1.

2,2,5,5-Tetramethyl-3,6-dicyanopiperazine,



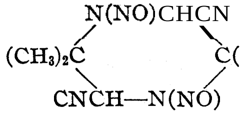
$$(CH_3)_2C\begin{matrix}NHCHCN\\ \\ CNCH{-}NH\end{matrix}C(CH_3)_2$$

—One hundred and eighty-five grams of potassium ferricyanide (0.56 mole) dissolved in 400 cc. of water, 10 g. of isobutyraldehyde (0.14 mole) and a solution of 14.3 g. of sodium hydroxide in 100 cc. of water were employed and the procedure was identical with that described in the preparation of the dihydropyrazine; the sodium hydroxide was added during thirty minutes, and the reaction mixture was then stirred for one hour longer at 80–85°. A small amount of oil formed on the surface of the reaction mixture. This on cooling solidified to crystals. The whole reaction mixture was continuously extracted for ten hours with 50-100 cc. of ether. The ether extract was mixed with a considerable quantity of white solid which was filtered off and dried between filter paper, m. p. 189–192°; yield, 2.0 g. The product after being twice recrystallized from benzene melted at 193–194.5°. The reaction mixture, after the ether extraction, was filtered from the fine red precipitate of ferric hydroxide, which when dried and ignited weighed 1.04 g. (0.0065 mole of Fe_2O_3, corresponding to 0.0130 mole of ferricyanide). The ether extract, after filtering off the solid already mentioned, was dried and distilled and the residue fractionated; the bulk of the product boiled at 170°; yield, 2.3 g. This fraction crystallized, but the crystals of the tetramethyldihydropyrazine were mixed with some thick oily materials.

Anal. Calcd. for $C_{10}H_{16}N_4$: C, 62.4; H, 8.4; N, 29.2. Found: C, 62.5; H, 8.6; N, 29.5. Mol. wt. Calcd. for $C_{10}H_{16}N_4$: 192. Found: (1) in acetone boiling-point method: 0.3360 g. (second increment) 14.2 g. of acetone; At, 0.211°, mol. wt., 187. (2) By the micro method in camphor: 206, 225.

The compound was also prepared by heating a 1% aqueous solution of 2,2,5,5-tetramethyldihydropyrazine at 100°, passing in hydrocyanic acid gas and allowing the mixture to stand for one hour at 70–90°. The dicyano compound separated as a white solid, the yield was 1.4 g. (theoretical). The identity of the material with that formed by the interaction of femcyanide and isobutyraldehyde was established by a mixed melting point.

Dinitroso-2,2,5,5-tetramethyl-3,6-dicyanopiperazine,



$$(CH_3)_2C\begin{matrix}N(NO)CHCN\\ \\ CNCH{-}N(NO)\end{matrix}C(CH_3)_2$$

—A solution of 1.0 g. of recrystallized 2,2,5,5-tetramethyl-3,6-dicyanopiperazine in 50 cc. of glacial acetic acid was treated with 1.2 g. (12% excess of theoretical for dinitroso derivative) of n-butyl nitrite at room temperature. After standing overnight the crystals which had separated were filtered off, washed with acetic acid and dried between filter paper, m. p. (with violet decomposition), 178° (placed in baths below this temperature and slowly heated, the decomposition point is always 178°, if placed in baths somewhat above 178°, some time elapses before the decomposition takes place), yield, 1.04 g., 80% of the theoretical. Recrystallization from benzene did not raise the melting point.

Anal. Calcd. for $C_{10}H_{14}N_6O_2$: C, 48.0; H, 5.64; N, 33.6. Found: C, 48.0; H, 5.9; N, 35.3.

Investigation of Acidic Products Formed by the Interaction of Ferricyanide and Isobutyraldehyde

(a) Experiments with Buffer Solutions.—3.29 g. of potassium ferricyanide and 4.22 g. of potassium ferrocyanide were dissolved in one liter of the borate buffer which was made by adding a solution of 326 cc. of 0.2 *M* sodium hydroxide to 1000 cc. of 0.2 *M* boric acid 0.2 M in potassium chloride. The mixture was heated to 80° and 0.724 grams (0.01 M) of freshly distilled isobutyraldehyde in 50 cc. of water was added with vigorous mechanical stirring. The oxidation proceeds fairly rapidly in this buffer at 80° as was shown by the change of potential of a platinum electrode in a number of similar experiments. The mixture was stirred for twenty minutes at 80° and then a further 3.29 g. of potassium ferricyanide was added and the mixture stirred for five hours at 80°. At the end of this time the mixture was cooled and 10 cc. of 35% sodium hydroxide added to neutralize all of the boric acid; the solution was evaporated under reduced pressure to a small volume, acidified with sulfuric acid, then continuously extracted for six hours with ether. The ether solutions thus obtained contained boric acid and had an odor of hydrocyanic acid. The ether was distilled off and the residue dissolved in water. An aliquot portion of the aqueous solution thus obtained was titrated with standard sodium hydroxide, using a quinhydrone electrode. The electrometric end-point showed that the amount of acid present corresponded to only 0.0030 mole in the original reaction mixture (compared with 0.010 mole of aldehyde employed). The potential of the mid-point corresponded to a K_A of 1.42×10^{-4} for the acid (K_A for formic acid $= 2.14 \times 10^{-4}$; for isobutyric acid, 1.48×10^{-5}). Parallel experiments in which isobutyric acid was added to the buffer solution showed that our procedure extracted at least 95% of the material from a 0.01 M solution. It was also established that a titration using the quinhydrone electrode was satisfactory in the presence of boric acid and small amounts of hydrocyanic acid and that the value of K_A for the acid present could be determined with an accuracy of 3040%.

The fact that the acid which was extracted was formic acid was further established by evaporating the solution and testing the salt for reducing properties. It reduced mercuric oxide and silver nitrate on heating. As a further confirmation that isobutyric acid was not obtained, the oxidation of isobutyraldehyde by ferricyanide was carried out as above, using a phosphate buffer of $P_H = 10.4$, 0.2 M in phosphate ion, in which the oxidation proceeds more rapidly. The ether extraction of the solution after concentration and acidification yielded only about 30% of the theoretical quantity of acid. This acid on conversion into sodium salt gave no crystalline *p*-toluide when heated with hydrochloric acid and *p*-toluidine; a blank with isobutyric acid showed this to be a sensitive test for this acid.

(b) Oxidation Using Minimum Quantities of Sodium Hydroxide.—One hundred and thirteen grams (0.343 mole) of potassium ferricyanide was dissolved in one liter of water in a 2-liter, round-bottomed flask fitted with a condenser, a stirrer, two bright platinum wire electrodes, a buret dropping funnel and a saturated potassium chloride bridge leading to a calomel electrode. The whole was heated to 80° by immersion in a bath at 80°. The electromotive force of the system was read on a potentiometer. 10.3 g. (0.143 mole) of isobutyraldehyde dissolved in 150 cc. of water was added from the dropping funnel. 1 *N* sodium hydroxide was added from the buret until the potential had fallen to a value which then remained constant, indicating that the reaction was complete; a total of 313 cc. of sodium hydroxide was added. The solution was removed from the bath and after cooling was found to be neutral to phenolphthalein and basic to methyl orange. Titration of a sample showed that 100 cc. of 1 N acid would be required to neutralize the entire batch to the methyl orange end-point; therefore 0.313 mole of sodium hydroxide was neutralized in the course of the reaction, calculated from the phenolphthalein end-point and 0.213 calculated from the methyl orange end-point. These amounts correspond to 2.19 and 1.5 moles per mole of aldehyde, respectively. On the basis of the reaction $2K_2Fe(CN)_6 + 2KOH \longrightarrow 2K_4Fe(CN)_6 + H_2O + 0$, it is seen that if one molecule of the aldehyde takes up one atom of oxygen to yield a neutral substance, two equivalents of hydroxyl ion are used up. The formic acid which was found to be produced to the extent of about 0.3 mole per mole of aldehyde by the decomposition of ferricyanide would be half taken care of by the potassium ions of the potassium ferricyanide; 0.15 mole of free acid would thus be produced and about 0.3 mole of the weakly basic dihydropyrazine. The dihydropyrazine is sufficiently basic to turn methyl orange but not phenolphthalein; the discrepancy between these two end-points is thus accounted for as well as the slight excess over two moles of alkali required for the complete neutralization to phenolphthalein.

Determination of the Amount of Potassium Ferrocyanide Formed by the Reduction of Potassium **Ferricyanide** at **80°** by *Iso***butyraldehyde.**—A solution of 5 cc. of 0.05 M potassium ferricyanide in 60 cc. of 0.2 N potassium sulfate was heated in a thermostat at 80° in a cell equipped with two bright platinum electrodes, a mechanical stirrer and a saturated potassium chloride bridge connecting it with a saturated calomel electrode. One cc. of a 0.125 M solution of isobutyraldehyde was run in, followed by the slow addition of 5 cc. of 0.517 *N* sodium hydroxide over five minutes. Rapid reduction took place, the potential falling from 0.256 volt to -0.022 volt after all the alkali had been added. A blank was run at 80° using potassium *ferrocyanide* instead of ferricyanide without adding isobutyraldehyde, but 5 cc. of 0.056 N sodium hydroxide was added. The excess alkali in both experiments was neutralized by the addition of the calculated amount of sulfuric acid and 7 cc. of 2 N acetic acid was added to each cell after cooling to room temperature. The amount of ferrocyanide was determined by electrometric titration with 0.01 N potassium dichromate,[5] the experiment with the pure ferrocyanide serving to standardize the procedure. In two experiments 14.9 and 15.8 cc. of 0.01 N dichromate were required as compared to 25 cc. calculated from the ferricyanide used and 22.5 cc. by standardization using ferrocyanide in the blank run. The yield of ferrocyanide was thus 63–70% of the theoretical.

Oxidation of Methyl Isopropyl Ketone with Potassium **Ferricyanide.**—A solution of 115 g. of potassium ferricyanide in one liter of water in a flask fitted with *a* reflux condenser, mechanical stirrer and dropping funnel was heated in a bath at 80°, 11.4 g. of methyl isopropyl ketone added and 320 cc. of 1.0 N sodium hydroxide dropped in slowly over twenty-five minutes with vigorous mechanical stirring. The reaction mixture was allowed to stand for about thirty minutes at 80° after the alkali had been added and then slowly distilled until one liter had passed over. The clear distillate was redistilled slowly through a long spiral column. A crystalline solid separated in the receiver; it weighed 2.9 g. and melted at 85–87". On again distilling the solution from which the the solid separated, more solid was obtained in the new distillate. The residue from the original reaction mixture also yielded a further quantity when after four days' standing 200 cc. was distilled from it. In this case the solid separated from the distillate without redistillation, which indicates that the four days' interval had caused the formation of the compound from some intermediate (presumably the a-amino ketone). In all 6.0 g. of hexamethyldihydropyrazine hexahydrate, m. p. 85–87°, was obtained, 33% of the theoretical amount. The identity of the compound[2] was established by the melting point of the hydrate (87–89° after steam distillation; Gabriel gives 88–89°) and anhydrous material (m. p. 65–63"; Gabriel gives 69–69.5°) and by analysis.

The Oxidation of Acetaldehyde by Potassium Ferricyanide at 80° in Alkaline Solution.—A solution of 180 g. (0.546 mole) of potassium ferricyanide in one liter of water in the same apparatus that was used in oxidizing iso-butyraldehyde under these same conditions was heated to 80° and a solution of 10.75 g. (0.245 mole) of acetaldehyde in 100 cc. of water was added. 1 N sodium hydroxide was then added slowly until the potential of two bright platinum electrodes in the solution against a

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[5] The point of inflection in the e.m.f.-cc. curve at the end-point during the titration of potassium ferrocyanide in acid solution with potassium dichromate at these concentrations is not as sharp as one would expect. The titration curves show certain abnormalities and deviate from the theoretical logarithmic curve, but experiments showed that the comparative results are quite accurate.

saturated calomel half-cell had fallen to a steady value, indicating that the reaction was complete; 598 cc. of 1 *N* sodium hydroxide was required. The solution after cooling was alkaline; 74 cc. of 1 N sulfuric acid was required to neutralize this solution. Thus 524 cc. of 1 N sodium hydroxide had been used up, which corresponds to 2.14 equivalents of alkali per mole and demonstrates that practically no acidic substance was produced during the oxidation of acetaldehyde. That reduction of the ferricyanide had taken place was shown by the fall in potential of the system from 0.345 volt to −0.0301 volt. Only a trace of iron oxide was precipitated.

A run exactly the same as the one above was evaporated in vacuum in a bath at 50–55° to a volume of 300 cc., the distillate being collected in an ice-cooled receiver. An equal volume of alcohol was added to the residue. The salts thus precipitated were filtered off. This material was apparently mostly potassium ferrocyanide, giving a blue precipitate with ferric chloride. The mother liquor from the alcohol precipitated was evaporated in a vacuum below 40° to a volume of 80 cc. and 150 cc. of alcohol was added to precipitate the rest of the salts. Very little material was thrown out by this procedure. The solution after filtering was evaporated almost to dryness in a vacuum. A thick sirup was left behind; weight, 2 g. Analysis by the Kjeldahl method showed that this material contained 5.6% of nitrogen. The distillates were examined for possible oxidation products of acetaldehyde but nothing was found.

The Products of Oxidation of Isobutyraldehyde by Potassium Dichromate in Dilute Acid Solution at 80°.—A solution of 27.2 g. (0.555 equivalent) of potassium dichromate and 30 cc. (1.08 equivalents) of concentrated sulfuric acid was placed in a 2-liter flask fitted with a reflux condenser, dropping funnel and mechanical stirrer. The flask and contents were heated in a bath at 80°. With vigorous stirring, 10.0 g. (0.139 mole) of *iso*-butyraldehyde was rapidly run in. The mixture was kept at 80° for three hours. The solution was then cooled. Its volume was 1040 cc. Titration of a sample with 0.05 M ferrous ammonium sulfate in acid solution, using potassium ferricyanide as outside indicator, showed that this solution was 0.072 N in dichromate. On refluxing a sample and again titrating, it was found that no more dichromate was used up. Thus 1 mole of *iso*butyraldehyde had used up 3.43 equivalents of potassium dichromate. From the solution 865 cc. was distilled at ordinary pressures. The first fractions had a distinct odor of acetone. By titration 0.0573 mole of isobutyric acid was found in the distillate. The distillate was neutralized and distilled slowly, using a long column. Three grams of material distilled over at 56.5° and the thermometer then rose rapidly to 99°. The first fraction on redistillation yielded 2 g. of a liquid, b.p. 56.5–60°, which was identified as acetone by the formation of dibenzalacetone.

The solution from which the acetone was distilled was concentrated to

20 cc., acidified with 15 cc. of 6 N sulfuric acid and extracted with ether. After drying with potassium sulfate the ether was distilled from the extract through a long column and the liquid residue fractionated: Fraction 1, 90–151°, water + *iso*butyric acid, 1.5 g.; Fraction 2, 151–153°, *iso*butyric acid, 2.02 g.

A similar experiment in which a-hydroxy-isobutyric acid was substituted for the *iso*butyraldehyde also yielded acetone.

Quantitative Study of the **α-Oxidation** of Isobutyraldehyde and *n*-**Butyraldehyde** in Different Concentrations. (a) Apparatus.—A 500-cc. round-bottomed, three-necked flask was fitted with a mechanical stirrer with a mercury seal, a reflux condenser connected to two U-tubes containing sulfuric acid and glass beads and provided with a tube going to the bottom of the flask, which served as a nitrogen inlet. A dropping funnel fitted with a pressure equalizer, in the form of a by-pass connected to the nitrogen stream, was fitted directly into this inlet tube. Nitrogen could be let through the by-pass so that it swept out the funnel and passed through the solution in the flask. The nitrogen was purified by passing through two towers of soda lime.

(b) Procedure.—A solution of potassium dichromate and sulfuric acid in 250 cc. of water was made in the flask and refluxed for one-half hour, keeping a current of nitrogen passing through the flask. The flask was then placed in a bath held at 80° and a weighed potash bulb similar to that used in combustions was connected to the other end of the two U-tubes containing sulfuric acid and glass beads. With rapid mechanical stirring the *iso*butyraldehyde either as pure liquid or solution was introduced and the reaction allowed to run at 80°. The solution was then refluxed for one-half to one hour to drive out all of the carbon dioxide. A slow current of carbon dioxide-free nitrogen was passed through the flask during the entire process. The bulbs were then disconnected and weighed with the usual precautions. The reaction mixture was then washed from the flask into a 500-cc. graduated cylinder, thoroughly mixed by blowing air through and its volume read to 2 cc. A buret was then filled with the solution and a titration made against a standard ferrous ammonium sulfate solution which was approximately 0.1 N, using dilute potassium ferricyanide as outside indicator. The volume in which the titration was carried out varied from 100–300 cc.; five cc. of concentrated hydrochloric acid per 100 cc. was always added. In the more concentrated solutions a portion of the reaction mixture was diluted before titration, so that the concentration of dichromate was about 0.1 N.

In all cases the completeness of the reaction was tested by subsequently refluxing the solution for two hours and titrating again. If there was no appreciable amount of dichromate used up the reaction was assumed to be complete.

The results are summarized in Table I; the per cent. a-oxidation is calculated directly from the amount of carbon dioxide and also from the number of equivalents of dichromate used up per mole, assuming for *iso*butyraldehyde the reaction

$$(CH_3)_2CHCHO + 30 \longrightarrow (CH_3)_2CO + CO_2 + H_2O$$

and for n-butyraldehycle

$$CH_3CH_2CH_2CHO + 40 \longrightarrow CH_3CH_2COOH + CO_2 + H_2O$$

TABLE I

THE AMOUNT OF α-OXIDATION IN THE REACTION OF BUTYRIC ALDEHYDES WITH POTASSIUM DICHROMATE AT 80° AT VARIOUS TEMPERATURES~

Expt.	Concd. H_2SO_4, cc.	K_2CrO_7, g.	Aldehyde, g.	Concentration H_2SO_4 normal	K_2CrO_7, normal	Aldehyde, molal	Eqts. per mole	CO_2 per mole	a-Oxidation Prom CO_2, %	From no. of equivalents, %
				(A) Isobutyraldehyde						
A1	30	27.3	10	4.3	2.23	0.555	3.20	0.286	28.6	30.0
A2	30	2.56	0.619*	0.43	0.208	.0344	3.70	.308	30.8	42.5
				(B) n-Butyraldehyde						
B1	7.5	6.82	1.244	1.08	.556	.0691	3 62	.2455	24.5	27.0
B2	5.0	3.413	0.631*	0.72	.278	,0351	4.19 .	.216	21.6	36.5
B3	2.5	1.706	.310*	.36	.139	.0173	4.42	.257	25.7	40.2
B4	2.5	1.706	.32	.36	.139	.0178	4.32	.283	28.3	38.7

[a] The sulfuric acid and potassium dichromate were dissolved in 250 cc. of water except when a star indicates that the aldehyde was added as a solution in 25 cc. of water. In these cases 225 cc. of water was used. In Experiment B1, the remainder of the reaction mixture was distilled in steam till no more acid came over. The distillate was diluted to 500 cc. Titration showed it to be 0.1702 N in acid. Allowing for the reaction mixture used in titration of dichromate, from this result we calculate that 0.666 moles of acid are yielded per mole of aldehyde.

Action of Potassium Dichromate on n-Butyric Acid and Isobutyric Acid in Acid Solution at **80°** in the Presence of Chromic Sulfate.—To a solution of 100 cc. of water, **3** cc. of concentrated sulfuric acid, 2.73 g. of potassium dichromate, and 9.27 g. of chrome alum (potassium chromium sulfate) was added 1.22 g. of isobutyric acid in one experiment and 1.22 g. of n-butyric acid in another. The mixtures were refluxed for four hours and the solution titrated for dichromate with ferrous ammonium sulfate as has been already described for the aldehyde oxidations. It was found that in both cases no detectable amount of potassium dichromate had been reduced.

The Oxidation of Isobutyraldehyde by Ceric Sulfate at 80°.—A mixture of 300 cc. of 0.6 M sulfuric acid and 3.0 g. (0.042 mole) of *iso*butyraldehyde was heated to SO° in a flask equipped with a stirrer, dropping funnel, reflux condenser and nitrogen-inlet tube. A total of 300 cc. of 0.156 N ceric sulfate solution (containing 10 cc. of sulfuric acid) mas dropped in slowly during two hours; the reduction of the ceric salt was evident by the decolorization. The reaction mixture was neutralized with 60 g. of sodium bicarbonate and slowly distilled through a long spiral column. Fractions of 3 to 10 cc. each were collected and tested with (a) Schiff's reagent (decolorized fuchsine), (b) Tollens reagent, (c) by adding a few drops of a saturated solution of p-nitrophenylhydrazine hydrochloride, (d) by adding a few drops of iodine solution followed by enough 10% sodium hydroxide to decolorize, (e) by boiling for thirty seconds with 3 drops of 10% sodium hydroxide and then applying test d. Distillation of a number of dilute solutions of acetone, isobutyraldehyde, and α-hydroxy-isobutyraldehyde (prepared by hydrolysis of α-bromo-*iso*butyraldehyde) showed that it was possible to identify these compounds in the presence of each other by means of this fractionation and these tests. The distillation of 37 cc. from 500 cc. of a 1 per cent, isobutyraldehyde solution is sufficient to remove so much aldehyde that subsequent fractions give no test with Schiff's reagent, whereas with the hydroxy aldehyde, the aldehyde continues to come over and give this test from even a 0.2% solution after 100 cc. have been distilled. The iodoform test (d) is specific for acetone and the same test after heating with sodium hydroxide (e) is specific for the hydroxy aldehyde in the absence of acetone. The acetone comes over completely in the first tenth; test (e) is then specific. The formation of an amorphous yellow precipitate with *p*-nitrophenylhydrazine (test c) and the Tollens test (test b) also persisted much longer when a solution of the hydroxy aldehyde was distilled. These several confirmatory tests were always available and exactly the same procedure was used in testing a reaction mixture that was used in the blank runs.

It was found that after one-tenth of the reaction mixture had been distilled tests a, b, c and e were still given strongly by the distillate. This proves the presence of hydroxy-isobutyraldehyde. By comparing the tests with those given by corresponding distillates from a solution of known concentration of hydroxy aldehyde, it was estimated that the reaction mixture contained 0.5 g. of a-hydroxy-isobutyraldehyde. The first fractions of the distillate gave the iodoform test in the cold, proving the presence of acetone.

The amount of isobutyric acid formed was estimated by acidifying with sulfuric acid the residue from the distillation just described and again distilling. The first 4 cc. was 0.025 N in acid as determined by titration; after 400 cc. had been collected the distillate was running only 0.0025 N in acid. The total acid distilled over up to this point was 0.00329 mole or only 14% of the aldehyde employed. In another similar experiment an estimate of the isobutyric acid was made by the method of Duclaux.[6] According to this author the ratio of acidity in the first three 10cc. portions is 1:0.83:0.64 and 25% of the acid distils in the first 10 cc. The corresponding numbers found on distilling the acidified reaction mix-

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[6] Duclaux, THIS JOURNAL, 39, 731, 746 (1917).

ture were 1: 0.82: 0.60. Assuming that 25% of the acid was distilled in the first 10 cc., the total *iso*butyric acid in the reaction mixture was found to be only 22% of the theoretical based on the aldehyde employed.

Oxidation of Isobutyraldehyde with Permanganate in Dilute Sulfuric Acid.—The experiments were carried out by dropping a dilute solution of the permanganate into a well-stirred solution of the aldehyde in molar sulfuric acid. In a typical experiment 0.025 mole of aldehyde in 200 cc. of molar sulfuric acid was treated with 0.008 mole of potassium permanganate in 100 cc. of water at 25°. On distilling through a fractionating column the fractions of the distillate gave strong positive tests for acetone and α-hydroxy-isobutyraldehyde. The method of testing was the same as that described above. The same result was obtained at 80°.

Oxidation of Acetaldehyde with Potassium Permanganate in Acid Solution.—The amount of carbon dioxide formed in the oxidation of acetaldehyde was determined in the same manner as that described above in the experiments with isobutyraldehyde and dichromate. The method was tested by the liberation of carbon dioxide from bicarbonate; the recovery of carbon dioxide was 80%. The temperature was 85–95°. Both the aldehyde and the permanganate in dilute solutions were slowly dropped into 200 cc. of molar sulfuric acid which was stirred. The maximum yield of carbon dioxide was obtained by operating in such a way that no excess of permanganate was ever present as determined by the color. One hundred cc. of 0.25 *M* permanganate and 100 cc. of 0.25 M acetaldehyde solution were employed. The extent of α-oxidation as measured by the carbon dioxide evolution varied from 3.2 to 22%. The amount of acetic acid formed was estimated by distilling over one-tenth and titrating the distillate. A blank run with 0.020 mole of acetic acid and the same volume of sulfuric acid and water showed that 6.2% of the acid distilled in the first tenth. Using this factor, the amount of acetic acid was found in a series of runs to vary from 0.022 mole to 0.017. The highest amount corresponded to the lowest yield of carbon dioxide and vice versa.

Oxidations of Isobutyraldehyde with Other Reagents.—Isobutyraldehyde (0.025 mole) in 670 cc. of 8 N sulfuric acid containing 0.055 mole of cobaltic sulfate (prepared by electrolytic oxidation) was allowed to stand at 0° for one hour and overnight at room temperature. The reduction of the cobaltic salt was evident at 0° by the color change. The material was distilled in the usual way and the fractions of the distillate were tested. Strong tests for acetone and α-hydroxy-isobutyraldehyde were obtained. The first tenth of the distillate was titrated and the total *iso*butyric acid calculated from a factor obtained in a blank run using the same sulfuric acid and pure isobutyric acid. The yield of isobutyric acid was estimated as 25% but there was some unchanged aldehyde so that not much significance can be attached to this figure.

A suspension of 0.020 mole of chloranil and 0.5 g. of palladium black in 400 cc. of water was heated to boiling in nitrogen and 0.011 mole of *iso*-butyraldehyde in 100 cc. of water slowly added. The reaction took one hour. After cooling and filtering, the solution was distilled in the usual way. The distillate gave a strong test for a-hydroxy-isobutyraldehyde but contained no acetone.

Summary

1. The oxidation of isobutyraldehyde by ferricyanide in alkaline solution at 80° yields 2,2,5,5-tetramethyldihydropyrazine and 2,2,5,5-tetramethyl-3,6-dicyanopiperazine and no isobutyric acid. From methyl *iso*-propyl ketone under the same conditions hexamethyldihydropyrazine is formed. The reaction involves the oxidation of the a-carbon atom and the gain of nitrogen from a fraction of the complex cyanide.

2. The oxidation of isobutyraldehyde with ceric sulfate at 80° in acid solution yields acetone and a-hydroxy-isobutyraldehyde as well as *iso*-butyric acid. The same products are formed in acid solution by potassium permanganate and cobaltic sulfate. Chloranil and palladium yield a-hydroxy-isobutyraldehyde.

3. Potassium dichromate in acid solution at 80° oxidizes *iso*butyraldehyde in the *α*-position, yielding acetone to the extent of 40% in very dilute solutions. The process of a-oxidation is favored by dilution. *n*-Butyraldehyde is also oxidized in the a-position, as shown by the formation of carbon dioxide.

4. Potassium permanganate oxidizes acetaldehyde in acid solution at 80°, yielding carbon dioxide as well as acetic acid if precautions are taken to keep the reactants in *very* dilute solution with an excess of aldehyde.

CAMBRIDGE 38, MASSACHUSETTS

[CONTRIBUTION FROM THE ROCKEFELLER PHYSICAL AND BAKER CHEMICAL LABORATORIES OF CORNELL UNIVERSITY]

THE ABSORPTION SPECTRA OF SOME PHTHALEINS AND SULFONEPHTHALEINS OF PHENOL AND ORTHO-CRESOL[1]

BY R. C. GIBBS AND C. V. SHAPIRO[2]

RECEIVED JULY 17, 1928 PUBLISHED OCTOBER 6, 1928

In continuation of our previous investigations[3] on the absorption spectra of compounds of the triphenylmethane series, data are now presented for some phthalein and sulfonephthalein derivatives of phenol and o-cresol.

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[1] The investigations upon which this article is based were supported by grants from the Heckscher Research Foundation for the Advancement of Research, established by August Heckscher at Cornell University.

[2] Heckscher Research Assistant in Physics and Chemistry, Cornell University, 1923–1928.

[3] Orndorff, Gibbs and co-workers, THIS JOURNAL, 47, 2767 (1925); 48, 1327. 1994 (1926); 49, 1541, 1545, 1588 (1927); 50, 819, 1755 (1928).

All of the compounds used in the course of the present research were prepared at this Laboratory under the direction of the late Professor W. R. Orndorff and were of analytical purity.

Some preliminary work here on the ultraviolet absorption of these compounds[4] in various solvents and a few reports on their absorption in the visual region in acid and alkaline solutions[5] have been published.

Phenoltetrachlorophthalein, o-cresolphthalein and *o*-cresoltetrachlorophthalein are typical lactoid phthaleins, which yield colorless solutions in neutral solvents. Their absorption spectra in absolute ethanol solution, together with that of phenolphthalein[6] in the same solvent, Fig. 1, are characterized by a pair of bands in the region of frequency numbers, 3500 to 3700. Similar bands have been found for a large number of benzenoid compounds of the triphenylmethane series,[7] of which many are lactones of the phthalein class, but some are carbinols of triphenylmethane derivatives. It is therefore believed that these bands are characteristic not of a single typical atom or group of atoms but rather of the molecule as a whole, when all three benzene nuclei are in their normal, benzenoid state.

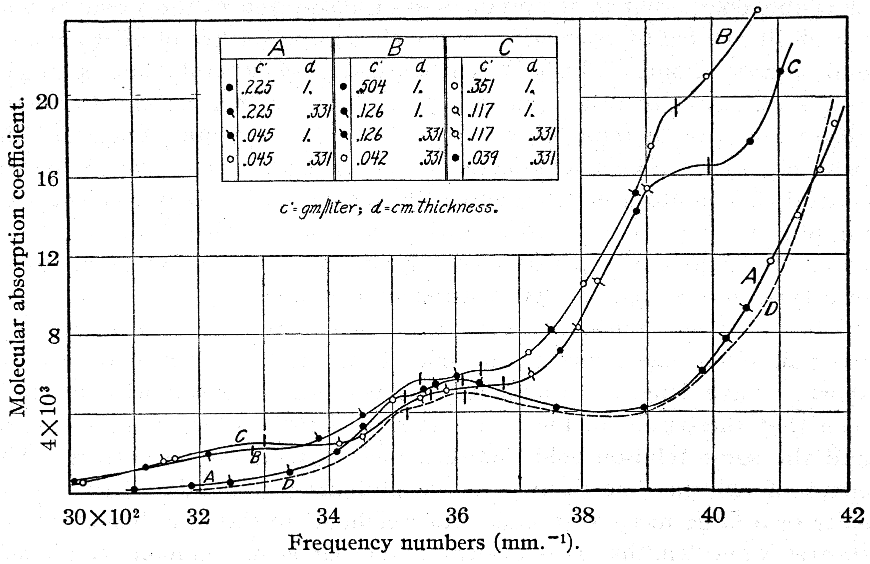

Fig. 1.—Absolute ethanol solutions: *A*, o-cresolphthalein; B, *o*-cresoltetrachlorophthalein; *C*, phenoltetrachlorophthalein; D, phenolphthalein.

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[4] Howe, *Phys. Rev.*, 8, 687 (1916); Howe and Gibson, *Phys. Rev.*, 10, 767 (1917); Orndorff, Gibbs, Scott and Jackson, Phys. *Rev.*, 17, 437 (1921).

[5] Formánek and Knop, *Z.* anal. Chem., 56, 273 (1917); Moir, *Trans. Roy. Soc. S. Africa*, 7, 8, 114 (1918); White and Acree, THIS JOURNAL, 40, 1092 (1918); Brode, *ibid.*, 46, 585 (1924); Holmes, *ibid.*, 46, 629, 633 (1924).

[6] Orndorff, Gibbs and McNulty, THIS JOURNAL, 48, 1994 (1926).

[7] Gibbs and Shapiro, *Proc.* Nat. *Acad. Sci.*, 14, 251 (1928).

It is extremely unlikely that the methane carbon atom in triphenylmethane derivatives, even when unsaturated as represented by the quinoid state of the molecule, can be the seat of absorption in the wave length range from the visible region down to the ultraviolet at about 2300 Å., as recently suggested by Vogt.[8] The aliphatic hydrocarbons exhibit absorption only in the extreme ultraviolet below 1900 Å. while the simple, unsaturated hydrocarbons have bands in the region of 2200 to 1900 Å.[9] On the other hand, as is well known, benzene shows strong, banded absorption in the middle ultraviolet from 2700 to 2300 Å. and the effect of changing from the benzenoid to the quinoid state with the production of visible color, that is, the production of absorption in the visual region, is well illustrated by comparison of the absorption spectra of hydroquinone and benzoquinone.[10] In a system consisting of several benzene nuclei and a methane, or other simple type of hydrocarbon carbon atom, the absorption will therefore be due entirely to the combined effects of the benzene nuclei. This hypothesis of the negligible part played by the central carbon atom in determining the absorption is neatly confirmed by unpublished results obtained at this Laboratory on the absorption spectrum of a triphenyl derivative of germanium,[11] which was found to be of a type very similar to that of triphenylmethane.

The tetrachlorophthaleins each have two more bands in addition to the pair cited above, one to the side of longer, the other to the side of shorter wave lengths. Comparing phenol- and o-cresolphthalein, it is seen that the bands for the latter are shifted toward longer wave lengths and the same relation holds between their tetrachloro derivatives. The effect of chlorine substitution in the phthalic acid residue, however, in spite of a large increase of molecular weight, is to shift the bands toward shorter wave lengths, as is evident if the bands in common for phenol- and phenoltetrachlorophthalein and for o-cresol- and *o*-cresoltetrachlorophthalein as given in Table I are compared.

TABLE I

FREQUENCY NUMBERS OF BANDS IN NEUTRAL ABSOLUTE ETHANOL SOLUTION

Phenolphthalein	..	3523	3613	..
Phenoltetrachlorophthalein	3300	3560	3675	3995
o-Cresolphthalein	..	3519	3608	..
o-Cresoltetrachlorophthalein	3281	3544	3638	3945

Phenolsulfonephthalein and *o*-cresolsulfonephthalein, in contrast with the corresponding phthaleins derived from phthalic anhydride, are colored

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[8] Vogt, *Z. physik. Chem.*, *132*, 101 (1928).

[9] Stark and co-workers, *Jahr. Radioakt. und Elektronik*, *10*, 139 (1913).

[10] Klingstedt, *Compt. rend.*, 175, 365 (1922); 176, 1550 (1923).

[11] Tabern, Orndorff and Dennis, THIS JOURNAL, 49, 2512 (1927).

substances whose constitution has been the subject of some debate.[12] Orndorff and Sherwood[12b] have suggested that, because phenolsulfonephthalein is a sulfonic acid derivative of benzaurin, a strongly basic compound, it probably forms an inner salt. In aqueous solution, however, they postulated the addition of a molecule of water, bringing about the formation of a quinoid hydrate. If this theory were correct, it is to be expected that both phenolsulfonephthalein and **o-cresolsulfonephthalein** would exhibit different types of absorption in aqueous and absolute ethanol solution, since in the latter solvent hydrate formation could not occur. It has previously been shown that a sharp differentiation between the quinoid and quinoid hydrate forms, as found in fresh and faded solutions, respectively, of fuchsone, benzaurin and aurin,[13] can be readily obtained by means of their absorption spectra. In the present instance the spectroscopic evidence completely confirms the existence of the quinoid form, or inner salt, in alcoholic, and the quinoid hydrate in aqueous solution. Figs. 2 and 3, respectively, show the absorption curves for phenolsulfonephthalein and o-cresolsulfonephthalein in both solvents. Curve A in each case is for the aqueous solution; the curves are entirely similar, with the bands for o-cresolsulfonephthalein shifted slightly toward longer wave lengths. For the absolute ethanol solutions Curves B of Figs. 2 and 3 are obtained and they are of a radically different type from the "A" curves. The

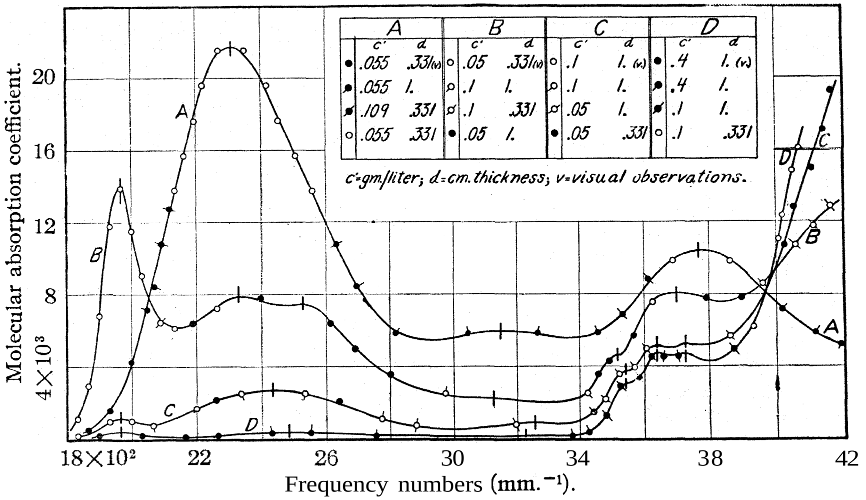

Fig. 2.—Phenolsulfonephthalein—neutral solutions: *A*, aqueous; B, absolute ethanol—fresh solution; *C*, solution B—after standing for one year; D, diethyl ether—absolute ethanol solution.

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[12] (a) White and Acree, This Journal, 40, 1092 (1918); 41, 1190 (1919); (b) Orndorff and Sherwood, *ibid.*, 45,490 (1923).

[13] Orndorff, Gibbs, McNulty and Shapiro, This Journal, 49,1546 (1927).

assignment of the inner salt configuration to these sulfonephthaleins in ethanol solution is based on the similarity of their absorption curves to those obtained for the sulfuric acid solutions, Pigs. 4 and 5. In the latter case salt formation occurs through the neutralization of the basic, quinoid oxygen by the sulfuric acid and it is reasonable to assume that the formation of an inner salt in neutral alcoholic solution by the sulfonic acid radical gives rise to a similar distribution of intramolecular forces, which uniquely determine the nature of the absorption spectrum. It is necessary to work in absolutely dry ethanol and with perfectly dry samples of the sulfonephthaleins in order to obtain this absorption characteristic of the inner salt, as the formation of the hydrate readily takes place in the presence of traces of water. The effect of minute traces of moisture, which cannot after all be completely avoided, is apparent in both of the "B" curves, for a weak band is found in the region of frequency number 2300 which is evidently related to the strong band occurring at the same approximate position for the aqueous solutions. If more water is present, as in a 95% ethanol solution, hydrate formation is complete and the solution has the bright yellow color of an aqueous solution instead of the salmon color in absolute ethanol. This accounts for the type of curve obtained by Howe and Gibson[4] for their "alcoholic" solution of phenolsulfonephthalein, which evidently contained a fair amount of water, since the absorption recorded by them resembles that here presented for an aqueous solution.

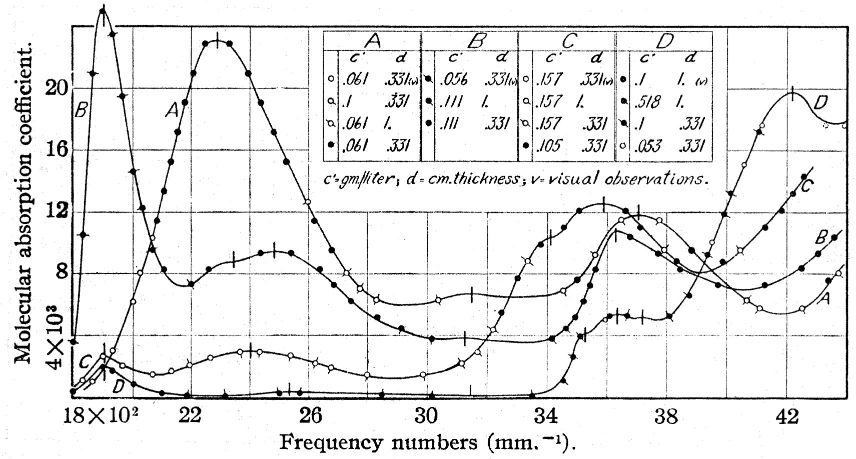

Fig. 3.—o-Cresolsulfonephthalein—neutral solutions: *A*, aqueous; *B*, absolute ethanol—fresh solution; *C*, solution B—after standing for one year; D, diethyl ether—absolute ethanol solution.

The formation of a hydrate in aqueous solution is not observed with all sulfonephthaleins. Hydroquinolsulfonephthalein[14] exhibits the same ab-

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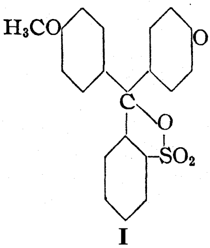
[14] Shapiro, This Journal, 50, 1772 (1928).

sorption in both aqueous and ethanol solution and this is of the acid type, as found for example in concentrated sulfuric acid. The introduction of more hydroxyl groups stabilizes the inner salt configuration, probably by enhancing the acid properties of the sulfonic acid radical. This effect on the acid properties of the phthaleins and sulfonephthaleins due to an increase of the number of hydroxyl groups appears to be quite general and will be discussed in a subsequent paper.

When the alcoholic solutions of phenolsulfonephthalein and *o*-cresolsulfonephthalein are allowed to stand in a dark room for a year in tightly stoppered pyrex bottles, the color decreases considerably in intensity and the solutions no longer give the characteristic color changes of the sulfonephthaleins in acid and alkaline solution. Curve C, Fig. 2, shows the absorption of such a faded solution of phenolsulfonephthalein. The band in the visual region at 1966 has not changed in position but it has only one-twelfth of its original intensity. In the ultraviolet region, however, the character of the bands has been completely modified. This is evidently due to the conversion of the phenolsulfonephthalein into its diethyl ether,[15] for by determining the absorption of the pure diethyl ether in ethanol solution, Curve D is obtained and it runs quite parallel to Curve C. Moreover, the absorption of the diethyl ether solution does not remain constant but slowly approaches that of the faded solution of the sulfonephthalein. There is thus indication that the diethyl ether, which can be obtained in the form of almost colorless crystals[15] and is considered as a lactoid derivative, I, sets up equilibrium in solution with a colored modification, which may be an ether–ester, II, or possibly a mixed quinoid hydrate, III.



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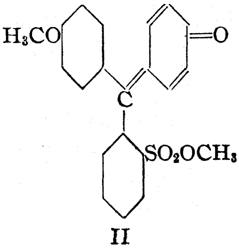
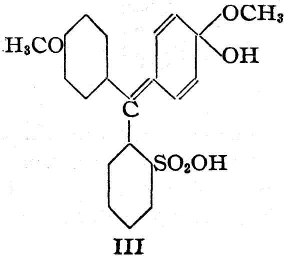


II



III

The existence of the lactoid form in the equilibrium mixture is confirmed by the presence of the characteristic pair of bands at 3540 and 3639, which have previously been associated with the benzenoid condition of the molecule.[7]

o-Cresolsulfonephthalein likewise fades to a considerable extent in ethanol solution, as shown in Curve C, Fig. 3, with the peak of the band at 1905 decreasing to one-tenth of its original intensity after one year. In the ultraviolet region, however, the absorption increases and new bands

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[15] Orndorff and Shapiro, THIS JOURNAL, 46, 2858 (1924).

develop which are not related either to those of the fresh solution, or to those of a freshly prepared solution of the diethyl ether of *o*-cresolsulfonephthalein, Curve D. In fact, at a still later stage (not shown on Fig. 3), the bands at 3411 and 3588 of Curve C had again increased 50% in intensity, with some indication that they were shifting closer together. The absorption of the pure diethyl ether of *o*-cresolsulfonephthalein, Curve D, is similar to that for the ether of phenolsulfonephthalein, except for the presence of a band in the extreme ultraviolet at 4218. It is probable that there is a corresponding band in phenolsulfonephthalein diethyl ether, but further in the ultraviolet and hence beyond the range of our spectrograph, since in general the bands for phenolsulfonephthalein are located to the side of higher frequency numbers with reference to the corresponding bands of o-cresolsulfonephthalein. The fading of the alcoholic solution of o-cresolsulfonephthalein cannot, therefore, be ascribed to ether formation in view of the relation between Curves C and D, but further observations will be continued on both of these solutions, in particular to follow any changes that may develop in that of the diethyl ether. The positions of the bands in the faded ethanol solutions of the sulfonephthaleins and in the ethanol solutions of their diethyl ethers are presented in Table II.

TABLE II

FREQUENCY NUMBERS OF BANDS IN ETHANOL SOLUTIONS OF

Phenol-sulfonephthalein, faded	o-Cresol-sulfonephthalein, faded	Phenol-sulfonephthalein, diethyl ether	o-Cresol-sulfonephthalein, diethyl ether
1966	1905	1966	1905
2434	2402	2485	2535
3255	..	3225	3145
3540	3411	3540	3527
3639	3588	3639	3634
3727	..	3727	3719
..	..	..	4218

Phenolsulfonephthalein and o-cresolsulfonephthalein readily dissolve in concentrated sulfuric acid to form orange colored solutions, in which the sulfonephthalein is presumably present as the sulfate. If hydrochloric acid is added to an aqueous solution of the sulfonephthalein, which is originally present therein as the quinoid hydrate, as we have indicated above, water is split off with the formation of the basic quinoid form, which then reacts to form a hydrochloride. The extent to which this srries of reactions proceeds depends, however, on the amount of acid present, and by determining the absorption spectrum at different concentrations of acid it is possible to follow the course of the salt formation. When the solution contains 10,000 molecules of hydrochloric acid to one of the sulfonephthalein, the same absorption bands are found as in the sulfuric acid solutions, but at intermediate concentrations of acid some of the "neutral" bands, that is, those characteristic of the quinoid hydrate form, persist. Phenolphthalein and o-cresolphthalein in concentrated sulfuric acid likewise form salts of a quinoid structure which should have the same molecular configuration as those of the sulfonephthaleins and should, therefore, give rise to the same type of absorption spectra. In the case of phenolphthalein, however, it has already been pointed out[6] that the occurrence of sulfonation is a complicating factor in its effect on the absorption spectrum and a similar result has now been found for o-cresolsulfonephthalein, as is evident from an inspection of their absorption curves.

Figure 4 shows the absorption curves for the phenol derivatives. Curve A for phenolsulfonephthalein in concentrated sulfuric acid and Curve B for the same compound in aqueous solution with the addition of 10,000 molecules of hydrogen chloride are fairly parallel, with the bands in the sulfuric acid solution shifted uniformly toward longer wave lengths. Curve C is a reproduction of our previously published curve for phenolphthalein in sulfuric acid,[6] with the addition of a band in the extreme ultraviolet at 4280, which has since been found. It is similar to Curves A and B up to frequency number 3230, beyond which the three broad bands are in sharp contrast with the single prominent band of phenolsulfonephthalein at 3771.

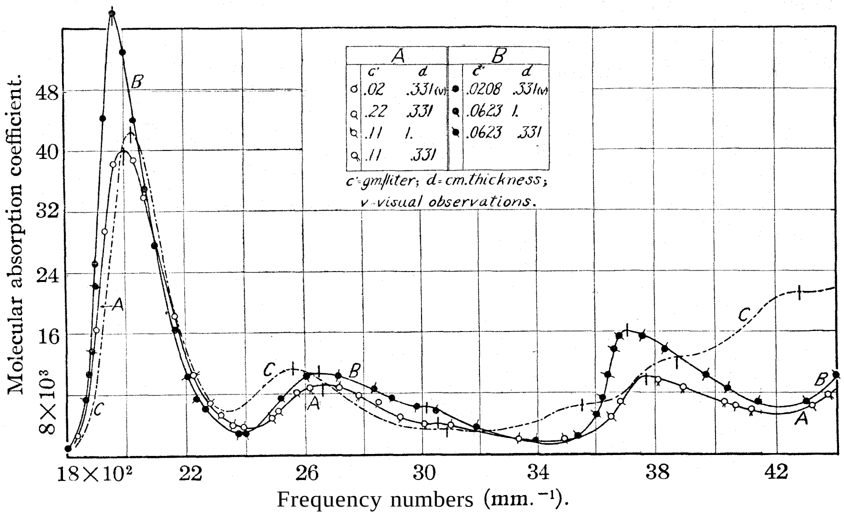

Fig. 4.—Acid solutions: *A*, phenolsulfonephthalein—concd. sulfuric acid; B, phenolsulfonephthalein—1 mole: 10,000 moles of hydrochloric acid; *C*, phenolphthalein—concd. sulfuric acid.

Figure 5 gives a similar set of curves for the o-cresol compounds. Curve A for *o*-cresolphthalein in sulfuric acid corresponds in all respects with the curve for phenolphthalein in the same solvent, Fig. 4. Evidence for progressive sulfonation was also obtained, in that the intensity of the absorption in the visual region was observed to diminish slowly in the course of several days. Curve B for o-cresolsulfonephthalein in concentrated sulfuric acid exhibits some peculiarities beyond 3400, in that instead of having a single, well-defined band, as with phenolsulfonephthalein, a shallow double band is produced. In aqueous hydrochloric acid, Curve C, the absorption is normal, with the bands having the same relative positions and intensities as for phenolsulfonephthalein in acid solution and for both sulfonephthaleins in absolute ethanol solution. The data for the positions of the band heads in these several neutral and acid solutions are summarized in Table III.

In alkaline solution, phenolsulfonephthalein and o-cresolsulfonephthalein exhibit their characteristic bluish-red color, due to the formation of the quinoid, di-basic salt. There are, however, two conditions under which this color is subject to modification. In the first place, at very low concentrations of alkali, corresponding to two molecules of the base to one of the sulfonephthalein and at low concentrations of the sulfonephthalein, hydrolysis occurs to a marked extent owing to the weak nature of the acid.

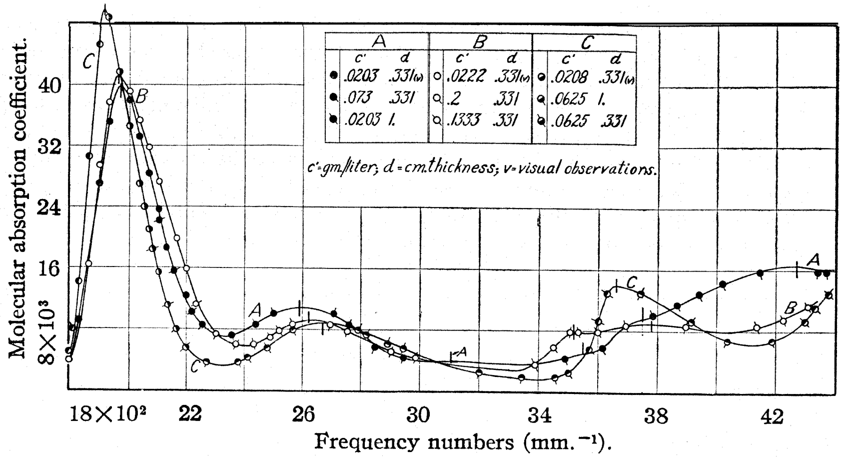

Fig. 5.—Acid solutions: A, o-cresolphthalein—concd. sulfuric acid; B, *o*-cresolsulfonephthalein—concd. sulfuric acid; *C*, *o*-cresolsulfonephthalein—1 mole : 10,000 moles of hydrochloric acid.

This is brought out in Fig. 6, Curves A and A', for the absorption of an aqueous solution of phenolsulfonephthalein containing the theoretical amount of alkali for producing the dipotassium salt. Curve **A** was for a solution containing 0.0609 g. of phenolsulfonephthalein to the liter and it will be noted that for the thinnest cell available, 0.331

TABLE III

FREQUENCY NUMBERS OR BANDS IN NEUTRAL AND ACID SOLUTIONS

Distilled water						
Phenolsulfonephthalein	..	2310	..	3148	..	3768
o-Cresolsulfonephthalein	..	2290	..	3148	..	3706
Absolute ethanol						
Phenolsulfonephthalein	1966	2330	2527	3125	3516	3700
o-Cresolsulfonephthalein	1905	2345	2483	3125	..	3620
Concentrated sulfuric acid						
Phenolphthalein	2025	2560	3085	3555	3875	4280
Phenolsulfonephthalein	2000	2659	3055	..	3771	..
o-Cresolphthalein	1970	2590	3105	3550	3752	4271
o-Cresolsulfonephthalein	1964	2623	..	3518	3780	..
1 mole of phenolpthalein: 10,000 moles of hydrochloric acid						
Phenolsulfonephthalein	1965	2647	3016	3709	..	..
o-Cresolsulfonephthalein	1920	2672	..	3663	..	..

cm., it was not possible to obtain the peak of the band in the visual region at 1782 indicated on the curve by a broken line. Upon diluting to a concentration of 0.0203 g. to the liter, the solution changed from its bluish-red color to an orange and the absorption in the visual and near ultraviolet regions, Curve **A'**, showed a large decrease in the intensity of the band at 1782 and a simultaneous increase of that at 2300, which is the first band in the neutral aqueous solution, Fig. 1, Curve A. At a ratio of 100 molecules of potassium hydroxide to one of phenolsulfonephthalein, Curve B, *the* full alkaline color developed and was then stable at all practical dilutions. It is now apparent on examining Curve A for the higher concentration of the sulfonephthalein in solution with two molecules of alkali that even undex these conditions hydrolysis is effective, for traces of two of the neutral bands still persist at 2250 and 3642.

The same phenomenon occurs with o-cresolsulfonephthalein in an aqueous solution containing two equivalents of potassium hydroxide, Fig. 6, Curve **A,** except **that** the *o*-cresol compound appears to be somewhat more susceptible to hydrolysis, for at a concentration of 0.061 g. to the liter the absorption curve has the same contour as that for phenolsulfonephthalein at a concentration of 0.0203 g. to the liter. It was found on examining a solution containing 0.1 g. of o-cresolsulfonephthalein to the liter, that the intensity of the first two bands was reversed, that at 1745 becoming much stronger than the one at 2287. With 100 molecules of potassium hydroxide present, the absorption becomes stable at all practical dilutions and Curve B is obtained, which is entirely comparable with that of phenolsulfonephthalein obtained under similar conditions. In each case there are three bands, with those for *o*-cresolsulfonephthalein shifted uniformly toward longer wave lengths.

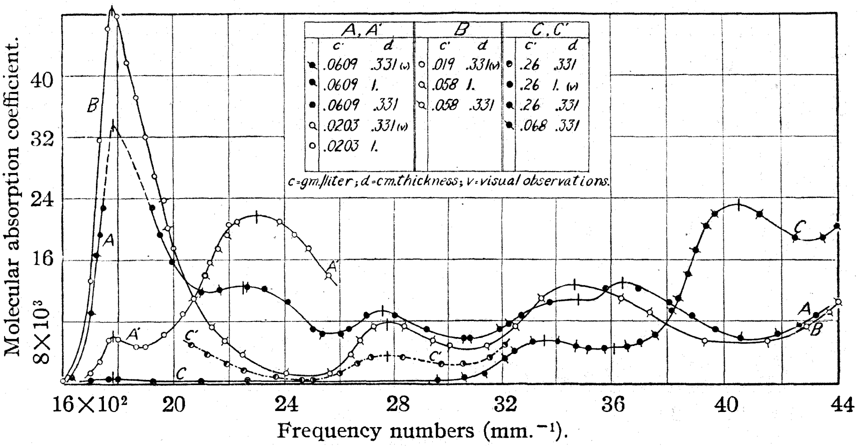

Fig 6.—Phenolsulfonephthalein in aqueous alkaline solutions: A, A′, 1 mole:2 moles of potassium hydroxide; B, 1 mole:100 moles of potassium hydroxide; *C*, C′, 33% potassium hydroxide—two days after preparation of solution.

As both phenolsulfonephthalein and o-cresolsulfonephthalein are commonly used as indicators for the absolute determinations of *P*H values, it is evident that when working with alkaline solutions of low concentration, if only slightly buffered or unbuffered, it is essential to carry out comparisons with the standard solutions under very nearly identical conditions of concentration of the alkaline medium and of the indicator. The use of the partially neutralized indicator, as recommended by **Clark,**[16] is evidently an improvement in the light of the above data, but the caution

[16] Clark, "The Determination of Hydrogen Tons," Williams and Wilkins Co., Baltimore, 1922, p 80

still applies for very low alkali concentrations. It is, furthermore, not safe, in view of the hydrolysis of the dibasic salts of the indicators, to assume as **Brode**[17] has done in the development of his spectrophotometric method for the determination of hydrogen-ion concentration, that Beer's law always holds over a range of concentrations.

The second of the two conditions under which the alkaline color of these sulfonephthaleins is modified is in the presence of high concentrations of alkali. In aqueous solutions containing 33% potassium hydroxide, the deep red color of phenolsulfonephthalein rapidly fades to a pale pink in two days, while o-cresolsulfonephthalein requires six months to reach the same stage. This fading, which is common to all phthaleins in strongly alkaline solutions, is due to the formation of the colorless tripotassium salt of the carbinolcarboxylic acid. With phenolsulfonephthalein an attempt was made to record the absorption of its solution in 33% potassium hydroxide immediately after its preparation but, owing to the rapidity of the fading, consistent data could not be obtained. Curve C', Fig. 6, represents a portion of the data thus obtained and brings out the band at 2774, which is missing in Curve C for the same solution, two days later. In the ultraviolet region, Curve C shows three bands, whereas in the solution containing 100 molecules of alkali to one of phenolsulfonephthalein there is only one in the same region.

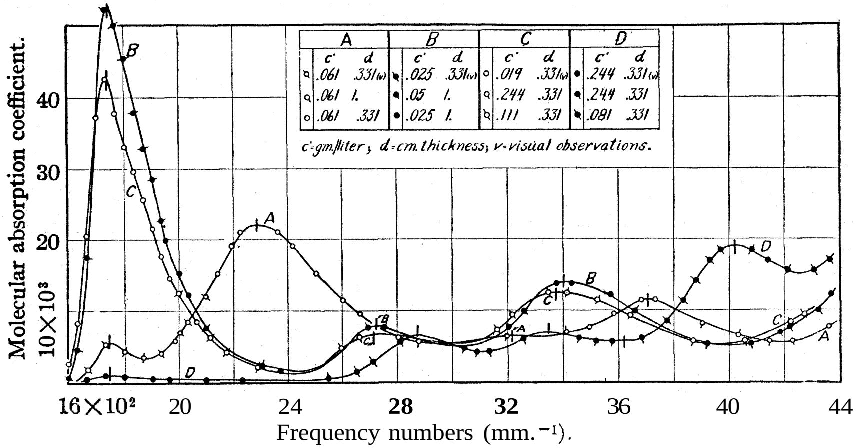

Fig. 7.—o-Cresolsulfonephthalein in aqueous alkaline solutions: *A*, 1 mole:**2** moles of potassium hydroxide; B, 1 mole:100 moles of potassium hydroxide; *C*, 33% potassium hydroxide—fresh solution; *D*, solution C—after standing for six months.

As the fading was so much slower in the case of o-cresolsulfonephthalein in 33% potassium hydroxide, it was possible to obtain the absorption of the fresh solution, Curve C, Fig. 7, and it will be noted that except for a

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[17] **Brode**, THIS JOURNAL, 46, 587 (1924).

slight decrease in intensity, which is probably due to an incipient fading, the bands are very close to those for an aqueous solution of *o*-cresolsulfonephthalein containing 100 molecules of potassium hydroxide, Curve B. At the end of six months, however, when the solution had changed to a pale pink, the absorption, Curve D, had likewise changed completely in character, yielding a curve very like that of phenolsulfonephthalein after two days, except that there remains a well defined band at 2874, for which there is no counterpart in the faded solution of the latter substance. The relatively greater stability of o-cresolsulfonephthalein in strongly alkaline solution, as indicated by the above data, renders it more desirable than phenolsulfonephthalein as an indicator under such conditions. The relation between the bands in the various alkaline solutions of these two sulfonephthaleins is well brought out in Table IV.

TABLE IV

FREQUENCY NUMBERS OF BANDS IN AQUEOUS ALKALINE SOLUTIONS OF PHENOLSULFONEPHTHALEIN AND *o*-CRESOLSULFONEPHTHALEIN

	1 mole: 3 moles of KOH	**1 mole. 100 moles of** KOK	33% KOH	33% KOH, **faded**
	1782	1782	1782	1782
	2250 (2300)			
Phenolsulfonephthalein	2756	2774	(2774)	
	3487	3474	(3378)	3355
	3642			3610
			(4058)	4052
	1745	1745	1742	1745
	2287			
o-Cresolsulfonephthalein		2725	2715	2874
	3215	3402	3373	3346
	3705			3620
				4021

Summary

1. The absorption spectra of phenoltetrachloro-, o-cresol-, and *o*-cresoltetrachlorophthaleins are discussed in their relation to that of phenolphthalein. Evidence is presented to support the view that the absorption of triphenylmethane compounds is due primarily to the joint effect of the three phenyl nuclei and not to the central methane carbon atom.

2. A consideration of the absorption spectra of phenolsulfonephthalein and o-cresolsulfonephthalein in neutral aqueous and ethanol, and in sulfuric acid solutions, leads to the conclusion that they possess the inner salt structure in ethanol solution but the quinoid hydrate in aqueous solution.

3. The absorption spectra of these sulfonephthaleins in weakly alkaline solutions bring out the progress of hydrolysis of the dibasic salts at low concentrations. The implications of this fact with respect to their use as indicators are pointed out.

4. In concentrated alkaline solutions, both phenolsulfonephthalein and o-cresolsulfonephthalein are converted largely into the colorless tribasic salts of the carbinolcarboxylic acid, although the reaction proceeds very much more rapidly with the former.

ITHACA, NEW YORK

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

DI-NORMAL-BUTYL ETHER AS A SOLVENT FOR THE GRIGNARD REAGENT

BY C. S. MARVEL, A. T. BLOMQUIST AND L. E. VAUGHN

RECEIVED JULY 19, 1928 PUBLISHED OCTOBER 6, 1928

The need for a solvent with a higher boiling point than that of diethyl ether for the preparation and use of the Grignard reagent has long been felt. The low boiling point of diethyl ether with the consequent loss of it in handling and danger of the formation of explosive mixtures of its vapor and air has limited the use of the Grignard reagent in commercial work to very rare cases. Numerous papers describing the use of higher aliphatic ethers, various phenyl ethers and high boiling hydrocarbons have appeared in the literature.[1]

It seemed likely that a suitable substitute for diethyl ether would be di-n-butyl ether, which has occasionally been used as a solvent in the Grignard reaction. This ether may be prepared in a pure condition easily and cheaply fron n-butyl alcohol and its boiling point is high enough so that it can be conveniently handled without excessive loss due to evaporation. Furthermore, distillation alone gives an ether free from moisture and butyl alcohol, thus avoiding the difficulties met in the purification of ordinary ethyl ether. While it has been suggested as a solvent in this reaction, there is very little information in the literature concerning the yields of the Grignard reagents from different halogen compounds or of the yields of products that may be obtained from Grignard reagents in this solvent. Gilman and McCracken[1] report a yield of 55.9% of phenylmagnesium bromide from bromobenzene and magnesium in di-n-butyl ether.

The present investigation has shown that the yields of the Grignard reagent from several typical halogen compounds when di-n-butyl ether is the solvent are nearly equal to those obtained in diethyl ether. It has also been shown that in a typical reaction of the Grignard reagent, such as that with carbon dioxide, as good a yield of product can be obtained in di-n-butyl ether as when diethyl ether is used. For a reaction such as that between the Grignard reagent and ethylene oxide, where an elevated temperature is needed to complete the reaction, di-n-butyl ether is more

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[1] A review of this topic is given in a recent paper by Gilman and McCracken, *Rec. trav. chim.*, **46**, 463 (1927).

convenient to use than is the usual mixture of ether and benzene. For the preparation of primary alcohols from the Grignard reagent and formaldehyde di-n-butyl ether has a decided advantage over diethyl ether since in the higher boiling solvent a temperature can be reached which will bring about depolymerization of paraformaldehyde in the reaction mixture. This obviates the necessity of depolymerizing the paraformaldehyde as a separate operation. One disadvantage that should be mentioned is that di-n-butyl ether cannot be used conveniently as a solvent in reactions used for the preparation of neutral substances which boil too close to its own boiling point (141°). The di-n-butyl ether may be recovered from these reaction mixtures with very little loss and after distillation is again ready for use.

Experimental Part

1. Preparation of Grignard Reagents in Di-n-butyl Ether.—In determining the yields of various Grignard reagents in di-n-butyl ether a standard procedure essentially the same as that devised by Gilman and his students[S] was used. A 200-cc., three-necked flask was fitted with a mechanical stirrer, separatory funnel, reflux condenser and thermometer. In the flask was placed about 40 cc. of di-n-butyl ether, 1.5 g. of magnesium turnings and a crystal of iodine. The theoretical amount of halogen compound dissolved in enough di-n-butyl ether to make a total volume of 30 cc. was placed in the separatcry funnel. A small amount of the solution of the halogen compound was added and the reaction flask was heated until the reaction started. This temperature varied somewhat with the different halogen compounds. When the reaction was once started, stirring was begun and the remainder of the solution of the halogen compound was added at a rate which allowed the reaction to proceed smoothly. After addition of the last of the solution of the halogen compound stirring was continued until the mixture had cooled to room temperature. The reaction mixture was then rapidly transferred to a volumetric flask and the reaction vessel rinsed with more solvent. The level of the liquid in the volumetric flask was brought up to the mark by the addition of more solvent and aliquot parts were titrated with standard acid.

The di-n-butyl ether used in these experiments was prepared from n-butyl alcohol and sulfuric acid. It was washed with sodium hydroxide solution and distilled twice. The fraction boiling at 140–142° was collected. The halogen compounds and magnesium were of the ordinary grade used for the preparation of the Grignard reagent.

The results of the experiments are listed in the following table.

TABLE I

YIELDS OR GRIGNARD REAGENT FROM VARIOUS HALOGEN COMPOUNDS AND MAGNESIUM IN DI-n-BUTPL ETHER

Halogen compound	Yield, %	Halogen compound	Yield, %
Ethyl bromide	91–93	Zsobutyl bromide	82–86
n-Propyl bromide	89–90	n-Heptyl bromide	73–81
Zsopropyl bromide	79–80	Cyclohexyl bromide	80–83
n-Butyl bromide	86–87	Bromobenzene	70–77
sec.-Butyl bromide	68–72	α-Bromonaphthalene	63–71
		β-Phenylethyl bromide	68–71

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[2] Gilman, Wilkinson, Fishel and Meyers, THIS JOURNAL, **45**, 150 (1623); Gilman and Meyers, *ibid.*, **45**, 159 (1923); Gilman and McCracken, *ibid.*, **45**, 2462 (1923).

The yields recorded in the table are the upper and lower yields (to the nearest whole number) of a number of runs..

2. Reactions of the Grignard Reagent in Di-n-butyl Ether. dl-Methylethylacetic Acid.—The standard procedure for the preparation of an acid from the Grignard reagent was followed[3] except that di-n-butyl ether was substituted for diethyl ether. The yield of dl-methylethylacetic acid (b. p. 173–175") from 274 g. of *sec.*-butyl bromide was 135 g. (66% of the theoretical amount). In diethyl ether the yield has been found to be 135–136 g.

n-Nonyl Alcohol.—The general procedure for the preparation of n-hexyl alcohol from n-butyl bromide[4] was followed with the exception that di-n-butyl ether was used as a solvent in place of the usual solvents, ether followed by benzene. The Grignard reagent was prepared from 179 g. of n-heptyl bromide in about 300 cc. of di-*n*-butyl ether. This solution was cooled to 0° and with stirring an excess of ethylene oxide was added. The temperature was maintained at 0° for one hour after the addition of the ethylene oxide and then allowed to rise to 40° and maintained at that point for one hour. Finally the mixture was heated on the steam-bath for two hours and then decomposed and the product was isolated according to the procedure used for n-hexyl alcohol. The yield of n-nonyl alcohol boiling at 95–100° (12 mm.) was 95 g. (65% of the theoretical amount).

Cyclohexyl **Carbinol.**—The proportions of the reagents used were those desc ibed for this preparation by Adams and **Noller.**[5] The general procedure was the same except that the Grignard reagent was prepared in di-n-butyl ether. The solution was heated to 100–110° and 100 g. of dry paraformaldehyde was added in small portions to the well stirred solution over a period of about two hours. The product was isolated as described for the preparation in diethyl ether. The yield of cyclohexyl carbinol (b. p. 88–93' (18 mm.)) from 163 g. of cyclohexyl bromide was 70 g. (60% of the theoretical amount). In diethyl ether the yield has been found to be 61–65% of the theoretical amount.

Summary

1. Di-n-butyl ether may be used in place of diethyl ether as a solvent for the preparation of the Grignard reagent without materially reducing the yield.
2. The three typical reactions of the Grignard reagent which were studied have been found to give as good yields in di-n-butyl ether as when diethyl ether is used as a solvent. In two of these reactions the procedure is simplified by the use of the higher boiling solvent.

URBANA, ILLINOIS

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[3] Gilman and Parker, "Organic Syntheses," John Wiley and Sons, Inc., New York, 5, 75 (1925).

[4] Dreger, "Organic Syntheses," John Wiley and Sons, Inc., New York, **6,** 54 (1920).

[5] Adams and Noller, "Organic Syntheses," John Wiley and Sons, Inc., New York, ***6,*** 22 (1926).

[Contribution from the Chemical Laboratory of the College of Liberal Arts,
Northwestern University]

THE REACTIVITY OF THE METHYLATED SUGARS. III. THE ACTION OF DILUTE ALKALI ON TETRAMETHYL-*d*-MANNOSE

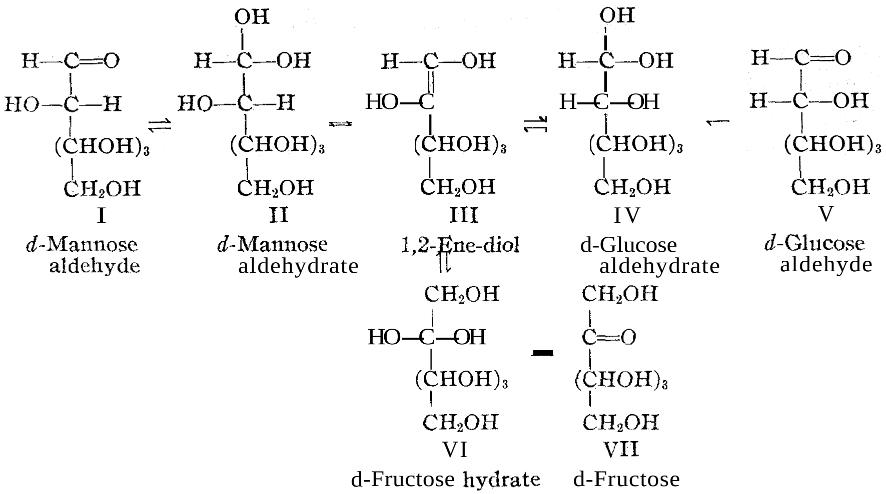
By Richard D. Greene[1] with W. Lee Leu-is

Received July 26, 1928 Published October 6, 1928

Attention has already been directed[2] to the fact that the methylated sugars offer excellent opportunities for testing experimentally the validity of certain of the theories developed to explain the reactivity of the simple sugars.

The interconversion of sugars by alkalies, first studied by Lobry de Bruyn,[3] and explained by him and also by Fischer[4] and by Wohl,[5] was exhaustively studied by Nef[6] and his students. Nef's study of the action of alkalies and alkaline oxidizing agents on the sugars led him to interpret the reactions on the basis of the formation of intermediate ene-diols. Thus the obtaining of isomeric hexoses from d-glucose in alkaline solution and of acids of from one to five carbon atoms by alkaline oxidation was readily explained by assuming progressive enolization. It is this theory of enolization and, more especially, the actual mechanism of enol formation when methylated mannose is treated with alkali, that is our chief concern here. Nef[6,7] explained enol formation by assuming that a given sugar can selectively add and lose water in such a way as to produce ene-diols, and from them various isomeric sugars.

On the basis of Nef's explanation the interconversion of *d*-mannose into d-glucose and d-fructose may be illustrated as follows



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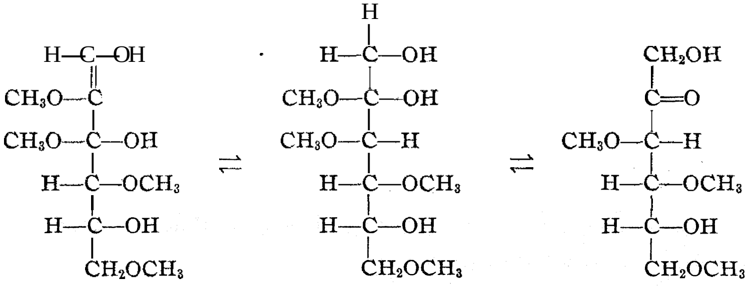
[1] Abstracted from a dissertation submitted by Richard D. Creene to the Graduate

By assuming that enolization continues down the carbon chain, Nef accounted for the formation of other products, as d-glutose and d-pseudofructose. If Nef's theory of enol formation is entirely correct, we can make certain predictions as to the behavior of the methylated sugars with alkali. Thus 2,3,4,6-tetramethyl-*d*-mannose should add water to form its aldehydrate, which would then lose water to form the 1,2-monomethyl ene-diol. This, in turn, by selective loss and addition of water, might form 2,3,4,6-tetramethyl-*d*-glucose. It might, however, equally well form an unstable hemi-acetal (IX), which would undoubtedly lose methyl alcohol to form 3,4,6-trimethyl-*d*-fructose.



VIII IX X

This trimethylfructose (X) would then be subject to a repetition of the same process of enolization and demethylation, and in the presence of oxidizing agents should yield fragments of from one to five carbon atoms (in the chain) just as in the case of the unmethylated sugars.

Actually the facts are not consistent with such behavior. The resistance of the methylated sugars to mineral acids and to fermentation is well known. It has been shown that they are much less reactive with Fehling's solution[8] than are the unmethylated sugars. The oxidation of tetramethyl-d-glucose with alkaline hydrogen peroxide[2"] yielded predominantly formic and carbonic acids with a methylated five carbon acid, whereas Nef's difficulty in obtaining any five carbon acid from unmethylated glucose is historic. It was further shown that tetramethyl-*d*-glucose[2b] under the action of dilute alkali yields a mixture of methylated glucose and mannose with a certain amount of the ene-diol common to them.

School of Northwestern University, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] (a) Gustus and Lewis, THIS JOURNAL, 49, 1512 (1927); (b) Wolfrom and Lewis, ibid., 50,837 (1928).

[3] Lobry de Bruyn and Van Ekenstein, *Rec. trav. chim.*, 14, 156, 203, **213** (1895).

[4] Fischer, *Ber.*, 28, 1149 (1895).

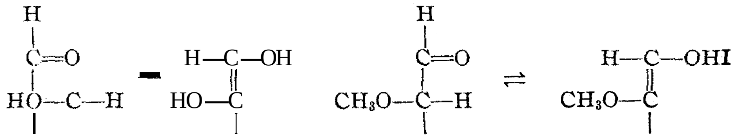
[5] Wohl and Neuberg, *Ber.*, 33, 3099 *(1900)*.

[6] Nef, ***Ann.***, 357, 214 (1907); 376, 1 (1910); 403, 204 (1914).

[7] Spoehr, ***Am. Chem. J.***, 43, 228 (1910).

[8] Purdie and Irvine, *J. Chem. Soc.*, *85*, 1060 (1904); Irvine, *ibid.*, 85, 1077 (1904).

The conclusion from these facts must be that enolization is definitely blocked at carbon 2 when the labile hydrogen of the sugar is replaced by the non-polar methyl group. Nef's theory as it stands does not account for the behavior of the methylated sugars and so must not be an entirely correct explanation of the reactivity of the simple sugars. By a simple modification, however, it can be made to fit all the facts. If the concept of enolization by addition and loss of water be modified in favor of a simple keto-enol tautomerism, we can harmonize the behavior of the substituted and unsubstituted sugars perfectly.



$$\begin{array}{c}H\\|\\C{=}O\\|\\HO{-}C{-}H\\|\end{array} \quad - \quad \begin{array}{c}H{-}C{-}OH\\\|\\HO{-}C\\|\end{array} \qquad \begin{array}{c}H\\|\\C{=}O\\|\\CH_3O{-}C{-}H\\|\end{array} \rightleftarrows \begin{array}{c}H{-}C{-}OHI\\\|\\CH_3O{-}C\\|\end{array}$$

We can now understand their difference in reactivity for we would not suspect that, under our conditions, methyl should go from oxygen to carbon. It seems highly reasonable then, that tetramethyl-d-mannose with alkali should produce a system containing only tetramethylated glucose and mannose.

In the further verification of this principle it was first necessary to find conditions under which mannose would produce a system containing considerable amounts of glucose and fructose, with minimum secondary effects. Having then applied identical conditions to the methylated sugar, we should be in a position to generalize correctly from the results.

A solution molar in mannose and 0.035 *N* in calcium hydroxide held at 35° for 200 hours fulfilled the above requirements. Tetramethyl-*d*-mannose, which had been obtained crystalline for the first time, was subjected to similar conditions. In the analytical investigation of the action of alkali on tetramethylmannose it was found that the specific rotation increased from +2.4° to an equilibrium value of $42". This is precisely the value obtained from a synthetic mixture of equal quantities of tetramethylmannose and tetramethylglucose. Determination of total methylated aldoses by iodine titration gave the surprising result of apparently increased aldose content. This is ascribed to the presence of a certain amount of the ene-diol, common to the two sugars, which seems to possess unusual stability. This view is confirmed by the fact that treatment with acid restores the original iodine value. Investigation of the alkaline solution of mannose did not show the presence of an unmethylated ene-diol of any stability.

The separation of the two tetramethyl sugars from the reaction mixture was accomplished by their conversion to the anilides, which were separated on the basis of their solubility in aniline, tetramethylglucose anilide being much the more insoluble.

This investigation, in showing that tetramethyl-d-mannose with alkali gives no methylated ketose and an undiminished amount of methylated aldose, affords direct evidence that the process of enolization involves the movement of hydrogen atoms rather than selective hydration and dehydration. In addition, the general enol explanation of sugar reactivity finds further support. While this work does not involve, and therefore does not answer, the question of the absolute ring structures of the two tetramethyl sugars dealt with, yet their interconvertibility indicates that they possess the *same* ring structure.

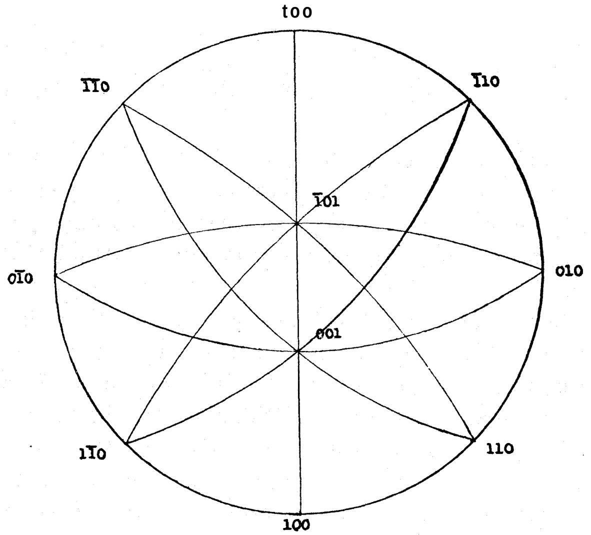


Fig. 1.—Stereographic projection of tetramethylmannose. Crystallography of Letramethylmannose.* Monoclinic. Resembles orthoclase, Fig 767, p. 457, Dana's "Mineralogy," 3d ed, W. E Ford Some crystals have (100) also slightly developed. 110 A $1\bar{1}0$ = 89° 1'; 100 A 010 = 45° 39'; 100 A 001 = 55° 30'; 100 $\wedge$ 101 = 55° 11'; 001 $\wedge$ 101 = 69° 19'. Cleavage: (100) perfect. Optically. Birefringence fairly strong, $(\gamma - \alpha) = 0.023$. $\alpha = 1.475$, $\beta = 1\ 495$, $\gamma = 1.498$ Ax. Pl.||(010) Extinction parallel. Dispersion, $p < v$.

* Acknowledgments are here made to A. J. Walcott, Department of Mineralogy, Northwestern University, for directing the crystallographic determinations.

Experimental Part

The Preparation of Crystalline Tetramethylmannose.—α-Methylmannoside was prepared from vegetable ivory nuts by the method of Hudson;[9] the yield was about 50%

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[9] Hudson, "Organic Syntheses," John Wiley and Sons, Inc., New York, 7, 64 (1927).

of the weight of vegetable ivory used. From the mannoside so obtained **the** completely methylated mannoside was prepared by the method of Haworth.[10] The tetramethyl-a-methylmannoside was a limpid, colorless liquid; b. p. 116° at 2 mm. It later solidified to a mass of prisms, m. p. 39–40°. The specific rotation in water was *[a],* = \$43.5" (c = 5). The mannoside was hydrolyzed with hydrochloric acid and the tctramethylmannose was isolated according to the method of Irvine.[11] Vacuum distillation had been employed by previous workers in the purification of tetramethylmannose, but with quantities not exceeding 30 to 40 g., perhaps. An attempt at vacuum distillation (2–5 mm.) of 258 g. of tetramethylmannose resulted in complete decomposition, with the formation of some tetramethylglucose and a large amount of partially demethylated products. A similar attempt at distillation of 633 g. promised the same result and the method of purification by distillation was abandoned.

Extraction with petroleum ether (b. p. 40–50°) was tried on a freshly prepared sample of tetramethylmannose as a means of removing the small amount of unhydrolyzed mannoside present. Equal volumes of the petroleum ether and tetramethylmannose were heated at about 55° in order to produce gentle refluxing, while the mixture was stirred vigorously. After one hour the mixture was allowed to demulsify and cool and the solvent layer was decanted. This treatment was repeated. The residual sirup (90% of the original) was almost entirely freed from solvent *in vacuo*. After several days standing the sirup crystallized completely. The large lot of undistilled material above (633 g.) crystallized largely after seeding. It was now possible to purify the sugar by recrystallization, as with tetramethylglucose. This operation was carried out in a continuous siphon extractor. In this way 270 g. of pure crystalline tetramethylmannose was obtained. The yield was not calculated because of the previous treatment of the material. Methoxyl was determined by the modified Zeisel method.[12]

Anal. Subs., 0.1492, 0.1209: AgI, 0.5862, 0.4762. Calcd. for $C_6H_8O_2(OCH_3)_4$:OCH_3, 52.5. Found: 51.9, 52.1.

The constants of the sugar were as follows

	Recrystallization $[\alpha]_D^{20}$ (c = 5 in all cases)			
	H_2O	CH_3OH	$CHCl_3$	M. p.
First	+2.4°	+27.6°	+23.0°	50–51°
Second	+2.4°	+27.6°	+23.0°	50.5–51.5°

The preparation of the tetramethylglucose and tetramethylfructose referred to in the course of this work is described by M. L. Wolfrom.[2b]

Preparation of **Tetramethylmannonic Lactone** from Crystalline **Tetramethylmannose**.—Ten *g.* of crystalline tetramethylmannose was oxidized with bromine according to the method of Purdie and Irvine [13] The crude lactone was purified by the sodium salt method of Haworth.[14] The pure lactone was a colorless sirup, which showed no tendency to crvstallize. Mol. wt. by titration, 235. Calcd. for $C_{10}H_{18}O_6$: 234. OCH_3, calcd., 53.0. Found, 52.2. A solution of the lactone in water (c = 2.97) changed in specific rotation *[a],* from +136.4° to +62.8° in six days. This agrees with the data of Upson and Whitnah[15] and confirms the conclusion of Haworth[14] that

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[10] Haworth, J. *Chem. Soc.*, 107, 8 (1915).

[11] Irvine and Moodie, *ibid.*, 87, 1465 (1905).

[12] Hewitt and Moore, *ibid.*, 81, 318 (1902).

[13] Purdie and Irvine, *ibid.*, 83, 1033 (1903).

[14] Charlton, Haworth and Peat, *ibid.*, 128, 89–101 (1926).

[15] Whitnah, "Dissertation," Nebraska University, 1925.

the tetramethylmannonic lactone prepared from "normal" tetramethylmannose is an "unstable" one.

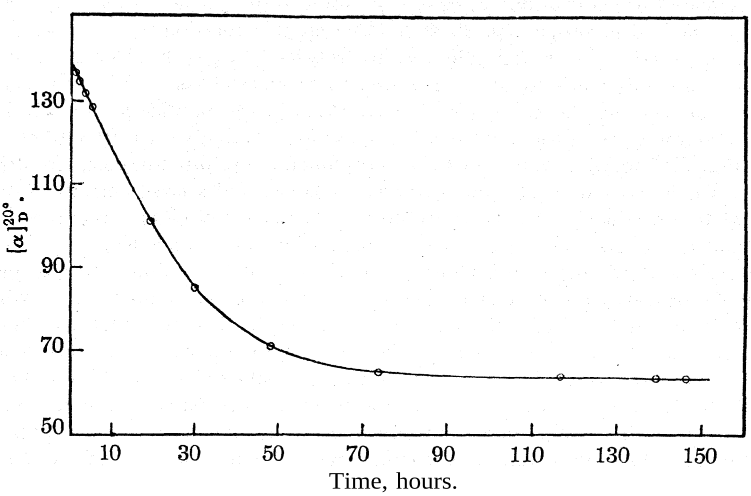

Fig. 2.—Change in specific rotation of tetramethylmannonic lactone in water (c = 2.969).

The Action of Dilute Alkali on Mannose.—It was proposed to find the optimum conditions for the interconversion of mannose and then to apply these to tetramethylmannose. A solution molar in mannose and 0.342 N in calcium hydroxide was allowed to stand at 35° for 200 hours. During this period the specific rotation changed from +14.3° to +0.6° (constant) and the solution had become neutral to phenolphthalein.

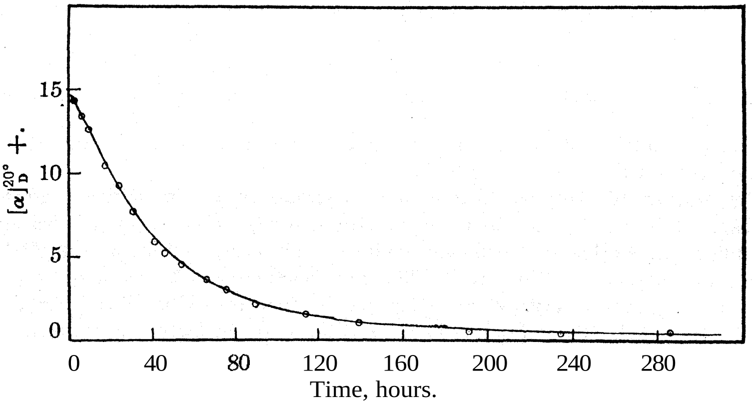

Fig. 3.—Change in specific rotation of mannose and alkali.

The amounts of glucose, mannose and fructose were determined periodically and finally. The percentages of the three sugars were calculated from the determination of reducing sugar by the Munsen-Walker method, aldoses by iodine titration[16] and mannose as

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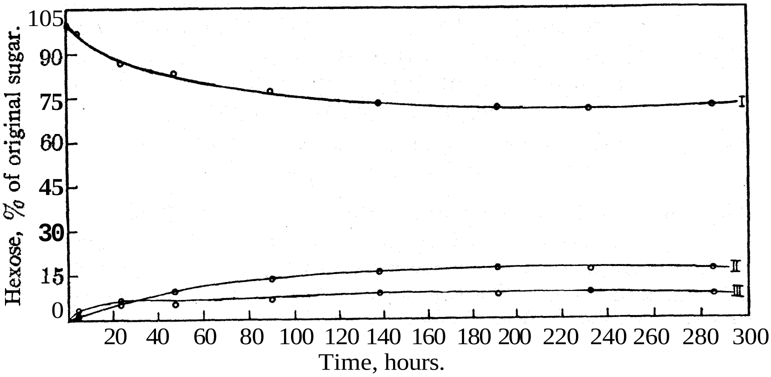
[16] Cajori, *J. Biol. Chem.*, 54, 617 (1922).

the phenylhydrazone.[17] The applicability of these methods had been tested on known solutions of the three sugars. The final percentages so determined were: mannose 71.7, glucose 8.9, fructose 16.9, non-sugar bodies, probably saccharinic acids (by diff.) 2.5. The polarimetric reading calculated from these percentages and the accepted specific rotations of the three sugars was −0.6° as against the observed value +0.6°. This is nearly as close agreement as the analytical determinations warrant.

In view of the evidence of the apparent stability of the methylated ene-diol, the reaction solution of the *unmethylated* sugar was tested. Iodine titration and Fehling's solution gave identical values with and without acidification, indicating no more than a transient existence of the simple ene-diol.

Preliminary Study of the Action of Alkali on Tetramethylmannose.—The action of 0.034 *N* calcium hydroxide on mannose had produced a considerable degree of interconversion and it seemed probable that the same conditions would be applicable to tetramethylmannose. Solutions of tetramethylmannose were made up molar in the sugar and with alkalinity of 0.03 N barium hydroxide, 0.035 *N* calcium hydroxide, 0.04 N barium hydroxide and 0.056 N barium hydroxide. Little or no specificity in the two alkalies was observed. These solutions were held at 35° and polarimetric observations were made at intervals. The specific rotation4 increased from the initial value of +2.4°, respectively, to +38.9°, +41.5°, +41.8° and +41.8° in about 200 hours. The alkalinity gradually decreased until the solutions were almost neutral. It is clear that a true equilibrium is involved since further increase of alkali beyond a certain point does not increase the specific rotation. The result has further interest, in view of the statement appearing frequently in sugar texts that rotation drops in alkaline solution.



I, mannose; II, fructose; III, glucose.

Fig. 4.—Formation of glucose and fructose from mannose and alkali.

The nature of this change was investigated by the method of iodine titration. This method was used in the determination of methylated aldoses in a known mixture of tetramethylmannose, tetramethylglucose and tetramethylfructose and found to be perfectly applicable.[2b] Determinations of the iodine values of the equilibrated solutions yielded results from 117 to 152% of the original, varying with the strength of alkali. This was taken as indicating the presence of a certain amount of the stable monomethyl ene-diol, which was capable of reacting with more iodine than the sugar. Treatment of the equilibrated solutions with acid caused a return to the original value

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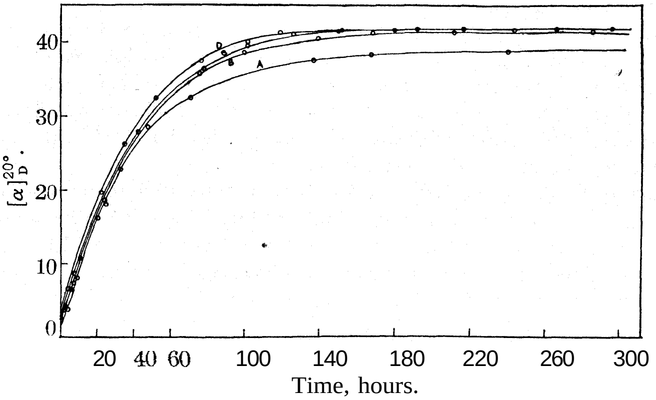
[17] Sherrard and Blanco, *J. Ind. Eng. Chem.*, *15*, 612 (1923).

of 100% tetramethyl aldohexose, indicating the absence of tetramethylfructose. The specific rotation of +42° was not appreciably altered by such treatment. Reference to the specific rotations of tetramethylmannose (+2.4°) and tetramethylglucose (+82°), shows that a mixture of equal quantities of the two sugars would have a specific rotation of +42°. Treatment of a mixture of equal quantities of the two sugars with 0.035 N alkali gave a constant specific rotation of +42°. The presumption of the presence of equal amounts of the two sugars in the equilibrated mixture is confirmed by the actual isolation of their anilides.



A, 0.03 N $Ba(OH)_2$; *B*, **0.035** N $Ca(OH)_2$; *C*, 0.04 N $Ba(OH)_2$; D, 0.056 N $Ba(OH)_2$.

Fig. 5.—Action of different strengths of alkali on tetramethylmannose.

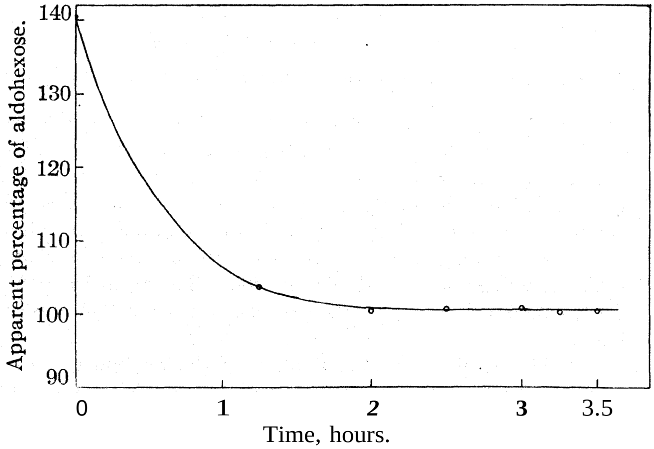


Fig. 6.—Rate of de-enolization of tetramethylmannose.

Optimum Conditions for **De-enolization.**—The complete reconversion of the enediol to sugar required a surprisingly strong acid treatment. Three N hydrochloric acid at 35° reduced the iodine from 152 to 100% apparent aldohexose in four hours. Since sulfuric acid could be removed more readily (as barium sulfate) it was substituted.

A portion of a reaction solution from 0.035 N calcium hydroxide was made 3 N in sulfuric acid and $M/2$ in sugar and held at 35° with the following results.

Interval, hours	(Original)	0	1.25	2	2.5	3	3.25	3.5
I, value, % app. aldohex.	140.4	103.7	100.4	100.8	100.7	100.1	100.3	

Further work showed that weaker acid at a higher temperature would render de-enolization complete. A solution 0.02 N in sulfuric acid and $M/5$ in sugar was heated at 95°. In fifteen minutes the iodine value dropped from 140.4 to 100.5% apparent aldohexose. In actual practice it was thought better to employ a temperature of 50° and a longer time.

Quantitative Recovery of the Sirup.—This phase of the work presented difficulties as serious as they were unexpected. Originally it was taken for granted that the sugar could be recovered quantitatively from the equilibrated solution without any special difficulty. While their known greater stability gave them an apparent advantage over the simple sugars, nevertheless the methylated sugars seem to possess a degree of volatility which necessitated the utmost care in their isolation from aqueous solution. After de-enolization of the equilibrated solution with sulfuric acid, the acid was removed by the addition of 0.1 N barium hydroxide drop by drop, until just faintly acid, and barium carbonate for the remainder of the acid. After removal of the barium sulfate by filtration, the water was evaporated at 25 mm. and 45–50°. The residual sirup was taken up in alcohol and finally in ether, any precipitate being removed before evaporating the solvent in *vacuo*. In this way but an 80–85% recovery of sirup was possible. The use of alcohol and ether was then discarded as unnecessary and the water was removed at 35° instead of at 45–50°. After these modifications a yield of 93.5% of sirup was obtained.

Methods of Separation and Identification.—Tetramethylglucose was established qualitatively as a product of the interconversion of tetramethylmannose, as follows. The equilibrated sirup from the experiment with 0.056 N alkali was seeded with tetramethylglucose. Crystallization occurred and the crystals were freed from sirup and recrystallized from petroleum ether. The following constants were obtained: $[\alpha]_D^{20}$ in water ($c = 1.14$) + 83.7°; m. p. 89–90°; identical with those of pure tetramethylglucose. Both equilibrated sirups and synthetic mixtures of equal amounts of the two sugars actually exhibited spontaneous crystallization of tetramethylglucose, in nearly equal amounts (10–15%) of the tetramethylglucose present. In this way substantial confirmation of the presence of equal amounts of the two sugars in the equilibrated solution was afforded. Attempts were made to separate the sugars as such quantitatively by crystallization and by the use of solvents, without success. Of their known compounds the anilides[18] appeared promising, being nicely crystalline and quantitative in formation. The two anilides were prepared

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[18] Irvine, J. Chem. *Soc.*, 93, 95 (1908); 97, 1449 (1910).

by heating for three hours at 100° a mixture of 8 moles of aniline with a 30% solution of the sugar in absolute alcohol. After recrystallization from absolute alcohol both anilides were obtained in a high degree of purity, with the following constants.

$[\alpha]_D^{20°}$ in Ethyl Alcohol with 0.001% Hydrochloric Acid (c = 5)

Anilide	Initial	Final	M. p.
Tetramethylglucose	+230°	+59°	138°
Tetramethylmannose	Variable	−8.5"	Variable

These anilides exhibit mutarotation with definite and reproducible equilibrium values, just as the sugars do. The tetramethylglucose anilide has a constant melting point, indicative of one solid form.

The original workers[18] had recorded such a wide variation in the case of hydrolysis of the two anilides that it seemed to promise a method of separation. This variability in case of hydrolysis was not confirmed, but the relative insolubility of the tetramethylglucose anilide in aniline was successfully utilized.

A trial separation was made on the anilides prepared from a mixture of equal amounts of the two sugars. Seven g. each of tetramethylmannose and tetramethylglucose was dissolved in 42 cc. of alcohol (absolute) and 42 cc. (8 moles) of redistilled aniline was added. The mixture was heated at 100° for three and one-half hours. After standing for eighteen hours the mass of crystals which had formed was filtered off. After removal of the alcohol a crop of crystals came out of the aniline and was filtered off. The aniline was completely removed from the remaining solution by distillation in *vacuo* and the mixed anilides were separated on the basis of fractional solubility in aniline. The more insoluble portions, high in tetramethylglucose anilide, were recrystallized from absolute alcohol. A melting point of 137–139° was taken as the criterion of purity. As the tetramethylmannose anilide content of the remainder was increased, crops were removed by crystallizing from alcohol. The purity of the tetramethylmannose anilide was later ascertained by determination of the specific rotation and that of the tetramethylglucose anilide also was confirmed in this way. Out of a calculated weight of 18.45 g. of mixed anilides, 7.59 g. of pure tetramethylglucose anilide and 8.02 g. of pure tetramethylmannose anilide were isolated. In addition to this a crystalline residue of 1.5 g. of mixed anilides remained, making 17.11 g. of crystalline anilides (92.8% calcd.) remaining at the end of the separation. In addition 0.8 g. of very dark, tarry matter remained. The enormous number of leachings with aniline and its subsequent removal induce progressive tar formation.

Tetramethylmannose with 0.0325 N Barium Hydroxide.—Tetramethylmannose (35.424 g.) was dissolved in an amount of 0.0407 *N* barium hydroxide sufficient to make a volume of 150 cc. This solution, 1 M in sugar, 0.0325 *N* in alkali (sp. gr, 1.043;

22.65% sugar) was kept at 35°. The specific rotation at 182 hours was +41.3°, indicating 49.5% tetramethylglucose and 50.5% tetramethylmannose. The iodine value was 125% of the original and the color of the solution was slightly yellow. The solution, now 139 8 cc. containing 33 02 g. of sugar, was combined with 185 cc. of 0.1 *N* sulfuric acid and 374 cc. of water. This solution, $M/5$ in sugar and 0.02 N in acid, was kept at 50° for four hours in order to de-enolize it. The iodine value was then 103.5%, indicating almost complete conversion of the enol.

The de-enolized solution, 701.8 g. containing 32.81 g. of sugar, was neutralized by the dropwise addition of 130 cc of 0.1 N barium hydroxide at 40°. The slight acidity left was removed by the addition of 0.4 g. of barium carbonate. After removal of the barium sulfate the iodine value of the solution was found to be 103.4%.

The amber colored solution, 1090 g. containing 32.66 g. of sugar, was evaporated *in vacuo* at 25 mm. and 35°. The evaporation was carried out in a one-liter Claisen flask with a removable glass column. The receiver was kept ice-cold. The flask was weighed every two hours after the removal of nearly all the water, and was found to reach constant weight after twenty hours of distillation. The residual brown sirup weighed 30.85 g., a yield of 94 5%. This, however, contained a slight dark-brown residue, which was separated in the subsequent removal of the sirup preparatory to making the anilides. By decanting the alcohol solution of the sirup, 0.32 g. of the dark residue remained, leaving 30.53 g., net, of sirup, or 93.5%. This residue was not investigated beyond ascertaining that it was soluble in water, insoluble in alcohol, was mainly organic and gave a test for barium. The iodine value of the sirup was 107.3%, a slight increase over the value previously obtained on the solution. The specific rotation was \$40.4". The iodine value of the aqueous distillate indicated the presence of 0.39 g. of sugar. Reckoning this in the yield, the total weight accounted for is 95.7% of the original.

After the removal of 3.83 g. of sirup as a specimen, the remaining 26.70 g. was dissolved in 82 cc. of absolute alcohol and 82 cc. of water white aniline was added. The mixture was heated in a glycerol bath at 100° for 3.2 hours, using an air condenser. After standing for two days, the solution had failed to yield any crystals. One-tenth of the solution (2.67 g. of sugar) was evaporated in *vacuo* and efforts were made to obtain crystals from it. A small amount of crystalline material was obtained, but it appeared that the formation oi the anilides had been quite incomplete, perhaps because of the presence of moisture from the original sirup. The test portion was kept separate and the main lot (2403 g. of sugar) was freed from alcohol and partly from aniline, in order to eliminate any possible water. The solution was then restored to the original concentrations of aniline and alcohol and heated at 100° for two hours. Now, after cooling, a reasonable crystallization occurred.

The reaction mixture at this stage was very black and from previous experience it seemed highly desirable to remove the crystalline mixed anilides from the dark material before attempting their separation. By progressive concentration of the alcohol solution 26.18 g. (83%, calcd.) of crystalline anilides was obtained. At this point it was necessary to precipitate some of the tar by dissolving the residue in alcohol–ether and adding petroleum ether (40-50°). Crystallization following this step raised the total to 90%. Some more tar was removed from the residue at this point by steam distillation. The light-colored, water-soluble portion (3 g.) was heated with 9 cc. of absolute alcohol and 9 cc. of aniline at 100° for three hours. By crystallization as before, in a desiccator held at 5°, the total weight of crystalline anilides was raised to 29.74 g., or 93.9% of the calculated weight (31.67 g.).

The mixed anilides were repeatedly leached with aniline, the undissolved portions being recrystallized from absolute alcohol (generally 1:5) to obtain pure tetramethylglucose anilide, m. p. 137–139°. As the remaining material increased in tetramethylmannose anilide content, it was also crystallized out. In the later work a superior method was developed. This consisted in dissolving the mixed anilides in 3 parts of aniline and allowing almost pure tetramethylglucose anilide to crystallize.

In this way 12.50 g. of tetramethylglucose anilide of m. p. 137–139° was obtained in 11 portions. A composite melting point with pure tetramethylglucose anilide showed no depression. The specific rotation (CH_3OH, $c = 2.36$) decreased from +228.7° to +58.9° on the addition of 0.001% of dry hydrogen chloride. A slightly greater amount of tetramethylmannose anilide. 12.79 g., was obtained in 6 lots, a composite of which yielded a specific rotation (CH_3OH, 0.0001%, hydrogen chloride, $c = 4.93$) of −8.5°, in agreement with the accepted value. A crystalline residue of 0.37 g. gave a specific rotation of +31.9° in the same solvent, indicating that this unseparated portion contained 60% of tetramethylglucose anilide and 40% of tetramethylmannose anilide. A tarry residue of 2.08 g. raises the total residual weight to 27.74 g., a loss of 2.00 g. in manipulation. The enormous number of transfers and lengthy treatment with aniline make this appear not unreasonable.

Reviewing the significant steps of the process, 32.66 g. of tetramethylmannose after treatment with alkali yielded 30.53 g. of recovered sirup, or 93.5%. Of this 30.53 g. of sirup, 24.03 g. (net) was converted to the anilides. Out of a possible 31.67 g. of anilides, 29.74 g. of crystalline material, or 93.9%, was obtained. From these mixed anilides 25.29 g. of the pure anilides was separated, a yield of 85%.

The nature of the processes and the yields obtained, along with the analytical data, justify the conclusion that the action of dilute alkali on tetramethylmannose, followed by suitable acid treatment, produces a mixture of equal amounts of tetramethylmannose and tetramethylglucose. From this we can only conclude that the interconversion of sugars is an enolic process involving migratory hydrogen atoms.

The authors wish to make grateful acknowledgments to Dr. F. C. Whitmore for valuable contributions to the theory and procedure of this problem.

Summary

1. The action of dilute alkali on mannose was investigated and conditions were found for conversion to glucose and fructose with minimum saccharinic acid formation. The composition of the solution at equilibrium was determined.

2. Tetramethylmannose was obtained in crystalline form for the first time.

3. On treating 100 g. of tetramethylmannose with dilute alkali, 93.5 g. of sugar was recovered. This yielded a weight of crystalline anilides equivalent to 87.8 g. of sugar. The weight of pure anilides separated from this was equivalent to 74.7 g. of sugar, of which 36.9 g. was tetramethylglucose and 37.8 g. was tetramethylmannose.

4. No methylated ketose was formed.

5. Evidence is presented for the presence of the monomethyl ene-diol common to tetramethylmannose and tetramethylglucose.

6. The ring structures of the normal forms of tetramethylmannose and tetramethylglucose are indicated to be identical.

7. The prediction of the ene-diol theory as applied to the action of dilute alkali upon tetramethylmannose has been confirmed.

EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF MIDDLEBURY COLLEGE]

REACTIONS OF ALPHA, BETA-UNSATURATED DINITRILES

BY BEN B. CORSON AND ROGER W. STOUGHTON

RECEIVED AUGUST 7, 1928 PUBLISHED OCTOBER 6, 1928

Malononitrile, by virtue of its methylene group, readily condenses with carbonyl compounds to yield α,β-unsaturated dinitriles.[1] In several instances we obtained two products, the usual α,β-unsaturated dinitrile (I) and a dimer (II) whose structure we are still investigating.

$$C_6H_5CHO + CH_2(CN)_2 \longrightarrow \underset{\text{I}}{C_6H_5CH{=}C(CN)_2} \quad \text{also} \quad \underset{\text{II}}{C_{20}H_{12}N_4}$$

This paper deals with condensation products corresponding to I.

There is a close resemblance between the reactions of α,β-unsaturated dinitriles and those of α,β-unsaturated aldehydes and ketones, the resemblance being due to the presence in both classes of substances of a reactive conjugated system, $C{=}C(C{\equiv}N)_2$ and $C{=}C{-}C{=}O$, respectively.

We have studied this resemblance in four reactions which are typical of α,β-unsaturated aldehydes and ketones, namely, the reaction with sodium bisulfite, oxidation by permanganate, reversal of reaction of formation (aldol or ketol condensation) by means of sodium hydroxide and the addition of the elements of hydrocyanic acid.

Benzalmalononitrile (I) and similar substances dissolve in sodium bisulfite solution—slowly in the cold, rapidly when warmed. The product thus formed (III) resembles the sulfonates (IV)[2] obtained from the reaction

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[1] (a) Heuck, *Ber.*, 28, 2251 (1895); (b) Walter, *Ber.*, 35, 1320 (1902); (c) Hinrichsen, *Ann.*, 336, 323 (1904); (d) Sachs and Appenzeller, *Ber.*, 41, 102 (1908); (e) Heller and Wunderlich, *Ber.*, 47, 1617 (1914); (f) Ostling, *Ofversick Finska Vetenskaps. Soc. Forhandl.*, **57A**, No. 11, 1 (1915); (g) Kauffmann, *Ber.*, 49, 1324 (1916); (h) **50,** 526, 1618 (1917); (i) 52, 1422 (1919); (j) Diels, Gartner and Kaack, *Ber.*, 55, **3439** (1922); (k) Diels and Conn, *Ber.*, 56, 2076 (1923); (l) Rosenmund and Boehm, *Ann.*, 437, 125 (1924); (m) Fischer and Nenitzescu, *Ann.*, 439, 175 (1924).

[2] (a) Pinner, *Ber.*, 15, 592 (1882); (b) Kerp, *Ann.*, 290, 123 (1896); (c) Knoevenagel, *Ber.*, 37, 4038 (1904); (d) Hofmann, *Ann.*, 201, 81 (1880); (e) Harries, *Ann.*, 330, 188 (1903); (f) Tiemann, *Ber.*, 31, 3297 (1898); (g) 32, 823 (1899); (h) 33, 561 (1900); (i) Baeyer and Henrich, *Ber.*, 28, 652 (1895); (j) Labbé, *Bull. soc. chim.*, [3] 23, 280 (1900); (k) Looft, *Ber.*, 15, 1538 (1882); (l) *Ann.*, 275, **377** (1893).

between α,β-unsaturated aldehydes and ketones and sodium bisulfite in that it is not reversed into the original components by means of acid or base. Lapworth and McRae[3] assumed a similar structure (V) for the product formed in the reaction between benzalcyano-acetic ester and sodium bisulfite.

$$[C_6H_5CH(SO_3Na)CH(CN)_2] \quad \text{III} \qquad C_6H_5CH(SO_3Na)CH_2COC_6H_5 \quad \text{IV}$$

$$[C_6H_5CH(SO_3Na)CH(CN)CO_2C_2H_5] \quad \text{V}$$

We were unable to isolate the sodium salt (III) in pure condition; Lapworth and McRae did not isolate V. However, by titration of the excess sodium bisulfite with iodine solution we found that one molecule of dinitrile reacted with one molecule of sodium bisulfite.

These a,@-unsaturated dinitriles are readily oxidized by potassium permanganate In acetone solution. Thus, benzalmalononitrile (I) yields benzoic acid; m-nitrobenzalmalononitrile, m-nitrobenzoic acid; o-methoxy benzalmalononitrile, o-methoxybenzoic acid.

It has long been known that acid, and especially alkali, reverses the reaction of formation of α,β-unsaturated compounds such as mesityl oxide. Likewise, the reaction of formation of these dinitriles is readily reversed. Benzalmalononitrile (I) shaken for ten minutes at room temperature with $N/5$ sodium hydroxide, produces benzaldehyde in good yield.

These α,β-unsaturated dinitriles add the elements of hydrocyanic acid. Hydrocyanic acid has been added to other α,β-unsaturated compounds by means of alkali cyanides[3,4] but the metallic derivatives of the addition products have not been isolated heretofore. Their appearance in this case is probably due to favorable solubility relations.

The general procedure was to treat the dinitrile with potassium cyanide solution, warm the mixture for a few minutes and acidify with hydrochloric acid. When the mixture was acidified, trinitrile was obtained. On the other hand, if the reaction mixture was allowed to stand without acidification, a potassium derivative was deposited. For example, starting with *p*-methoxybenzalmalononitrile (VI) we obtained a 95% yield of trinitrile (VII) if we acidified the solution after the reaction with potassium cyanide had taken place. However, if the reaction mixture was allowed to stand without acidification, a 90% yield of a potassium deriva-

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[3] Lapworth and McRae, *J. Chem. Soc.*, 121, 1704 (1922).

[4] (a) Pinner, *Ber.*, 14, 1072 (1881); (b) Lapworth, *J. Chem. Soc.*, **85**, 1214 (1904); (c) **83**, 995 (1903); (d) 89, 945, 1869 (1906); (e) Clarke and Lapworth, *ibid.*, 89, 1869 (1906); (f) Knoevenagel, *Ber.*, 37, 4065 (1904); (g) Anschütz, *Ber.*, 26, 827 (1893); (h) Wigginbotham and Lapworth, *ibid.*, **121**, 49 (1922); (i) Baker and Lapworth, *ibid.*, 127, 560 (1925); (j) Lapworth and Baker, "Organic Syntheses," John Wiley and Sons, Inc., New York, 8, 89 (1928).

tive was obtained whose nitrogen and potassium content agreed with the percentage composition of compound VIII

$$\begin{tikzcd} & \underset{\text{VII}}{p\text{-}CH_3OC_6H_4CH(CN)CH(CN)_2} \\ \underset{\text{VI}}{p\text{-}CH_3OC_6H_4CH{=}C(CN)_2} + KCN + HOH \arrow[ur] \arrow[dr] & \\ & \underset{\text{VIII}}{C_{12}H_8ON_3K} \end{tikzcd}$$

These trinitriles function as weak acids, dissolving in bases to form salts. The trinitrile (VII) obtained by the addition of the elements of hydrocyanic acid to *p*-methoxybenzalmalononitrile (VI) dissolves easily, even in such weakly alkaline solutions as potassium cyanide or dilute ammonium hydroxide solution. Recovery of trinitrile was practically quantitative from the potassium and from the ammonium salts. The yield from the silver salt was 73% of the theoretical amount.

$$p\text{-}CH_3OC_6H_4CH(CN)CH(CN)_2 \underset{HCl}{\overset{NH_4OH}{\rightleftarrows}} C_{12}H_8ON_3^- + NH_4^+$$

A white silver salt precipitates when dilute silver nitrate solution is added to a dilute solution of either the potassium or the ammonium salt. We analyzed several potassium and silver salts but the percentage of metal was usually high (around 5% high). The high values for silver and potassium may be due to the presence of some di-salt, for example, p-$CH_3OC_6H_4CAg(CN)CAg(CN)_2$.

The potassium derivative alkylates to give a carbon–carbon linkage. The potassium salt (IX) corresponding to α-phenyl-α,β,β-tricyano-ethane (XV) reacts with methyl iodide to form a methyl derivative (X) whose structure was established by conversion into the corresponding succinic acid (XI).

$$\underset{\text{IX}}{C_{11}H_6N_3K} \longrightarrow \underset{\text{X}}{C_6H_5CHCNCCH_3(CN)_2} \longrightarrow \underset{\text{XI}}{C_6H_5CH(CO_2H)CH(CH_3)CO_2H}$$

The melting point of this acid (XI) agreed with that given in the literature but since only a small amount of the product was obtained it seemed wise to synthesize a larger amount for purification and comparison. This was accomplished by means of the following series of transformations.

$$\begin{tikzcd} \underset{\text{XII}}{C_6H_5CH{=}C(CN)CO_2CH_3} \arrow[r] & \underset{\text{XIII}}{C_6H_5CHCNCH(CN)CO_2CH_3} \arrow[dl] & \\ \underset{\text{XIV}}{C_6H_5CHCNCCH_3(CN)CO_2CH_3} \arrow[r] & \underset{\text{XI}}{C_6H_5CH(CO_2H)CH(CH_3)CO_2H} \end{tikzcd}$$

There is nothing certain about the constitution of these salts. We see no evidence to justify any conclusion as to their structure, whether they be carbides or nitrides, that is, $C_6H_5CH(CN)CK(CN)_2$ or $C_6H_5CH(CN)$-$C{=}C{=}NK(CN)$, respectively.

The structure of the trinitriles was established by relating it to that of succinic acid. The structure of the α,β-unsaturated dinitriles follows from their method of formation and also from their relationship to the trinitriles.

$$RCHO + CH_2(CN)_2 \longrightarrow RCH{=}C(CN)_2 \longrightarrow RCHCNCH(CN)_2 \longrightarrow RCH(CO_2H)CH_2CO_2H$$

Incidentally, this is a very convenient set of reactions for use in proof of structure of many substances with the following constitutions, $RCH{=}C(CN)CO_2R$ and $RCH{=}C(CN)_2$. The nitrile groups in such substances are very resistant to hydrolysis.[5]

In order to hydrolyze a nitrile group so situated, hydrogen must first be introduced into the molecule in a position alpha to the nitrile group. This can be accomplished by reduction, which leads to complications because the product is apt to be a mixture of cyano and amino compounds.[5b]

$$RCH{=}C(CN)CO_2R \longrightarrow RCH_2CH(CN)CO_2R + RCH_2CH(CH_2NH_2)CO_2R$$

The better method for the introduction of alpha hydrogen is that employed in the present instance, namely, the addition of the elements of hydrocyanic acid to the α,β-unsaturated nitrile.

Experimental Part

I. Dinitriles

Preparation.—Equivalent quantities of aldehyde and malononitrile were dissolved in a suitable solvent and a few drops of piperidine added with shaking. The solution warmed up somewhat and became more or less reddish. Within fifteen minutes the mixture was solid with crystalline condensation product. It is advisable to carry out the reaction in an open beaker in order to facilitate removal of the solid. These condensations can be run without solvent but the products are apt to be dark colored. Solvent is desirable.

In the case of furfural the condensation must be run in a high dilution of water and in the presence of a weak catalyst (a pinch of sodium acetate). When the usual procedure was followed, the product was a sticky red gum with which we could do nothing. However, it is only in the condensation of furfural that special precautions are necessary.

For catalyst we usually used piperidine. However, other alkaline reagents also bring about condensation, for example, sodium methylate, sodamide, sodium acetate, ammonium carbonate, diethylamine and aniline. Reaction proceeded slowly in the presence of small amounts of formic and acetic acids. We have run several condensations between benzaldehyde and malononitrile without addition of any catalyst. Without catalyst the reaction required a day or so, whereas with piperidine the reaction was done in fifteen minutes. However, it is not to be concluded from this experiment that the condensation really takes place without the aid of a catalyst. Our materials were not sufficiently pure to preclude the presence of a trace of some basic or acidic impurity which might act as catalyst.

The condensation procedure can be best illustrated by the two following sets of directions, one for the preparation of piperonalmalononitrile (XIX), the other for furfuralmalononitrile (XXIII).

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[5] (a) Heller and Wunderlich, *Ber.*, **47**, 1617 (1914); (b) Kohler and Corson, THIS JOURNAL, **45**, 1975 (1923); (c) Rosenmund and Boehm, *Ann.*, **437**, 125 (1924).

Condensation of Piperonal with Malononitrile.—To a solution of 30 g. of piperonal (0.2 mole) and 15 g. of malononitrile (0.24 mole) in 130 cc. of n-butyl alcohol was added with stirring, 8 drops or so of piperidine. The solution became somewhat reddish and warmed up a little. Within five minutes the mixture was solid. After cooling to room temperature the product was jammed up, filtered by suction, washed with water containing a small amount of acetic acid and finally air dried. The yield was 38 g. or 96% of the theoretical amount. A small yield (±1 g.) slowly crystallized from the mother liquor. The product is lemon yellow; it has no irritant action upon the nose or eyes. The analytical sample was crystallized 3 times from acetic acid and dried at 100" in a vacuum over quicklime. It melts at 199–200°.[6]

Condensation of Furfural with Malononitrile.—Forty-eight g. of furfural (0.5 mole) and 33 g. of malononitrile (0.5 mole) was added to 250 cc. of water contained in a wide-mouthed Erlenmeyer flask equipped with a mechanical stirrer. The stirrer was started and a pinch of sodium acetate added to catalyze the condensation reaction. A flocculent yellow solid soon appeared. There was perhaps a slight rise in the temperature of the reaction mixture. At the end of half an hour the mixture was filtered by suction. After air drying the product weighed 70 g., which corresponds to 80% of the theoretical amount. The mother liquor slowly deposited 2 g. more of the product. The analytical sample was crystallized 4 times from carbon tetrachloride and finally air dried. Furfuralmalononitrile **(XXIII)** is straw yellow and melts at 72.5--73".

Physiological Properties.—Certain of these dinitriles have the effect of sneeze and tear gases. They are harmless when wet but to handle the dry powder is diastrous. When crystallizing *m*-nitrobenzalmalononitrile, for instance, the alcohol solution should not be boiled very much since the alcohol vapor has a peppery sting. In sneezing caused by *m*-nitrobenzalmalononitrile (XVIII) the mucous discharge from the nose becomes bright yellow on exposure to air. In sneezing caused by *o*-chlorobenzalmalononitrile (XX) the face smarts, especially if damp. The smarting is intensified-by washing. Most of the discomfort can be avoided if a gas mask is worn whenever dry solid is to be handled. However, the majority of the dinitriles reported in this paper have no irritant effect, as furfuralmalononitrile (XXIII) and *p*-methoxybenzalmalononitrile (VI).

Solubilities of Dinitriles.—As a general rule these substances are very soluble in acetic acid, acetone, benzene, chloroform and methyl acetate; less soluble in the higher alcohols, carbon tetrachloride and ether; sparingly soluble in carbon bisulfide, petroleum ether and water. The crystallizing properties of these dinitriles are excellent—they crystallize readily from a variety of solvents.

Solubility in Sodium Bisulfite Solution.—All these a,β-unsaturated dinitriles are soluble in sodium bisulfite solution with the exception of cyclohexylidene malononitrile (XXI). One and one-half grams of finely ground benzalmalononitrile (I) was suspended in 100 cc. of saturated sodium bisulfite solution and the mixture mechanically shaken at room

[6] All melting points reported in this paper are corrected for exposed thread and were read from a thermometer which had been calibrated against one which had been examined by the U. S. Bureau of Standards.

TABLE IA

α,β-UNSATURATED DINITRILES

No.	Malononitrile	Reaction solvent	Crystallizing solvent
I	Benzal-[a]	*Tert.*-$C_5H_{11}OH$	*n*-C_3H_7OH, *n*-C_4H_9OH, *tert.*-C_4H_9OH, *tert.*-$C_5H_{11}OH$
VI	*p*-Methoxybenzal-[b]	CH_3OH	CH_3CO_2H
XVI	o-Methoxybenzal-	*Tert.*-C_4H_9OH	*Iso*-$C_5H_{11}OH$
XVII	*p*-Hydroxybenzal-	CH_3OH	CH_3CO_2H, H_2O, *tert.*-$C_5H_{11}OH$
XVIII	m-Nitrobenzal-	C_2H_5OH	Any alcohol
XIX	3,4-Dioxymethylene-	*n*-C_4H_9OH	*Iso*-C_3H_7OH, *n*-C_4H_9OH
XX	o-Chlorobenzal-	*Tert.*-$C_5H_{11}OH$	Any alcohol, CS_2, CCl_4
XXI	Cyclohexylidene-	None	C_2H_5OH, *iso*-C_3H_7OH
XXII	3-Methoxy-4-hydroxy-benzal-	C_6H_6	CH_3CO_2H, C_6H_6, $C_6H_4(CH_3)_2$
XXIII	Furfural-[c]	H_2O	CCl_4

[a] Reported as melting at 87° by Heuck, Ber., 28, 2251 (1895).

[b] Reported as colorless and melting at 110° by Hinrichsen, Ann., 336, 323 (1904).

[c] Reported by Heuck as melting at 76°.

TABLE IB

, α,β-UNSATURATED DINITRILES

No.	Formula	Color	Physiol. action	Yield, %	M. p., °C.	Nitrogen, %[a]	
						Calcd.	Found
I	$C_6H_5CH{=}C(CN)_2$	None	Sneeze and tear	96	83.5–84	18.2	18.0
VI	*p*-$CH_3OC_6H_4CH{=}C(CN)_2$	Corn	None	93	114.5–115	15.2	15.1
XVI	*o*-$CH_3OC_6H_4CH{=}C(CN)_2$	Straw	None	90	84–84.5	15.2	15.1
XVII	*p*-$HOC_6H_4CH{=}C(CN)_2$	Lemon	None	77	188.5–189.5	16.5	16.4
XVIII	*m*-$NO_2C_6H_4CH{=}C(CN)_2$	Light cream	Sneeze	90	104.6–105	21.2	21.3
XIX	3,4-$CH_2O_2C_6H_3CH{=}C(CN)_2$	Lemon	None	96	199–200	14.1	14.0
XX	*o*-$ClC_6H_4CH{=}C(CN)_2$	None	Sneeze and skin irritant	85	95–96	14.9	14.7
XXI	$C_6H_{10}{=}C(CN)_2$	Pale straw	None	±30	173.5–174.5	19.2	19.0
XXII	3,4-$CH_3O(HO)C_6H_3CH{=}C(CN)_2$	Lemon	None	85	133.5–134.5	14.0	14.1
XXIII	$C_4H_3OCH{=}C(CN)_2$	Pale straw	None	80	72.5–73	19.5	19.6

[a] Kjeldahl analysis with mercury catalyst.

temperature. At the end of twenty-four hours the substance had gone into solution. The same substance dissolved immediately when the mixture was warmed to 70° or so.

It would seem that the salts of sulfonic acids are formed since the dinitriles are not regenerated on addition of excess acid or base. In spite of several attempts we were unable to isolate any of these sodium salts. However, by determining the amount of bisulfite used we were able to show that one molecule of sodium bisulfite reacted with one molecule of dinitrile. Two examples follow.

To a warm solution (±65°) of 1.657 g. of sodium bisulfite in about 50 cc. of water was added 1.443 g. of benzalmalononitrile. The mixture was shaken for fifteen minutes or so until all the dinitrile had dissolved. The solution was then cooled to room temperature and diluted to 100 cc. A portion of this solution was titrated against a solution of iodine, 1 cc. of which was equivalent to 0.00506 g. of sodium bisulfite. The excess of bisulfite was found to be 0.567 g. since 17.63 cc. of the solution required 19.88 cc. of iodine solution. Therefore, 1.443 g. of benzalmalononitrile used up 1.091 g. of sodium bisulfite, which is in the molecular ratio of 1.00 to 1.12.

Using the same analytical procedure, 2.014 g. of furfuralmalononitrile was treated with 1.976 g. of sodium bisulfite. After dilution to 100 cc., 27.66 cc. required 19.99 cc. of iodine solution. Therefore, 2.014 g. of furfuralmalononitrile had used up 1.610 g. of sodium bisulfite, which is in the molecular ratio of 1.00 to 1.09.

Oxidation with Permanganate.—α,β-Unsaturated dinitriles are readily oxidized in acetone solution by means of potassium permanganate. These substances break at the ethylene double linkage. We isolated benzoic and substituted benzoic acids. Our method is illustrated by the following procedure.

One gram of m-nitrobenzalmalononitrile (XVIII) was dissolved in 200 cc. of acetone. To this solution was added with shaking a hot aqueous solution of *2* g. of potassium permanganate (25% excess) in 100 cc. of water. Manganese dioxide appeared as soon as the solutions were mixed. The mixture was warmed on a steam-bath for fifteen minutes and then filtered; perrnanganate color had disappeared. The filtrate was freed from acetone by heating on a steam-bath. Norite was added and the solution filtered. The solution was cooled and then extracted with ether in order to remove non-acidic organic material and next heated over a flame and evaporated to a volume of 50 cc. This *50* cc. of solution was poured with stirring into 50 cc. of concentrated hydrochloric acid. The m-nitrobenzoic acid was extracted with ether and the ether extract dried with anhydrous sodium sulfate. After evaporation of the ether the organic acid was crystallized from 50 cc. of 1% hydrochloric acid. Crystallization yielded 0.32 g. of pure m-nitrobenzoic acid; ether extraction of the mother liquor gave an additional yield of 0.13 g. The total yield was 0.45 g. or 50% of the theoretical amount. The product melted at 140° and was identifidd by comparison with an authentic sample of m-nitrobenzoic acid prepared by the method of Kamm and Segur.[7]

Using the same procedure we obtained a *60%* yield of benzoic acid by the oxidation of benzalmalononitrile (I). The product was identified by means of a mixed melting point comparison. Starting with 0.9 g. of *o*-methoxybenzalmalononitrile (XVI) and 1.6 g. of potassium permanganate, we obtained 0.43 g. of impure o-methoxybenzoic acid (60% yield). Crystallization from water yielded pure o-methoxybenzoic acid melting at 100.5–101°. The melting point of *o*-methoxybenzoic acid is recorded in the literature as 98.5, 98.5–99 and 99°.[8] We had no authentic sample on hand for a mixed melting point comparison.

Reversal by Means of Sodium Hydroxide.—Benzalmalononitrile decomposes readily in the presence of sodium hydroxide. A good yield of benzaldehyde is obtained after shaking for ten minutes at room temperature in contact with *N*/5 aqueous sodium hydroxide.

In order to obtain an idea as to the extent of this reversal, we carried out the following procedure. To a dilute solution of sodium hydroxide contained in a 250cc. distilling flask connected to a water condenser was added a known amount of dinitrile. The alkaline mixture was boiled and about 50 cc. of distillate collected. The odor of ammonia was apparent after distillation had proceeded for a few minutes. The benzaldehyde in the distillate was precipitated by means of an acidic aqueous solution of phenylhydrazine hydrochloride. The precipitate was collected in a fretted glass

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[7] Kamm and Segur, "Organic Syntheses," John Wiley and Sons, Inc., New York, 3, 73 (1923).

[8] (a) Graebe, ***Ann.,*** 139, 139 (1865); (b) Bromwell, *Am.* ***Chem.*** **J , 19,** 577 (1897); (c) Lander, J. *Chem. Soc.,* 77, 745 (1900).

Gooch, dried and weighed. The product thus obtained was shown to be benzaldehyde phenylhydrazone by means of a mixed melting point comparison with an authentic sample. We obtained 1.48 g. of benzaldehyde phenylhydrazone from 1.93 g. of benzalmalononitrile; this corresponds to 60% of the theoretical amount. We ran a blank with pure benzaldehyde against our phenylhydrazine reagent in order to test the analytical procedure. Starting with 0.6194 g. of benzaldehyde we obtained 0.8847 g. of benzaldehyde phenylhydrazone, 77.3% of the theoretical amount. This indicates that the yield of phenylhydrazone in the reversal experiment was 60/77.3 × 100% or 77.6%.

In like manner we obtained 2.80 g. of p-methoxybenzaldehyde phenylhydrazone from 3.58 g. of *p*-methoxybenzalmalononitrile. This corresponds to 45% of the theoretical amount. The identity of the product was established by means of a mixed melting point comparison with an authentic sample.

II. Trinitriles

We obtained trinitriles from four of the unsaturated dinitriles, namely, benzal- (I), *p*-methoxybenzal- (VI), o-methoxybenzal- (XVI) and dioxymethylene benzalmalononitrile (XIX). The crude trinitriles from *p*- and o-methoxybenzalmalononitrile were fairly pure and the yields almost quantitative. The crude yield from piperonalmalononitrile was the smallest and the least pure. The general procedure follows.[9]

Addition of Hydrocyanic Acid to *p*-Methoxybenzalmalononitrile.—To 13.5 g. (0.74 mole) of finely ground **p-methoxybenzalmalononitrile** (VI) wet with 15 cc. of ethyl alcohol was added a hot, filtered solution of 9.5 g. (1.5 moles) of potassium cyanide in 15 cc. of water. The mixture was stirred and heated for two to three minutes on a steam-bath. The dinitrile dissolved. The red solution was then diluted with an equal volume of water. If the reaction had proceeded to completion the solution remained clear on dilution. Sometimes, however, a flocculent, tan-colored precipitate appeared. This substance seemed to be neither the original dinitrile nor the trinitrile sought. This precipitate should be removed by filtration before proceeding. Usually, however, the solution remained clear. A large excess of concentrated hydrochloric acid was stirred into the clear solution. A milkiness appeared, then a rather dark, heavy oil which quickly solidified and granulated (stirring should be continued for a few minutes after precipitation). The mixture was filtered by suction and the solid air dried. The crude product weighed 15.5 g.; one crystallization cut the yield down to 14.5 g. or 95% of the theoretical amount. The analytical sample was recrystallized several times from tertiary amyl alcohol with one or two treatments with Norite and finally dried in a vacuum at 80° over concentrated sulfuric acid. The pure substance is light cream colored and melts at 122–122.5°.

Solubility, Color and Physiological Action of **Trinitriles.**—The solubilities of the trinitriles are similar to those of the dinitriles, usually very soluble in acetic acid, acetone, benzene, chloroform and methyl acetate; less soluble in alcohols, carbon tetrachloride and ether; sparingly soluble in carbon bisulfide, petroleum ether and water. The trinitriles are lighter colored than the dinitriles. It may be that further purification would totally decolorize them. None of the trinitriles have the irritant physiological action of the dinitriles.

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[9] This is practically the procedure outlined by Lapworth and Baker (ref. 4j) for the addition of hydrocyanic acid to ethyl benzalcyano-acetate.

TABLE IIA

TRINITRILES

No	Tricyano-ethane	Crystallizing solvent
XV	α-Phenyl-α,β,β-	*n*-C_4H_9OH
VII	α-(*p*-Methoxyphenyl)-α,β,β-	*Tert.*-$C_5H_{11}OH$
XXIV	α-(*o*-Methoxyphenyl)-α,β,β-	Aq. CH_3CO_2H, *iso*-C_3H_7OH, *iso*-$C_5H_{11}OH$, *tert.*-$C_5H_{11}OH$
XXV	α-(3,4-Dioxymethylenephenyl)-α,β,β-	*n*-C_4H_9OH

TABLE IIB

TRINITRILES

No.	Formula	Color	Yield, %	M. p., °C.	Nitrogen, % Calcd.	Nitrogen, % Found
XV	$C_6H_5CH(CN)CH(CN)_2$	None	90	124.5–125	23.2	23.0
VII	*p*-$CH_3OC_6H_4CH(CN)CH(CN)_2$	Cream	95	122–122.5	19.9	19.7
XXIV	*o*-$CH_3OC_6H_4CH(CN)CH(CN)_2$	Cream	95	140.5–141	19.9	20.0
XXV	3,4-$CH_2O_2C_6H_3CH(CN)CH(CN)_2$	Light orange	80	153–153.5	18.7	18.4

Potassium Derivative as Intermediate.—When the reaction with potassium cyanide was carried out according to the preceding directions, the trinitrile was obtained directly without the intermediate appearance of a potassium salt. However, when the following modified procedure was employed a potassium derivative could be isolated.

Benzalmalononitrile (I) and potassium cyanide were mixed as in the preparation of trinitrile. The mixture was stirred and warmed for two to three minutes. The solution was then quickly filtered by suction. Large pink crystals of the potassium derivative (IX) crystallized from the filtrate. We were unable to purify this potassium salt by recrystallization. We could, however, remove the greater part of the pink color by grinding in a mortar with dry ether or n-butyl acetate. The salt darkens and shrivels around 180°; it partially melts around 190°. It is very soluble in water; rather soluble in acetone and acetic acid (the acetic acid solution soon deposits trinitrile); less soluble in the alcohols; insoluble in benzene, ether, n-butyl acetate and carbon bisulfide. It crystallizes poorly from n-butyl alcohol. The analytical sample was washed with ether and dried in a vacuum at 100°.

Anal. Calcd. for $C_{11}H_6N_3K$: N, 19.2; K, 17.8. Found: N, 19.0; K, 17.6.

Starting from *p*-methoxybenzalmalononitrile (VI), the corresponding potassium derivative was obtained in 88% yield. The high figures for potassium suggest that a second active hydrogen has undergone partial salt formation.

Anal. Calcd. for $C_{12}H_8ON_3K$: N, 16.9; K, 15.7. Found: N, 16.7; K, 17.5, 17.6.

These potassium salts decompose slowly in water solution. A water solution was made by dissolving 1.6 g. of the potassium derivative of α-phenyl-α,β,β-tricyanoethane in 12 cc. of water. There resulted a clear, red solution, alkaline to litmus. In three hours considerable brown sediment had settled out. We were unable to identify this solid. It reminds one of the flocculent precipitate which occasionally appears on diluting the reaction mixture in the preparation of the trinitriles. This water solution was allowed to stand for two months and became thick with dark solid. A strong odor of ammonia developed and perhaps there was an odor of hydrocyanic acid.

Neutralization of Trinitriles.—The trinitriles, as acids, dissolve in bases—even in such weakly alkaline solutions as potassium cyanide solution and dilute ammonium hydroxide. Solution takes place readily.

Acidification of Salts.—Trinitrile is obtained pure and in quantitative yield on acidification of the corresponding potassium or ammonium salt. Three grams of the potassium derivative of α-phenyl-α,β,β-tricyano-ethane ($C_{11}H_6N_3K$, IX) was dissolved in 50 cc. of water and the red solution was acidified with a slight excess of acetic acid. Trinitrile (XV) was precipitated immediately. The yield of pure, dry trinitrile was 2.55 g., the theoretical amount being 2.50 g.

In another instance, 1.31 g. of α-(*p*-methoxyphenyl)-α,β,β-tricyano-ethane (VII) was dissolved in a mixture consisting of 10 cc. of concentrated ammonia water and 50 cc. of water. The resulting solution of ammonium salt was slightly yellow. Trinitrile was precipitated by addition of 20 cc. of concentrated hydrochloric acid. The yield of dry trinitrile was 1.29 g., which corresponds to 98.5% of the theoretical amount.[10]

Silver Salt.—To a dilute solution of the ammonium salt of *p*-$CH_3OC_6H_4CHCNCH(CN)_2$ was added, in the dark, with stirring, a dilute solution of silver nitrate. The silver salt immediately appeared. The salt is pure white at first but soon darkens, especially if exposed to the light. The solid was washed, first with methyl alcohol, finally with ether. It was dried, in the dark, over sulfuric acid in a vacuum desiccator. Choking fumes were given off during ignition of the silver salt.

Anal. Calcd. for $C_{12}H_8ON_3Ag$: Ag, 33.9. Found: Ag, 39.9.

Another sample of the silver derivative of *p*-$CH_3OC_6H_4CHCNCH(CN)_2$ was made by adding silver nitrate solution to a solution of the potassium salt.

Anal. Calcd. for $C_{12}H_8ON_3Ag$: Ag, 33.9. Found: Ag, 38.0.

Both of these analyses are high and they also disagree between themselves to the extent of 2%.

The silver salt behaves like the potassium and ammonium salts in that it regenerates the corresponding trinitrile upon acidification. The yield, however, is not quantitative. A sample of the silver salt (which had become dark upon standing) of *p*-$CH_3OC_6H_4CHCNCH(CN)_2$ was acidified with dilute nitric acid. The product was contaminated with so much silver (from previous decomposition of the salt) that the quantitative results were of no significance. We recrystallized the product and showed that trinitrile (*p*-$CH_3OC_6H_4CHCNCH(CN)_2$) was present.

Better results were obtained by acidifying the silver salt before it had a chance to darken. Trinitrile (1.105 g. of *p*-$CH_3OC_6H_4CHCNCH(CN)_2$) was dissolved in dilute ammonia water and the excess of ammonia neutralized with dilute nitric acid. To the clear solution of ammonium salt was added silver nitrate solution in excess. A white precipitate of silver salt appeared. The silver salt was immediately decomposed by the addition of dilute nitric acid. The precipitated trinitrile was filtered on a fretted glass crucible, dried and weighed. The product was pure *p*-$CH_3OC_6H_4CHCNCH(CN)_2$, 0 800 g. (73% of the theoretical amount). There was no odor of hydrocyanic acid upon acidification.

Alkylation of Potassium Derivative to Form $C_6H_5CHCNCCH_3(CN)_2$.—Eighteen grams of the potassium derivative of $C_6H_5CHCNCH(CN)_2$ was suspended in 25 cc. of methyl alcohol. The mixture was treated under a reflux with 6 cc. of methyl iodide. Within five minutes the alcohol had come to a boil. After the force of the reaction

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[10] In a recent interesting investigation by Rising and Zee, THIS JOURNAL, 50, 1699 (1928), (see Rising and Zee, *ibid.*, 49, 541 (1927)), certain sodium derivatives (seemingly similar to the salts encountered in this work but of smaller molecular weight) were found to yield hydrocyanic acid on treatment with acid This was construed as evidence for the nitride formula, that is, $C_6H_5CH{=}C{=}NNa$ and $C_6H_5C(C_2H_5){=}C{=}NNa$.

had subsided, an additional 10 cc. of methyl iodide was added and the mixture allowed to stand for six hours. The reaction mixture was finally poured into water. In the course of a day a white solid appeared. The yield was small. The substance was crystallized several times from isobutyl alcohol; it melts at 83–84'. It is soluble in acetone, acetic acid, ether and the alcohols; less soluble in carbon tetrachloride.

Anal. Calcd for $C_{12}H_9N_3$: N, 21.5. Found: N, 21.3.

Proof of Structure of **Alkylated Nitrile, $C_6H_5CHCNCCH_3(CN)_2$.**—In order to establish the structure of the alkylated nitrile we transformed it into the corresponding succinic acid (XI). This was accomplished by refluxing for several hours with 20% hydrochloric acid. An acid was obtained which melted at 182–183° with a little bubbling. This is one of the melting points recorded in the literature for α-phenyl-β-methyl succinic acid.[11]

Methyl **α-Phenyl-α,β-dicyano** Propionate, $C_6H_5CHCNCH(CN)CO_2CH_3$.—The elements of hydrocyanic acid were added to methyl benzalcyano-acetate (XII) in the usual manner. An oil was obtained upon acidification. The mixture of oil and water was aspirated for several hours until the oil had solidified into a hard lump. The product was crystallized three times from *iso*propyl alcohol and, finally, once from methyl alcohol. It melts at 100–101°. It is very soluble in acetone, acetic acid and methyl acetate; rather soluble in benzene, ether and the alcohols; less soluble in carbon bisulfide and carbon tetrachloride; sparingly soluble in petroleum ether and water.

Anal. Calcd. for $C_{12}H_{10}O_2N_2$: N, 13.1. Found: N, 12.7.

Methyl α-Phenyl-α,β-dicyano-β-methyl Propionate, $C_6H_5CHCNC(CN)CH_3$-CO_2CH_3.—Thoroughly dried nitrile ester (XIII) prepared above was dissolved in a cold methyl alcohol solution of sodium methylate (1 equivalent of sodium methylate, based on $C_6H_5CHCNCH(CN)CO_2CH_3$). The yellowish solution was treated with an excess of methyl iodide. The mixture came to a slight boil. After standing in warm water for one hour, the reaction mixture was poured into water and extracted with ether. An oil was obtained from the ether extract. We tried to distil the product under 5 mm. pressure but it decomposed. However, the crude oil solidified upon long standing. The solid was crystallized from methyl alcohol. We did not have sufficient material to determine its solubility in the various solvents. The colorless crystals melt at 87–88'.

Anal. Calcd. for $C_{13}H_{12}O_2N_2$: N, 12.3. Found. N, 12.3.

α-Phenyl-β-methylsuccinic Acid, XI.—Methyl α-phenyl-α,β-dicyano-β-methyl propionate was refluxed for several hours with 20% hydrochloric acid. A good yield of phenylmethylsuccinic acid resulted. It was purified by several crystallizations from hot water. It melted at 182–183° with some effervescence. A mixed melting point comparison showed it to be identical with the acid obtained from $C_6H_5CHCNCCH_3(CN)_2$

Anal. Calcd. for $C_{11}H_{12}O_4$; 0.5316 g. requires 25.54 cc. of $N/5$ KOH. Found 25.69 cc. 0.1875 *g*. requires 18.01 cc. of $N/10$ KOH. Found: 17.88 cc.

The silver salt was prepared, dried in a vacuum and analyzed. It is quite stable toward light as had already been observed by Zelinsky and Buehstab.

Anal. Calcd. for $C_{11}H_{10}O_4Ag_2$: Ag, 51.15. Found: Ag, 50.96.

III. Hydrolysis of Trinitriles to Succinic Acids

The trinitriles were transformed into succinic acids by refluxing for several hours (three to ten hours, depending on the substance) with a con-

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[11] *(a)* Zelinsky and Buchstab, *Ber.*, 24, 1876 (1891); (b) Ruhemann, *J. Chem. Soc*, 81, 1216 (1902); (c) Upson and Thompson, THIS JOURNAL, 44, 185 (1922).

siderable excess of 20% hydrochloric acid. The products were recrystallized from hot water.

Ten grams of a-phenyl-a,β,β-tricyano-ethane (XV) yielded upon hydrolysis and decarboxylation 9.6 g. of phenylsuccinic acid (90% of the theoretical amount). Its identity was established by comparison with an authentic sample prepared by the method of Bredt and Kallen.[12]

Ten grams of α-(*p*-methoxyphenyl)-α,β,β-tricyano-ethane (VII) yielded 7 g. of colorless p-methoxyphenylsuccinic acid **(67%** of the theoretical amount). It was recrystallized several times from hot water and finally dried at 100° in a vacuum over sulfuric acid. Its melting point depends upon the speed of heating. Heated slowly it melts at 204–206°; heated rapidly it melts at 207–208°. Uncertain melting point is often characteristic of dibasic acids and is doubtless due to the formation of a small amount of anhydride, the presence of which lowers the melting point. The faster the heating, the less anhydride formed and, therefore, the higher the melting point.

Anal. Calcd. for $C_{11}H_{12}O_5$: **0.4448** g. requires **19.85** cc. of $N/5$ KOH. Found: **19.83** cc.

p-Methoxyphenylsuccinicacid has been reported by Baker and Lapworth[13] as melting at 194–195° (10° below our melting point). Chrzaszezewska[14] describes it as pale yellow and melting still lower, 189–190°.

Because of this disagreement in melting points we prepared the anhydride for further comparison. The acid was refluxed for one hour with acetyl chloride. The acetyl chloride was removed by vacuum evaporation at room temperature and the residual solid crystallized from chloroform–petroleum ether mixture. The product melts at 91–92°, which agrees well with the melting point of **90.5"** observed by Baker and Lapworth.

Dimethyl *p*-Methoxyphenylsuccinate, p-$CH_3OC_6H_4CH(CO_2CH_3)CH_2CO_2CH_3$.—The dimethyl ester was obtained in 50% yield by refluxing **6.5** g. of the corresponding trinitrile (VII) with a solution of **9** cc. of concentrated sulfuric acid in **25** cc. of **98%** methyl alcohol. After boiling for five hours, the solution was poured into ice water and the mixture extracted with ether. The colorless product was recrystallized several times from methyl alcohol. It melts at **93–94'.** We were unable to obtain consistent analyses for the carbon content. **A** qualitative test showed nitrogen to be absent.

Anal. Calcd. for $C_{13}H_{16}O_5$: C, **61.9;** H, **6.0.** Found: **C, 57.8, 56; H, 5.5, 5.7.**

***o*-Methoxyphenylsuccinic** Acid, o-$CH_3OC_6H_4CH(CO_2H)CH_2CO_2H$.—Ten grams of the corresponding trinitrile (XXIV) yielded **6** g. of substituted succinic acid **(57%** of the theoretical **amount**).[15] The product, however, was a mixture. Fractional crystallization from water separated it into two fractions. The more soluble fraction melted cloudy around 122°; the melt cleared around **185"** and bubbled at about **197".** We did not investigate this fraction. The less soluble fraction was *o*-methoxyphenylsuccinic acid. It melts with slow heating at 182–184°; with rapid heating at 184–185°.

Anal. Calcd. for $C_{11}H_{12}O_5$: C, **58.9;** H, **5.4.** Found: C, **59.1;** H, **5.5.** Calcd.:

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[12] Bredt and Kallen, Ann., 293, **342 (1896).**

[13] Baker and Lapworth, **J.** *Chem. Soc., 127,* **560 (1925).**

[14] Chrzaszezewska, *Roczniki Chem.,* 5, 1–3, **33–76 (1925);** *C.* A., **20, 1078 (1926).**

[15] Lapworth and McRae, **J.** *Chem. Soc.,* 121, **1704** (1922), found that a very similar compound, o-$CH_3OC_6H_4CHCNCH(CN)CO_2R$, carbonized badly on refluxing with hydrochloric acid.

0.3743 *g*. requires 16.67 cc. of $N/5$ KOH. Found: 16.67 cc. Calcd.: 0.2106 g. requires 18.79 cc. of $N/10$ KOH. Found: 18.78.

Piperonylphenylsuccinic acid was obtained in poor yield by the alkaline hydrolysis and decarboxylation of $3,4\text{-}CH_2O_2C_6H_3CH(CN)CH(CN)_2$ (XXV). The product was very pale yellow and melted at 210–212°, which agrees with the melting point of 211° observed by Lapworth and McRae.[16]

This work was assisted by a grant from the Cyrus M. Warren Fund of the American Academy of Arts and Sciences.

Summary

1. Several new condensation products of malononitrile with aromatic aldehydes are reported.

2. These α,β-unsaturated dinitriles closely resemble α,β-unsaturated aldehydes and ketones in that they (a) dissolve in sodium bisulfite solution, (b) are oxidized by potassium permanganate, (c) are reversed into the original components by sodium hydroxide and (d) add the elements of hydrocyanic acid.

3. The trinitriles, resulting from the addition of hydrocyanic acid to the dinitriles, function as weak acids, dissolving in bases to form salts. Acidification of the potassium, ammonium and silver salts results in regeneration of trinitrile. The potassium salt alkylates with methyl iodide to give carbon–carbon alkylation.

MIDDLEBURY, VERMONT

[CONTRIBUTION FROM THE LABORATORY OF FOODS AND SANITATION, UNIVERSITY OF WISCONSIN]

THE ACTION OF SELENIUM MONOCHLORIDE UPON FATTY OILS

BY ELLERY H. HARVEY AND H. A. SCHUETTE

RECEIVED AUGUST 10, 1928 PUBLISHED OCTOBER 6, 1928

The discovery by Parkes[1] that rubber could be vulcanized by immersing it in sulfur monochloride, followed by his observation[1] that "articles having properties analagous to those from india-rubber or gutta percha" could be made from fatty oils by the action of this substance, eventually gave rise to its introduction into the field of analytical chemistry by Warren[2] and then by Fawsitt.3 Warren's conclusions, which were based upon the nature of the reaction product, were subsequently questioned.[4] Fawsitt's

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[16] Lapworth and McRae, *J. Chem. Soc.*, **121**, 1708 (1922).

[1] Parkes, British Patents 11,147, Sept. 25, 1846, and 2359, Oct. 22, 1855.

[2] Warren, *Chem. News*, **55**, 134 (1887); **56**, 222, 231, 243, 262 (1887); **57**, 26, 43, 113 (1888); 58, 4, 15 (1888).

[3] Fawsitt, *J. Soc. Chem. Ind.*, *7*, 552 (1888).

[4] Lewkowitsch, "Chemical Technology and Analysis of Oils, Fats and Waxes," Macmillan Co., London, **1921**, 6th ed., Vol. I, p. 474.

suggestion that the accompanying thermal effect might be utilized after the manner of Maumené's sulfuric acid number of fatty oils[6] received but scant attention and attempts to revive the former proposal by improving the technique of the method and following closely guarded experimental conditions, which measurements of this type require, have served to indicate that this feature of the reaction is impractical in so far as it might be used as a diagnostic "number" of fatty oils.[6]

The relationships which obtain in the oxygen family of the chemical elements and the renewed interest which has centered within recent years around selenium and its compounds suggested to the authors the desirability of observing the action of its monochloride upon the fatty oils under conditions? which simulate those once proposed by Fawsitt,[3] except that a diluent was to be used to facilitate the formation of a homogeneous reaction mixture.

Apparatus, Materials and Procedure.—The nested beakers of Fawsitt with cotton-filled intervening space were replaced by a silvered 300-cc. Dewar flask 55 mm. in diameter and 160 mm. in height. The latter was packed in kieselguhr and covered with a flanged Bakelite cap drilled to accommodate a stirrer, thermometer and pipet, respectively.

For experimental material there were selected twenty-two fatty oils representative of nine groups in the classification of Mitchell.[8] Their purity, in the sense that they conformed in' name to that for which they were sold, was experimentally verified. Selenium monochloride, b. p. 130°, was prepared from elementary selenium by the method of Divers and Shimos[9] and the sulfur monochloride was purified from a commercial preparation by that of Pope.[10]

For the purpose of measuring the thermal effect in the contemplated reaction, 25 g. of the fatty oil in question and a like amount of pure, drv xylene were weighed into the calorimeter. There was then quickly introduced (15 sec.) 1 cc. of the reagent at the same temperature as the fatty oil solution, the stirrer was started and the maximum temperature rise and the time of reaching this point were noted. Since the loss of heat through the glass is negligible from the standpoint of the purposes for which this reaction serves, and since the only escape of heat is from the surface exposed to the outer air, radiation losses were corrected for by the formula $C = 0.5t(R_1 \pm R_2)$, in which R_1 and R_2 represent the initial and maximum temperatures, respectively, and t is the number of minutes which elapsed from the moment that the reagent was added to the time at which the maximum temperature was reached.[11]

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[5] Maumené, *Compt. rend.*, 35, 572 (1852).

[6] Harvey and Schuette, unpublished data.

[7] By making allowance for the heat capacity of the apparatus and the specific heats of the solvent, oil, sulfur monochloride and reaction product it should be possible to calculate the exact amount of heat evolved, but since this reaction was studied from the standpoint of its probable suitability for analytical purposes, the observed rise of temperature is fully efficient.

[8] Allen, "Commercial Organic Analysis," Blakiston, Philadelphia, 1924, 5th ed., Vol. II, pp. 109–113.

[9] Divers and Shimos, *Chem.* News, 49, 212 (1884).

[10] Pope, J. *Chem. Soc.*, *37*, 356 (1880); Harvey and Schuette, THIS JOURNAL, 48, 2065 (1926).

[11] Stillman, "Engineering Chemistry," Chemical Publishing Co., Easton, Pennsylvania, 1910, 4th ed, p. 137.

The experiments were repeated in that the corresponding sulfur compound was substituted for the selenium monochloride so that comparative data might be obtained in the action of these substances under similar conditions. Data pertinent to these observations are recorded in the accompanying table.

TABLE I

THERMAL REACTIONS OF SULFUR AND SELENIUM MONOCHLORIDES AND FATTY OILS

		Sulfur monochloride			Selenium monochloride		
Group	Fatty oil	Max. rise, °C.	Time, min.	Rise per min., °C.	Max. rise, °C.	Time, min.	Rise per min., °C.
Olive oil	Almond	13.0	65	0.20	12.95	5	2.60
	Olive	10 0	165	.06	13.10	6	2.20
	Peanut	12.6	73	.16	10.90	2	8.40
Rape oil	Rapeseed	14.3	73	.19	12.80	6	2.10
Cotton seed oil	Soy bean	12 5	100	.12	14.85	3	4.95
	Sesame	11.7	75	15	13.75	3	4.58
	Corn	11.9	100	.11	18.80	1	18.80
	Cottonseed	11.0	160	06	14.90	4	3.70
Linseed oil	Tung	13.5	50	.27	8.55	4	2.14
	Linseed	17.3	65	.26	15.70	3	5.20
Castor oil	Castor	17.5	8	2.10	10.50	4	2.60
Cacao butter	Palm	12 9	20	0.64	11.40	13	0.87
Lard oil	Neatsfoot	16.1	50	.32	12.75	8	1.60
	Lard (oil)	16 0	55	.29	15.10	1	15.10
Tallow and butter	Tallow (beef)	.	..	. .	12.85	5	2.57
	Butterfat	5 1	80	.06	11.85	10	1.18
	Lard	8.5	95	.08	13.10	4	3.30
Whale oil	Whale	15.4	50	.30	15.80	1	15.80
	Menhaden	18.3	25	.73	13.40	2	6.70
	Codliver	13.4	45	.30	14.00	4	3.50
Fatty acid	Oleic acid	15.0	*50*	.30	14.80	0.5	29.60

Discussion

Selenium monochloride is, in the light of thermometric measurements, more energetic in its action upon the fatty oils than is the corresponding sulfur compound. Although on the one hand the action of the latter appears to be, under the conditions set forth in this communication, of a rather complicated nature—an action which is characteristic not of groups whose members bear some resemblance to each other in their physical properties or chemical natures, but rather of individuals and one which cannot be ascribed alone to the nature of the fatty acid radicals present —on the other hand the action of selenium monochloride is more far reaching. In addition to substitution and addition, which results wholly if not in part with the sulfur compound, here there must also be taken into consideration the effect of the decomposition of the selenium compound itself. The deposition of elementary selenium in many case points to this conclusion. Ditmar[12] advances the opinion that at low temperatures

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[12] Ditmar, Kunststoffe, 4, 292 (1914).

the reaction with sulfur monochloride is one of addition and that at normal temperatures substitution accompanies this phenomenon. Lack of specificity is even more pronounced in this case. The thermal rise which was observed with approximately one-half of the oils whose behavior was studied is about the same as with the sulfur monochloride, but of greater significance is the fact that the rise per minute is appreciably greater. Palm oil is the only one which showed any suggestion of a similar behavior.

Conclusions

The thermal effect which is observed when selenium monochloride acts upon fatty oils is an additive one produced not only by substitution and addition but by the decomposition of the reagent itself. In view of this situation, the use of selenium monochloride under conditions which simulate in a measure those of sulfuric acid[5] is impractical as a test which has any diagnostic value for the fatty oils.

MADISON, WISCONSIN

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

THE ACTION OF SILVER ON DIPHENYL-TERTIARY-BUTYLETHYNYLBROMOMETHANE

BY PAUL L. SALZBERG AND C. S. MARVEL

RECEIVED AUGUST 10, 1928 PUBLISHED OCTOBER 6, 1928

It was recently[1] shown that hexa-*tert.*-butylethynylethane reacted with liquid sodium-potassium alloy and with liquid sodium amalgams to give the corresponding alkali metal derivative of tri-*tert.*-butylethynylmethyl, thus indicating that aliphatic acetylenic groups possess the properties necessary to cause weakening of the central bond in a substituted ethane. These results would lead to the prediction that the replacement of two phenyls in hexaphenylethane by acetylenic radicals would not greatly decrease the dissociation. However, Moureu, Dufraisse and Houghton[2] have shown that the action of metals on diphenylphenylethynylchloromethane gives rise to a hydrocarbon which is much more stable than would be expected of *sym.*-tetraphenyldiphenylethynylethane. To gain further knowledge of the effect of acetylenic groups on the stability of hexa-substituted ethanes, a study of the closely related tetraphenyldi-*tert.*-butylethynylethane has been undertaken.

Diphenyl-*tert.*-butylethynylcarbinol was easily prepared from *tert.*-butylethynylmagnesium bromide and benzophenone. The bromide was prepared by the action of phosphorus tribromide on the carbinol. When an ether solution of this bromide was shaken with molecular silver in an

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[1] Salzberg with Marvel, THIS JOURNAL, 50, 1737 (1928).

[2] Moureu, Dufraisse and Houghton, *Bull. soc. chim.*, [4] **41**, 56 (1927).

atmosphere of nitrogen, a greenish-yellow solution with a very slight red fluorescence was obtained. The fluorescence disappeared when a stream of oxygen was run into the flask over the surface of the solution and then reappeared when the supply of oxygen was cut off. This indicated that the solution contained a free radical which was being oxidized. However, when an attempt was made to determine quantitatively the amount of oxygen absorbed it was found that only a very small amount (a few tenths of a cc.) was taken up by the solution. Furthermore, evaporation of the ether left a pure, stable, colorless hydrocarbon and not a peroxide.

This hydrocarbon had the composition of $C_{38}H_{38}$, corresponding to the expected ethane. However, there is some question as to its exact structure. It melts higher (155°) than hexa-*tert.*-butylethynylethane (131°) and this is unexpected since the bromide melts lower than tri-*tert.*-butylethynylbromomethane. The ethane was not cleaved at the ethane linkage by either 40% sodium amalgam or sodium–potassium alloy, as would be expected. It does react with them to give colored solutions of the metal derivative. Carbon dioxide decolorizes this solution but no appreciable amount of water-insoluble acid could be recovered from the reaction mixture. Furthermore, this hydrocarbon was stable toward heat.

In view of the ease with which hexa-*tert.*-butylethynylethane rearranged with heat to give a higher melting hydrocarbon, it was thought that rearrangement might have occurred during the formation of the hydrocarbon $C_{38}H_{38}$ obtained in this work. In order to test this theory, the reaction between the bromide and silver was carried out in the presence of oxygen, which should prevent the rearrangement by the formation of a peroxide. When this reaction was run, oxygen was rapidly absorbed and considerable heat was evolved. When the temperature was not controlled, two or three times the theoretical amount of oxygen was absorbed. By keeping the temperature at 0° the absorption of oxygen was only about one and one-half times the theoretical amount. However, all attempts to isolate a peroxide were unsuccessful. An oily material was obtained that had the odor of benzophenone.

The absorption of oxygen in this experiment is due to some reactive intermediate, presumably diphenyl-*tert.*-butylethynylmethyl. When tri-*tert.*-butylethynylbromomethane was treated with silver in the presence of oxygen, the absorption of oxygen was negligible. This shows that the percentage of free radical normally present in a reaction mixture of this type is not enough to cause oxygen absorption.

The most logical explanation of these observations seems to be that silver reacting with diphenyl-*tert.*-butylethynylbromomethane produces a free radical diphenyl-*tert.*-butylethynylmethyl which in the presence of oxygen is oxidized to products which are of lower molecular weight. In the absence of oxygen the free radical undergoes some rearrangement to produce a stable hydrocarbon $C_{38}H_{38}$. The structure of this hydrocarbon is now under investigation.

Experimental Part

Diphenyl-*tert.*-butylethynylcarbinol.—The Grignard reagent was prepared from 38 g. of *tert.*-butylacetylene by adding it from a dropping funnel to 115 cc. of a 4.116 N ether solution of ethylmagnesium bromide over a period of ten hours. The heat of the reaction caused the ether to reflux and a very efficient condenser filled with water at 0–5° was needed to avoid loss of the acetylene. When this reaction was finished a saturated solution of 85 g. of benzophenone in dry ether was added during one hour. The reaction mixture was then stirred for six hours, allowed to stand overnight and finally refluxed for about an hour. The reaction mixture was then decomposed by pouring it onto 500 g. of cracked ice and adding 25 g. of ammonium chloride and just enough dilute hydrochloric acid to dissolve any precipitate of basic magnesium salts The ether layer was separated, dried over sodium sulfate, filtered and heated on a steam-bath to remove the solvent. The residue was dissolved in an equal volume of petroleum ether (b. p. 40–60°) and the solution was cooled to −15°. The carbinol separated as white crystals; m. p. 63–66.5°. This grade of product was used for preparing the bromide. Recrystallization gave a very pure product which melted at 66.5–67.5°.

Anal. Subs., 0.2370: CO_2, 0.7502; H_2O, 0.1625. Calcd. for $C_{19}H_{20}O$: C, 86.36; H, 7.58. Found: C, 86.32; H, 7.67.

In the first run considerable difficulty was experienced in obtaining a crystalline compound. The crude product was distilled under reduced pressure and the main portion boiled at 132–135° at 0.4–0.5 mm. The supercooled liquid had the following constants: n_D^{25}, 1.5550; sp. gr. $\frac{25}{25}$ = 1.0124. This material crystallized after standing for a few days at −15°.

Diphenyl-*tert.*-butylethynylbromomethane.—Three g. of the carbinol was dissolved in 25 cc. of petroleum ether and the solution cooled to 0°. Then 1 g. of phosphorus tribromide was added and the solution was stirred for one-half hour. To the mixture was added 100 cc. of 10% sodium bicarbonate solution and stirring was continued for ten minutes. The petroleum ether solution was separated, dried over sodium sulfate, filtered and evaporated under reduced pressure at room temperature. The residue was dissolved in 5 cc. of dry ether, 5 cc. of absolute alcohol was added and then the solution was evaporated under reduced pressure until crystals began to form. The mixture was then allowed to stand at 0° overnight in order that all of the bromide might crystallize. The bromide was collected on a filter and dried in a vacuum desiccator. The yield of crude product (m. p. 56.5–59.5°) was 3 g. (81% of the theoretical amount) Recrystallization from alcohol and ether gave a product melting at 58.5–60.5° (corr.)

Anal. (Stepanow). Subs., 0.2626, 0 2112: 17.62, 14.21 cc. of 0.0450 N $AgNO_3$ Calcd. for $C_{19}H_{19}Br$: Br, 24.43. Found: Br, 24.12, 24.22.

The Reaction between Diphenyl-*tert.*-Butylethynylbromethane and Silver

(a) In Air or Nitrogen.—A solution of 1 g. of the bromide in 15 cc. of dry ether was shaken in a mechanical shaker with 1 g. of molecular silver in a 30-cc. round-bottomed flask for about ten hours. A greenish-yellow solution with a slight red fluorescence resulted. The fluorescence disappeared when a stream of oxygen was passed over the surface of the solution but reappeared after the solution had stood in the air for a few minutes. This could be repeated three or four times before the color failed to reappear. The ether solution was concentrated until crystals began to appear. The mixture was then cooled to 0° until crystallization was complete. These crystals

(m. p. 151.5–154.5, corr.) were collected on a filter. Recrystallization from alcohol and ether gave a product which melted at 153.5–155° (corr.).

Anal. Subs., ***0.1786:*** CO_2, ***0.6011;*** H_2O, ***0.1265.*** Calcd. for $C_{38}H_{38}$: C, ***92.31;*** ***H, 7.69.*** Found: C, ***91.78;*** H, ***7.92.*** *Mol. wt.* Subs., ***0.1527;*** benzene, 13.465; ***At,*** 0.134°. Constant for benzene, ***5.32.*** Calcd. for $C_{38}H_{38}$: mol. wt., ***494.*** Found: ***434.***

One run was made to determine the absorption of oxygen. One g. of the bromide in 5 cc. of toluene was shaken with 1 g. of molecular silver for fourteen hours in a sealed tube. Then the tube was broken in an oxygen chamber connected with a eudiometer. There was no absorption of oxygen after twenty hours. The mixture was then filtered and worked up as before. After two crystallizations ***0.45*** g. (39% of the theoretical amount) of the same hydrocarbon was isolated. Analysis of the silver–silver bromide residue showed that the bromine had been removed to the extent of over 90% of the theoretical amount.

Similarly, when the hydrocarbon was prepared in an atmosphere of carbon dioxide and then transferred to an oxygen atmosphere, there was no absorption. Fresh molecular silver was added to this reaction mixture and shaking continued without effect.

(b) In Oxygen.—A solution of ***2*** g. of the bromide in ***10*** cc. of toluene was shaken with ***2*** g. of molecular silver in a 30-cc. round-bottomed flask filled with oxygen and connected to a eudiometer filled with oxygen. When shaking was started, oxygen was rapidly absorbed and the temperature of the reaction mixture rose to 40–50°. On attempting to isolate the reaction products only about ***0.1*** g. of the hydrocarbon was obtained. One similar run made in ether solution and maintained at about 25° by means of a water-bath gave some white crystals melting at 96–102°. An attempt to purify these yielded an oil with a strong odor of benzophenone.

Several runs were made in xylene solutions in a tube surrounded by water to maintain the temperature at about 25–30°. In every case the absorption of oxygen was ***2*** to ***3*** times the theoretical amount. In one run using ***0.3*** g. of the bromide, the absorption of oxygen seemed to stop after the theoretical amount ***(10.3*** cc.) for the formation of a peroxide had been taken up. However, on further shaking the absorption was renewed and finally about three times the theoretical amount of oxygen ***(34.9*** cc.) was used.

In another run using ***0.3*** g. of the bromide the oxygen absorption was measured while the reaction mixture was held at about 0° by surrounding the reaction tube with ice water. After thirty-eight minutes, ***14.8*** cc. ***(144%*** of the theoretical amount for the formation of a peroxide) of oxygen was absorbed.

Reaction of the Hydrocarbon $C_{38}H_{38}$ with Sodium Amalgam.—Two cc. of 1% sodium amalgam and ***0.25*** g. of the hydrocarbon in ***10*** cc. of absolute ether were shaken in an atmosphere of nitrogen. No color was developed. The 1% amalgam ***was*** then replaced by ***40%*** amalgam and shaking was continued. The solution turned red in less than a minute. After shaking overnight, the mixture was treated with dry carbon dioxide for an hour. The excess alloy was frozen and the reaction mixture was separated and decomposed with water and hydrochloric acid. The ether layer was extracted with 10% potassium hydroxide and the alkaline solution was filtered and then acidified with hydrochloric acid, No water-insoluble acid was obtained.

In a second run, ***0.36*** g. of the hydrocarbon in ether was shaken with ***3.5*** cc. of the 40% sodium amalgam in an atmosphere of nitrogen. A deep red color developed in seven minutes and after nine hours the color was almost black. Dry carbon dioxide was then passed into the mixture until the color had disappeared. On working up this mixture as described above, a few yellow crystals melting at 168–170° resulted. Not enough material was obtained for identification.

Reaction of the Hydrocarbon $C_{38}H_{38}$ with Liquid Sodium–Potassium Alloy.—A solution of **0.38** g. of the hydrocarbon in ether was shaken for three hours with 4 cc. of the liquid sodium–potassium alloy in an atmosphere of nitrogen. The solution turned red in one minute. Dry carbon dioxide was led into the mixture until the red color had disappeared, and then the ether solution was poured off and any suspended particles of alkali metal were decomposed with moist carbon dioxide. The ether solution was then extracted with water and the aqueous extract acidified with dilute hydrochloric acid. Only a slight turbidity resulted. Evaporation of the ether layer with dilute hydrochloric acid left only potassium and sodium chlorides

Attempts to Rearrange the Hydrocarbon $C_{38}H_{38}$.—A solution of 0.44 g of the hydrocarbon in **5** cc. of absolute alcohol was heated for one hour in a sealed tube at 100°. The solution was cooled to 15° and the original hydrocarbon (m. p. **150–151**°) was isolated. The recovered hydrocarbon weighed 0.36 g.

Summary

1. Molecular silver removes the halogen from diphenyl-*tert.*-butylethynylbromomethane, and a hydrocarbon $C_{38}H_{38}$ is obtained when the reaction is carried out in air or nitrogen. In an atmosphere of oxygen this reaction does not produce a hydrocarbon but oxygen is absorbed very rapidly by the reaction mixture.

2. The hydrocarbon, $C_{38}H_{38}$, reacts with liquid sodium–potassium alloy and with 40% sodium amalgam to produce colored alkali metal derivatives but apparently the molecule is not cleaved as would be expected if it has the structure of tetraphenyldi-*tert.*-butylethynylethane.

3. To explain these observations the suggestion is made that tetraphenyldi-*tert.*-butylethynylethane is formed by the action of silver on diphenyl-*tert.*-butylethynylbromomethane but it rapidly dissociates and rearranges to some other more stable structure. If oxygen is present in large amounts the free radicals produced by the dissociation of tetraphenyldi-*tert.*-butylethynylethane are oxidized before this rearrangement occurs.

URBANA, ILLINOIS

NEW BOOKS

An Introduction to General Chemistry. By **WILLIAM MARTIN BLANCHARD**, Ph.D., Professor of Chemistry, De Pauw University. Doubleday, Doran and Company. Inc., Garden City, New York, 1928. ix + 588 pp. 90 figs. **11** plates—nearly full page photogravures of famous chemists 10 charts. 14 X 21 cm. Price **93.00.**

In the preface the author states that in the preparation of the text he has made his constant guide those difficulties with chemistry encountered by the average college student, and that he has endeavored to present the more common facts and fundamental laws and theories of general chemistry in a clear, concise and orderly fashion. The product of his efforts adds another ranking member to the rapidly growing list of conventional texts written for first year college students of general chemistry. The author is conservative in the choice of topics, adhering to the usual content and order but he defers the study of ozone and hydrogen peroxide till the chapter on selenium and tellurium is reached. Chemical equations are introduced almost at the outset in Chapter 2—Oxygen. In chapters 1 to 15 inclusive each topic is taken up and developed in logical sequence with new inquiries growing out of topics that preceded. Most of the fundamental theories and principles are incorporated in these chapters. Beginning with chapter 16--Sulfur and Hydrogen Sulfide—the book becomes mainly descriptive. Throughout the book the practical applications--old and recent—are introduced. The student must thus become impressed with the debt our present-day complex society owes to the pioneers in chemistry.

Nowhere in the volume does the author indulge in any unusual tactics to capture the interest of the reader but he maintains a clear, simple, logical development which will help the student over many difficulties. Each chapter closes with a set of thought questions and exercises but no answers are given to problems. Neither have simple literature references been introduced to guide and stimulate the wide-awake student in supplementary reading. Some of the exercises, however, will send the student to the reference library. For example, while but scant attention is given to primary cells, nevertheless, p. 481, the student is asked to explain the operation of the zinc–zinc sulfate–copper–copper sulfate cell; and on p. 531 he is directed to look up the latest reports on chromium plating.

Radioactive changes and the structure of the atom are logically presented in the chapter with the periodic law, but much more could be done later in applying the electron concept to electrolysis, ionic reactions, oxidation and reduction, primary cells. A thorough integration of electron transfer and sharing into these topics has not been attempted. The proton is not mentioned; instead, hydrogen nucleus is used. The admixture of electrons with explanations given largely in terms of positive and negative charges, rise and fall of valence, etc., so common in this transition period to most of our texts, is bound to be rather confusing to the neophyte whose radio contacts have already made the electron a reality.

The proof reading has been well done and little mistakes are few in number. The opening of sentences with the pronoun "this" could be curtailed to advantage; charcoal is spoken of as a good conductor of electricity, p. 313; electrons in discharge tubes do not attain the velocity of light as stated on p. 179; Millikan's classical experiments established the value of the charge on the electron not its mass, p. 179; the millimicron should not be represented by the double letter, $\gamma\gamma$. The laws of Boyle and Charles, p. 30, are not stated in their usual precise form; Cl^- and $\mathrm{OH}-$ are called chloride and hydroxide ions; the Avogadro number appears to have been overlooked. The omission of the now obsolete laws of multiple and reciprocal proportions, p. 50, would be of no serious harm to the atomic theory and would remove a distressing hazard from the joyous progress of the average freshman.

The chapter on "The Colloidal State" is well written. Experimental evidence is introduced repeatedly establishing the molecular formulas of gases, e. g., oxygen, hydrogen sulfide, sulfur dioxide, ammonia, nitrous oxide. The theory of ionization in aqueous solution is presented early—chapter 14, p. 148—but subsequently ionic equations occur only here and there. Figures of apparatus have been greatly simplified and rarely show the complete set-up. The principle of Le Chatelier is stated in unusually simplified form, p. 276, but in the examples cited the old terms "strain" and "stress" make their appearance. Some instances are given of the interesting parallel between the reactions of substances with liquid ammonia and their reactions with water, p. 257.

Finally the reviewer ventures to repeat the question raised by Kendall in the preface to Smith-Kendall, "General Chemistry," "Is not the time ripe to begin to reduce the amount and variety of material offered to first year college students in chemistry?" Few indeed are the teachers who have classes which are able to cover in a satisfactory way the whole of the material contained in the standard college texts. Should not the emphasis be shifted somewhat too by omitting altogether a large bulk of the descriptive material offered in the chapters which generally follow sulfur and hydrogen sulfide, and substituting therefor more about the recent marvelous advances which modern chemistry is making?

HERMAN SCHLUNDT

First Principles of Chemistry. BY P. W. DOOTSON, M.A., Sc.D., F.I.C., University Lecturer and Demonstrator in Chemistry, Cambridge, and **A. J. BERRY, M.A.,** Fellow of Downing College, University Demonstrator in Chemistry, Cambridge University Press, Cambridge, England, 1927. vii + 339 pp. 43 figs. 13.5 X 20 cm. Price, $2.00.

This textbook is designed more particularly for the use of students who practically begin the study of chemistry at the University. It is to be studied as an adjunct to the lecture method of teaching, and should conserve the time taken up by writing notes in class and secure better attention to the demonstrations.

General principles and general methods are emphasized, and details have only been stressed where they have a special significance. But little attention is given to the Periodic Law, "while the now obsolete Laws of Multiple and Reciprocal Proportions have been omitted altogether." The Law of Definite Proportions, however, is stressed in the introductory chapter and illustrated by two sets of well chosen experiments. At the outset the student is introduced to the atomic theory, the chemical equation, Avogadro's theory, isotopes, heats of reaction.

In Chapter II, on water, hydrogen, oxygen, etc., water is studied first, and here we find introduced among other topics, the phase rule, Le Chatelier's theorem, aqueous solutions, water softening. This chapter also includes Gay-Lussac's Law of Combining Volumes, hydrolysis, equivalent weights, the laws of Boyle and Charles, reversed combustion.

The Ionic Theory is deferred to Chapter 10, p. 249, and its applications are introduced in the next chapter on "Metals and Their Compounds." The closing chapter, 12, describes methods of determining molecular and atomic weights.

The book contains many refreshing passages and several elegant lecture demonstration experiments are described. The various chapters contain none of the modern teaching devices, such as thought questions, problems, literature references, etc. A knowledge of logarithms is assumed in expressing hydrogen-ion concentration in terms of P_H values. The book serves the purpose for which it was written but it is probably not adapted for freshmen in this country who have had a year of high school chemistry.

On p. 106 the boiling point of iodine is given as lower than its melting point: the reverse is true. The reviewer questions the statement on p. 17 that the compression of water by the pressure of the atmosphere results in a lowering of the general sea level by rather more than one hundred feet.

HERMAN SCHLUNDT

La Notion d'Espece en Chimie. (The Idea of Molecular Species in Chemistry.) BY JEAN TIMMERMANS, Professor of Physical Chemistry at the University of Brussels Gauthier-Villars et Cie., 55 **Quai des Grands-Augustins, Paris, France, 1928. iii + 134 pp. 15 figs. 14 X** *22* **cm.**

This little book undertakes a discussion of the most favorable conditions for the determination of physical–chemical constants. Its three main divisions are devoted to answering three questions. 1. How is a physical–chemical system to be defined unambiguously?—the problem of molecular species in chemistry. 2. How is such *a* system to be realized?—the problem of pure substances. 3. How are the constants to be measured with precision and exactness?

The first section outlines in interesting fashion the historical evolution of the idea of molecular species and the application of the phase rule to both simple and intricate cases. Section two discusses the meaning of the term pure, methods of dehydration, the theory of fractional distillation and of fractional crystallization and the limitations of methods used for these latter operations. Part three contains a discussion of the ultimate standards in use, the theory of least squares as applied to experimental data and a list of the principal national laboratories undertaking the determination of constants. There is also a list of the principal reference tables on physical–chemical constants. The chapter on the evaluation of existing data, with benzene taken as an example, is particularly interesting.

The limitation of the text to a little over a hundred pages has of course made it necessary that the theoretical treatment be frequently dogmatic rather than explicit, and the quotation of specific data meager. Necessarily also the matter contained can hardly be new to experts, and is too condensed to suffice for novices in the field. Nevertheless it will make most interesting and most helpful reading to both classes, for nowhere has there been in a single publication such a complete codification of the conditions and the problems to be kept in mind by the experimenter during the work of measuring physical–chemical constants.

ARTHUR E. HILL

Grundzüge der Körperlehre. (The Basis of a Science of Material Objects.) BY DR. J. V. HOFMANN. Emil Pahl, Dresden, 1926. Portrait. vii + 80 pages. 15.5 × *23.5* cm. Price, $1.00 net from the son of the author, William E. Hofmann, 1849 Bronxdale Avenue, New York City.

This book contains three popular lectures delivered in 1870 by Joh. Val. Hofmann (a German private scholar who was not connected with a university) in exposition of the views which he had earlier set forth in his "Somatologie oder Lehre von der inneren Beschaffenheit der Korper," Gottingen, 1863. It contains a polemical chapter in which evidence is given that Kirchhoff adopted and put forward as his own in 1865 the views which Hofmann had set forth in his book. Also, it prints a letter, with facsimile, from Professor Carl Naumann in acknowledgment of the dedication of the hook to him.

Hofmann speculated about the density of atoms and about the spaces between them, etc. He held that the purely mechanical theory of heat as then recently developed by Mayer, Joule, Thomson and Helmholtz is inadequate to account for the phenomena of physics and chemistry—and that the particular properties of the kind of matter which is involved must be taken into the reckoning. He was apparently the first to see the necessity for a special science—Somatology—which should develop from the same causes the phenomena of chemistry, of crystallography, and of physics. To that extent he laid the early foundations for the work of van der Waals, Richards, Bragg and Bohr.

The present little book does not contain any very remarkable deductions. It has some reasoning which appears to be fallacious. But it is an important historical document for the reason that it shows the feeble beginnings of the speculations and experimentation which are giving to the science of the structure of matter the status that Hofmann (and Kirchhoff) thought that it deserved.

TENNEY L. DAVIS

Mechanische Eigenschaften flüssiger Stoffe. Volumen, Dichte, Kompressibilitat, Oberlächenspannung, Innere Reibung. (Mechanical Properties of Liquid Substances. Volume, Density, Compressibility, Surface Tension, Viscosity.) By R. Kremann, Professor at the University of Graz. Handbuch der allgemeinen Chemie, Band V. Akademische Verlagsgesellschaft m. b. H., Markgrafenstrasse 4, Leipzig, Germany, 1928. xii + 597 pp. 75 figs. 18 × 25.5 cm. Price, unbound, M 46.50; bound, M 49.

The scope of this work is indicated by the subject matter treated in the various chapters. The first main division, on volume relations of liquids, includes relation of volume to pressure, temperature and constitution, and volume relations of binary mixtures. In the second main division, dealing with viscosity, the topics dealt with are: general discussion and definitions, methods and apparatus, influence of temperature and pressure, turbulent flow, relation between viscosity and other properties and its dependence upon chemical constitution, the viscosity of mixtures and various applications of the measurement of viscosity. Under surface tension the topics treated are general discussion and definitions, methods of determining surface tension, the effect of temperature, pressure and other variables, the relation to chemical constitution, the surface tension of mixtures and solutions, and further applications for the measurement of surface tension.

The author's own labors in these fields have well prepared him for the monumental task which he has accomplished. Anyone at all familiar with the literature in any one of the three main fields treated is aware of the enormous amount of work involved in its presentation in book form. The scope of the book and the extent of the literature covered by it have naturally made it necessary to write a résumé rather than a highly critical presentation. While this is a disadvantage from certain points of view, it will greatly aid a research worker in these fields in surveying the large amount of work previously done. Incidentally it is likely to impress him with the unsatisfactory character of much of it, and with the great need for a concerted attack upon the problems of the liquid state, for it is surely true that our knowledge of the liquid state of matter is far less satisfactory than that of the gaseous and solid states. Over and over again one discovers that the only formulation of certain relationships is in terms of the notoriously inaccurate van der Waals equation. A perusal of this book should serve to suggest many important researches, which is perhaps the highest service such a work can perform.

It may seem captious to complain of omissions from a book which represents such a stupendous review of physico-chemical publications; but the reviewer has felt, in reviewing this as well as other continental publications, that some of the work done on this side of the Atlantic is either absent from European libraries or receives but casual attention. To mention only two examples: in reviewing the effect of pressure upon surface tension, there is no reference to the thermodynamic formula given by Lewis and Randall; and in connection with the surface tension of metals, values obtained by Siedentopf in **1897** are used rather than the values of Hogness obtained in **1921.** There are also instances where the author has been content merely to state a discrepancy or to quote contradictory opinions, although some of these matters, to the reviewer's knowledge, have been critically discussed in American publications. The reviewer does not wish, however, that these remarks should be taken too seriously, for he realizes that any work of such scope prepared by a single author would be subject to similar criticism.

JOEL H. HILDEBRAND

Reaktionskinetik gasförmiger Systeme. (The Kinetics of Chemical Change in Gaseous Systems.) BY C. N. HINSHELWOOD, Lecturer at Oxford University. Translated by Dr. ERICH PIETSCH and Dr. GERTRUD WILCKE. Akademische Verlagsgesellschaft m. b. H., Markgrafenstrasse 4, Leipzig C 1, Germany, 1928. xii + 246 pp. 12 figures. 16 × 23.5 cm. Price, unbound, M 15; bound, M 16.

The translators have included an extensive bibliography which was not present in the English edition. The period covered is from **1887** to **1927.** The first two hundred and fifty papers are of a general nature. More than five hundred references are then given, classified according to the reactions studied. An index to the bibliography lists some seventy-five reactions.

H. E. BENT

Photochemical Processes. BY GEORGE B. KISTIAKOWSKY, Research Associate in Chemistry, Princeton University. American Chemical Society Monograph Series. The Chemical Catalog Company, Inc., 419 Fourth Avenue, New York City, 1928. 270 pp. 8 figs. 15.5 × 23.5 cm. Price, $5.50.

The book is divided into six chapters with the following headings: "The Concept of Light Quanta and Photochemical Kinetics," "The Equivalence Law," "Chain Reactions," "Photosensitisation," "Catalysis and Inhibition," and "Frequency of Radiation, Temperature and the Rate of Photochemical Reactions."

The first chapter is the shortest one of the book. In it is given a brief non-mathematical discussion of some of the fundamental concepts underlying the field of photochemistry. The Grotthuss-Draper law, Fresnel's law, Lambert's law, Beers' law, light scattering and photo-kinetics are covered in rapid succession. Follow a brief discussion of light quanta and mention of the principal theories of the primary process in photochemical reactions. This chapter does not contain all of the theoretical discussion given in the book, the details being reserved for later discussion, largely in connection with specific reactions. The chapter is quite readable and clear. One might wish amplification of certain points, particularly in the relationship of modern theories of band spectra to photochemical theory.

In the second chapter the author has limited discussion to some thirty odd reactions for which the data warrant discussion of possible mechanisms. The difficulties involved in the choice of reactions are great and probably no two photochemists could be found who would choose identical lists of reactions to be discussed. The chapter is quite readable in spite of the large amount of detail it contains and the author has usually been quite frank in stating that no definite conclusions can be drawn with regard to certain reactions. In many cases several reaction mechanisms may be used to derive equations which are equally applicable to the data. The author must, however, be lauded for his impartiality and the chapter is a good summary of the reliable data in this field.

In the third chapter a large fraction of the space is devoted to discussion of reactions involving halogens, particularly chlorine, since these reactions have been more studied than other reactions having quantum efficiencies much larger than unity. In view of the fact that the mechanisms of few, if any, of these reactions have been satisfactorily elucidated from all standpoints, one might feel that this chapter is too long in relation to the size of the book. The chapter is, however, interesting to read even if a great deal of the work included may eventually prove to be meaningless.

In the chapter on "Photosensitisation" are included discussion of gas reactions, reactions in solution and such matters as the sensitization of photographic emulsions and chemiluminescence. The author has presented the various experimental facts clearly and where possible has given discussion of reaction mechanisms. One might wish the inclusion of more of the physical aspects of the problem, since the author seems to have accepted one point of view entirely in the discussion.

The chapter on catalysis and inhibition contains a discussion of ozone decomposition, hydrogen peroxide decomposition, chlorine water decomposition, reactions of cobaltic complexes and autoxidations. The chapter is well written and the work on these reactions is quite fully given. Definite conclusions are not always arrived at, but the various aspects of the subject are presented in such a way that the reader obtains a clear idea of the field.

The final chapter contains a lot of loose odds and ends, some of which might well have been included earlier in the book. The discussion of the temperature coefficient of photochemical reactions is particularly interesting.

The style of the book is, on the whole, very good. The author has obviously not intended to give complete bibliographies for each of the reactions discussed, but has confined himself to papers permitting of some interpretation. The fact that the reading is difficult at times is not due to any fault of the author, but to the nature of the subject, since so many self-contradictory and illogical statements are found in the literature. Some slight mistakes in literature references and in statements of the points of view of some authors have crept in, but these are not serious. One might wish a fuller theoretical discussion, but the book is a worth while summary of the work on a large number of reactions.

The reviewer takes pleasure in commending the book to anyone interested in the subject of photochemistry.

W. ALBERT NOYES, JR.

Der **gegenwärtige** Stand der Spannungstheorie. (The Present Status of the Strain Theory.) BY WALTER HÜCKEL. Fortschritte der Chemie, Physik und physikalischen Chemie, Band 19, Heft 4, Serie A. Gebrüder Borntraeger, W 35 Schoneberger Ufer 12a, Berlin, Germany, 1927. iv + 101 pp. 12 figs. 17 × 25.5 cm. Price, M 7.60.

In one respect the present status of the strain theory is much less satisfactory than was its status ten years ago. The facts no longer permit one to state the theory neatly and in a few words. Von Baeyer, who invented this one of the few really important theories of organic chemistry, adopted the improbable assumption that all rings are uni-planar. This made it unnecessary to contemplate the rather overwhelming possibility that the number of atoms in a cycle might be any positive integer from 2 to infinity, or that even a simple alicyclic hydrocarbon might exist in stereoisomeric forms. The fact of the existence of large rings was established by the recent but already classical work of Ruzicka, and the experimental verification of the implications of the idea of non-planar and strainless rings (Sachse-Mohr) has received important additions at the hands of Walter Hückel, who is therefore in position to discuss all of these researches authoritatively and in detail.

The last third of the book is devoted to a criticism of Ingold's hypothesis of valency angles. Von Baeyer assumed that for carbon this angle is always 109° 28' (or that the deviation from this angle was a measure of the strain involved). The use of this improbable assumption makes possible a great many more positive predictions than its denial. Ingold not only repudiated this assumption, but he pretended to be able to calculate the manner in which substituents would affect the valency angles. He thus made the theory more explicit than before. Ingold and Thorpe defend themselves against Hückel's adverse criticism in the *Journal of the Chemical Society, 1928,* 1318.

As a result of the industry which led to the repudiation of Von Baeyer's simplifying assumptions, chemists now have opened before them a quite endless expanse of stereo-chemical problems. Some of these are discussed very suggestively in the present volume. A further result is that the strain theory no longer constitutes a quite homogeneous and self-complete chapter of organic chemistry. Such a chapter would perhaps be constituted by a complete story of the stereo-chemistry of cyclic compounds. This realm is considerably wider than the compass or intention of Hückel's brief study but it is one to which a monograph might very well be devoted.

There can be no doubt that a knowledge of the stereo-chemistry of cyclic compounds will be increasingly important to the most diverse branches of modern organic chemistry—one might mention, for example, sugars and polysaccharides and petroleum.

WALLACE H. CAROTHERS

Schiess- und Sprengstoffe. (Powder and Explosives.) BY DR. PH. NAOÚM, Director of the Research Laboratory of the Dynamite Joint Stock Company, formerly Alfred Nobel and Company. Theodor Steinkopff, Dresden and Leipzig, 1927. xi + 199 pages. 12 figs. 15.5 × 22 cm. Price, unbound, RM 12.50; bound, RM 14.

This volume is No. XVI of a series of *Technische Fortschrittsberichte,* the purpose of which is to summarize recent progress in the various branches of applied science. It has chapters on the theory of explosives, on black powder, nitroglycerine, nitrocellulose and the other nitrated carbohydrates, smokeless powder, dynamite, ammonium nitrate explosives, chlorate and perchlorate explosives, safety explosives, liquid oxygen explosives (chapter written by Dr. K. F. Meyer) and on primary explosives, primers, detonators, etc. It contains a surprisingly large amount of information and mentions or discusses many things which have not heretofore been brought together in a single book—the use of centralite in smokeless powder, the manufacture without solvent of powder containing a low percentage of nitroglycerine, non-fulminate primers containing thiocyanates, explosive superoxides, and cyclotrimethylenetrinitramine, or Hexogen as the Germans call it, which has a velocity of detonation of 8400 meters per second and is the most brisant of all explosives—to mention a few instances. As might be expected in a book of this character, there are a number of omissions. Guanidine nitrate is described but nitroguanidine does not appear to be mentioned, the preparation of trinitrobenzene by the oxidation of trinitrotoluene is not described, and no light is given on the chemistry of the sulfite, or better bisulfite, method for the purification of TNT. The statement that nitro-urea has good chemical stability is evidently an error.

The book is distinctly one for the specialist and gives an excellent account of recent progress in explosives. It will be of value to those who are concerned with that field, whether in research or in the manufacture and testing of the products.

TENNEY L. DAVIS

Creatine and Creatinine. By ANDREW HUNTER, M.A., M.B., F.R.S. Can., Professor of Biochemistry in the University of Toronto. Longmans, Green and Co., 55 Fifth Avenue, New York City, 1928. vii + 281 pp. 15.5 × 24.5 cm. Price, $5.00.

Nearly a century has elapsed since the discovery and designation of creatine in 1832 by the distinguished French chemist Chevreul. The identification of creatinine by Liebig occurred fifteen years later. These are two organic compounds widely distributed in the tissues of vertebrates, of questionable occurrence in invertebrates, but apparently present in some of the higher plants. Creatine seems to be concentrated in the muscles, which contain as much as 98% of all of the substance that is present in the vertebrate body. One or both of the compounds circulate in the blood (though the details of their occurrence there are by no means established beyond debate). Creatinine is a never-failing constituent of the urine; the appearance of creatine therein varies under conditions as yet little understood. The chemical origin, the physiological function, the abnormal occurrence and the biochemical fate of these long recognized body constituents cannot yet be presented in larger outline with any considerable degree of certainty. The problems that Professor Hunter has discussed, often with meticulous detail, still lead to a story that is full of "gaps and guesses." As Hunter himself has remarked in reviewing some of the uncertainties: "The safest position for the present is probably the admission of ignorance" (page 241).

Here, then, are themes for investigation that challenge the ingenuity of the ablest biochemists. One is not called upon to deal with tars or gums, with ill-defined products of unknown composition. The substances in question are readily crystallizable compounds of well-known structure; their biological significance is obviously notable; the need of new interpretations is pressing. Progress has been hampered, as in so many other instances, by the apparent lack of suitable methods of investigation. Progress was decidedly slow until the introduction of Folin's colorimetric methods of estimation in 1904. These are indirect and by no means devoid of pitfalls and uncertainties. New procedures seem imperative. It might be conducive to advance if much that has been published about the physiology of creatine and creatinine were temporarily forgotten so that the new students of the subject would acquire independent, unbiased starting points and impressions. In any event Professor Hunter's monograph is a *vade mecum* of inestimable value.

LAFAYETTE B. MENDEL

The Journal of the
American Chemical Society

VOL. 50 NOVEMBER, 1928 No. 11

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

STUDIES ON THE PERIODIC SYSTEM.
I. THE IONIC POTENTIAL AS A PERIODIC FUNCTION[1]

BY G. H. CARTLEDGE

RECEIVED APRIL 7, 1928 PUBLISHED NOVEMBER 6, 1928

In the more recent modifications of the periodic system emphasis has been placed upon the structure of the elements as the basis of classification. All forms of classification, however, suffer from the same essential difficulty, namely, that the elements have too protean a nature to be adequately classified by reference to any single atomic characteristic. For chemical use it is highly desirable that a periodic arrangement be devised which shall be based upon a more comprehensive and quantitative view of the elements and shall also provide a place for all valence forms of all elements. It is one of the serious defects of the Mendelejeff system that it has no quantitative basis, so that it is unable to indicate gradations in properties within a series or a family.

While the comparison of atomic structures gives a partial indication of variations in chemical behavior, even this is not adequate, inasmuch as the properties of *compounds* are to an important extent determined by the sizes of their ionic constituents as well as by their structures. The role of the ionic radii has been emphasized by Grimm,[2] and by v. Hevesy.[3] Grimm has also given a periodic classification in which the direction of variation in radii is represented.[4] The importance of certain electronic structures in giving different valence forms of the same element has been shown by Grimm and Sommerfeld.[5]

In order to obtain a more comprehensive representation of the properties of compounds, it is proposed in this paper to take account of the charge, structure and *size* of the ionic constituents of compounds, and to develop a form of representation in which it will be possible to include all valence forms of all of the elements. As a consequence of this broader and quanti-

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[1] In memory of Ira Remsen.

[2] Grimm, *Z. physik. Chem.*, **98**, 353 (1921); *ibid.*, 102, 113, 141 (1922).

[3] G. v. Hevesy, *Z. anorg. allgem. Chem.*, **147**, 217 (1925).

[4] Grimm, *Z. physik. Chem.*, **101**, 410 (1922).

[5] Grimm and Sommerfeld, *Z. Physik*, 36, 36 (1926).

tative basis of classification, the new arrangement eliminates the earlier difficulties with respect to the classification of hydrogen, the properties of the rare earths, the higher valence forms of copper, silver and gold, and the relations of the eighth-group elements. Being based upon ions rather than atoms it gives a clearer representation of the chemical relationships.

The Ionic Potential

In determining the properties of substances, increasing ionic charge and increasing ionic radius act in opposite directions; thus, the lattice energy of a binary polar crystal is chiefly determined by the Coulomb term, $Z^2e^2/(r_+ + r_-)$, in which e is the electronic charge and Z and r are, respectively, the valence and radius of the ions. In the same way, oxides are increasingly acidic the higher the charge or, for constant charge, the smaller the radius of the positive ion. This consideration suggests that the ratio of charge to radius should be an important property of ions and closely related to many characteristics of substances. If the ion in a crystal is regarded as a charged sphere of definite extension in space, this function is the *ionic potential* and will be represented by ϕ; that is, $\phi = Z/r$. Of course the ion in a crystal is not a conducting sphere in the strict sense, so that in calling this function the ionic potential we are using a somewhat hypothetical concept as a basis of classification. Ions actually have a real charge and a real extension in space, however, and these characteristics are observed to have a determining influence upon the properties of their compounds, so that the ratio of charge to radius is a real property of the ion.[6]

In this method of treatment it is not necessary to assume the free existence as ions of such substances as S^{6+} or C^{4-}. In crystals such as sodium chloride the lattice is undoubtedly ionic, while the intra-ionic bonds in sulfate ions, for instance, are generally regarded as non-polar. Since ions of the same structure have radii which are inversely proportional to the effective nuclear charge, the radius may be found for the electrical system corresponding to S^{6+}, even though this may not exist as a separate entity. It is only in this sense that S^{6+} will be called an ion. If it is a transition from polar to non-polar binding which is associated with the variation in properties in going through a periodic series, then it appears that this transition is directly related to the magnitude of the ionic potential, which therefore becomes an index of properties, even though calculated for hypothetical ions such as S^{6+}.

Ionic radii have been calculated from crystal data by Grimm and

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[6] Another similar function might be used, namely, the electrostatic energy of the ion, $Z^2e^2/2r$. This possibility has been investigated, and a classification results similar to the one here given. The simpler function is to be preferred, however, in most cases.

Wolff[7] and, more recently, on the basis of the wave mechanics, by Pauling.[8] The data of Pauling have been used, as far as they go, in calculating the ionic potentials. For this purpose the ionic charge Z corresponding to the valence is divided by the radius in Ångström units. These arbitrary units of potential are sufficient to indicate the comparisons desired.

In order to obtain ionic potentials for all the elements it is necessary to use indirect methods in certain instances. The available data on the radii have been extended in the following manner.

(a) The ionic potential is directly related to the ionization potential for the removal of the *last* electron in the production of the ion in question. As was found by Millikan and Bowen,[9] there is a linear relation between the atomic number and the square root of the energy corresponding to the removal of the electron in a series of ions of the same structure. This is an extension of the Moseley rule for x-ray frequencies into the region of optical spectra. Correspondingly, for positive ions it is found that *the square root of the ionic potential increases in very approximately equal steps as the ionic charge increases without alteration in structure.* For this reason the square root of the potential is given in some of the graphs and tables which follow, and unknown potentials may be very closely estimated by this *method of constant increments.* The increment $\Delta\sqrt{\phi}$ becomes less as the principal quantum number of the outermost electrons in the ion increases. This method has been used in finding values for Ta^{5+}, W^{6+}, (75^{7+}) and Os^{8+}, the calculations being based on the potentials for Lu^{3+} and Hf^{4+}, as found in the way described in (c) below; for Po^{6+} and (85^{7+}) by reference to Bi^{5+}; and for the series Ra^{++} to U^{6+} by reference to Ra^{++} and Th^{4+}.

(b) Within the alkali and alkaline earth families there is a linear relation between the ionization potential and the square root of the ionic potential, from the sodium to cesium series, inclusive. From this relation and the known ionization potential of radium, the value of $\sqrt{\phi}$ for radium is found to be 1.24. This value, combined with that for thorium (1.90), gives the increment in $\sqrt{\phi}$ as **0.33** for unit change in charge in the series Ra^{++} to U^{6+}.

(c) Radii for the rare earth ions were computed by Grimm and Wolff[7] from the lattice spacing of the oxides as given by Goldschmidt.[10] These measurements show that the ionic radius decreases from lanthanum to lutecium, the jump being apparently larger from La^{3+} to Ce^{3+} than it is elsewhere in the series. In order that all of the radii used in estimating potentials may be consistent with each other, the radius of Lu^{3+} has been calculated from that of Y^{3+} as given by Pauling by taking the lengths of the unit cells in the cubic forms of Y_2O_3 and Lu_2O_3 as 10.60 Å. and 10.37 Å., respectively. This gives 0.88 Å. as the radius of Lu^{3+}, corresponding to $\sqrt{\phi} = 1.85$. Values for the other rare earths have been interpolated, following the data of Grimm and Wolff.

Since the external structures are alike in the series Cs^{+} to Ce^{4+} and Hf^{4+} to Os^{8+}, and since these ions belong to the same periodic series, it is reasonable to assume that the increment in $\sqrt{\phi}$ per group is the same in both parts of the series. The value 0.40 as obtained from Ba^{++} and Ce^{4+} is used for $\Delta\sqrt{\phi}$ in estimating the potentials from Lu^{3+} to Os^{8+}.

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[7] Grimm and Wolff, *Z. physik. Chem.*, 119, *234 (1926);* Grimm, *ibid.*, 122, 177 (1926).

[8] Pauling, THIS JOURNAL, 49, 765 (1927).

[9] Millikan and Bowen, *Phil.* Mag., [7] *4,* 561 (1927).

[10] Goldschmidt, *Skrifter Norske Videnskapsakad. Oslo, I, Matemat.-natur. Klasse,* 1926, No. 2.

(d) The potential of the hydrogen ion $H^{\cdot}$ can be estimated only indirectly and approximately, owing to the unique character of the ion in all respects. As will be pointed out subsequently, the heat of hydration of the gaseous ion is related to the ionic potential. There is a linear relation for the alkali ions, and if this is used in connection with the heat of hydration of the H^+ ion, it gives a value of about 2 for $\sqrt{\phi_{H^+}}$. The ionization potential of the alkali elements also varies in the same order as the ionic potential, and extension of the curve indicates an ionic potential for H^+ corresponding to $\sqrt{\phi} = 4$ approximately. On account of the unique structure of the hydrogen ion it is hardly to be expected that any single constant can be obtained which will be a quantitative indication of all the properties of its compounds; this divergence in the values is not surprising, therefore, since they correspond to very different types of behavior. Nevertheless, as will be seen below and in the subsequent paper, a mean of the values obtained above serves to indicate properly the general relation of hydrogen compounds, such as hydrogen chloride and water.

Table I gives the square root of the ionic potentials obtained in the ways just described. The values are in arbitrary units, the charge being taken as the valence and the radius being expressed in Ångström units. A negative sign is attached to the values for the anion potentials. No attempt has been made to estimate potentials for ions which have an electron pair in the ion, such as Ge^{++}. Aside from the paucity of data for such cases, there is the further complication that tautomerism is apparently a common phenomenon in such valence forms, for example,

TABLE I

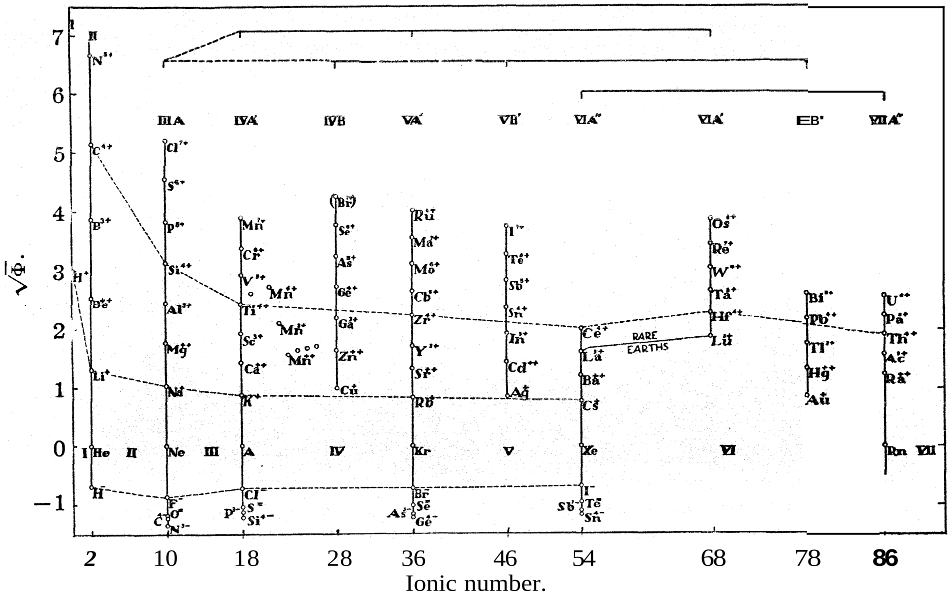
SQUARE ROOT OF IONIC POTENTIALS (ARBITRARY UNITS)

				H^+							
				3							
			H^-	Li^+	Be^{++}	B^{3+}	C^{4+}	N^{5+}	(O^{6+})	(F^{7+})	
			−0.69	1.29	2.54	3.87	5.16	6.71	(8.19)	(10)	
C^{4-}	N^{3-}	$O^{=}$	F^-	Na^+	Mg^{++}	Al^{3+}	Si^{4+}	P^{5+}	S^{6+}	Cl^{7+}	
−1.24	−1.32	−1.19	−0.86	1.02	1.76	2.45	3.13	3.83	4.55	5.20	
Si^{4-}	P^{3-}	$S^{=}$	Cl^-	K^+	Ca^{++}	Sc^{3+}	Ti^{4+}	V^{5+}	Cr^{6+}	Mn^{7+}	
−1.22	−1.19	−1.04	−0.74	0.87	1.42	1.92	2.43	2.92	3.39	3.90	
				Cu^+	Zn^{++}	Ga^{3+}	Ge^{4+}	As^{5+}	Se^{6+}	(Br^{7+})	
				1.02	1.64	2.20	2.74	3.26	3.78	(4.24)	
Ge^{4-}	As^{3-}	$Se^{=}$	Br^-	Rb^+	Sr^{++}	Y^{3+}	Zr^{4+}	Cb^{5+}	Mo^{6+}	Ma^{7+}	Ru^{8+}
−1.21	−1.16	−1.00	−0.715	0.82	1.33	1.79	2.24	2.66	3.11	3.56	4.01
				Ag^+	Cd^{++}	In^{3+}	Sn^{4+}	Sb^{5+}	Te^{6+}	I^{7+}	
				0.89	1.44	1.92	2.36	2.84	3.27	3.74	
Sn^{4-}	Sb^{3-}	$Te^{=}$	I^-	Cs^+	Ba^{++}	La^{3+}	Ce^{4+}				
−1.17	−1.10	−0.95	−0.68	0.77	1.21	1.61	2.00				
						Lu^{3+}	Hf^{4+}	Ta^{5+}	W^{6+}	Re^{7+}	Os^{8+}
						1.85	2.25	2.65	3.05	(3.45)	3.85
				Au^+	Hg^{++}	Tl^{3+}	Pb^{4+}	Bi^{5+}	Po^{6+}	85	
				0.85	1.35	1.78	2.18	2.60	3.02		
				87	Ra^{++}	Ac^{3+}	Th^{4+}	Pa^{5+}	U^{6+}		
					1.24	1.57	1.90	2.23	2.56		

$Ge(OH)_2 \rightleftarrows HGeOOH$, sulfurous acid, and others, so that the electrical system is not well defined.

Radii are known for some of the transition ions, so that their ionic potentials may be found. During the completion of an 8-shell, as from Ca^{++} to Zn^{++}, there is a distinct contraction as the first electrons are added, so that the transition ion has a higher potential than the equivalent ion with the inert-gas structure: $\phi_{Mn^{++}} > \phi_{Ca^{++}}$. The data are inadequate to permit tracing the variation during the complete transition from Ca^{++} to Zn^{++} or from Sc^{3+} to Ga^{3+}, for example, but the trend is indicated by the following values, some of which are included in Fig. 1.

Ion	Ca^{++}	Mn^{++}	Fe^{++}	Co^{++}	Ni^{++}	Ti^{4+}	V^{4+}	Mn^{4+}	Zr^{4+}	Cb^{4+}	Mo^{4+}	Ru^{4+}
$\sqrt{\phi}$	1.42	1.57	1.64	1.67	1.70	2.43	2.61	2.72	2.24	2.44	2.46	2.52



Electron shells	2	10	18	28	36	46	54	68	78	86
K	2	2	2	2	2	2	2	2	2	2
L		→ 8	8	8	8	8	8	8	8	8
M			→ 8	→ 18	18	18	18	18	18	18
N					→ 8	→ 18	18	→ 32	32	32
O							→ 8	8	→ 18	18
P										→ 8

Fig. 1.—Square root of the ionic potentials.

Ionic Potentials and the Periodic System

There are obviously three characteristics of the ions that should be represented in the periodic system, namely, the electronic structure, the net charge and the ionic potential. For simplicity we shall define the *ionic* number as the number of extra-nuclear electrons in the *ion*, corresponding to the atomic *number* for atoms. For graphical representation the square root of the ionic potential is plotted against the ionic number in Fig. 1. A still clearer representation is given by a three-dimensional model, a photograph of which is shown in Fig. 2. In this the ionic number and ionic charge are the axes in the plane of the board, while the height of the rods is proportional to $\sqrt{\phi}$ (omitting the negative sign of the anion potentials).

These arrangements emphasize the predominance of certain ionic structures, as was suggested in Kossel's diagram.[11] The periods also are clearly shown in accordance with the requirements of the Bohr theory, the periods being designated by a number equal to $n + 1$, in which n is the quantum number of the outer electrons in the ion.[12] While by no means all known valence forms of the elements are shown in Fig. 1, holes have been drilled in the board in the model for all of them, and the potential of any ion may be estimated by considering the general order of variation. In Pigs. 1 and 2 several valence forms of manganese are shown in order to illustrate the principle.

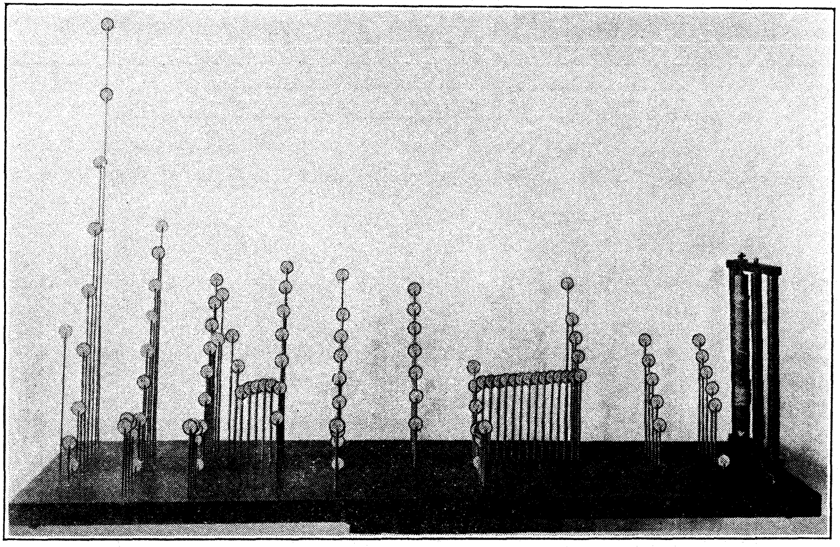


Fig. 2.—Model of the periodic system of ions. From left to right, ionic numbers; front to back, ionic charges ($^{4-}$ in front to $^{8+}$ at back); height of rods gives $\sqrt{\Phi}$.

The rapid variation in properties in the series Li^+ to N^{5+} is revealed

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[11] Kossel, Ann. *Physik*, 49, 229 (1916).

[12] In this way positive ions that are fully oxidized belong to the ionic series of the same numerical designation as is used by Bohr for the series of elements. Partly reduced positive ions (Fe^{++}, P^{3+}) are given the same series number as the fully oxidized ions, while fully reduced anions, such as Cl^-, belong to the next higher ionic series.

by the large increment in $\sqrt{\phi}$. This makes these ions more or less unique in comparison with corresponding ions of the series below. The dual character of hydrogen in giving both an alkali-like ion H^+ and a halogen-like ion H^- is shown by its double location in the system. The numerical value of $\sqrt{\phi_{H^+}}$ shows, however, that H^+ resembles the alkali ions only in valence, its potential placing it along with Si^{4+} and Ti^{4+}, while H^- is quite like a halide ion in general relations. Correspondingly, liquid HCl and $SiCl_4$ are volatile, non-conducting substances, while $LiCl$ and LiH are high-melting substances which conduct electrolytically in the fused state.

It is obvious that the eighth-group triads are provided for in a logical manner, as is also the case with Cu^{++}, Ag^{++} and Au^{3+}. The disposition of the rare earths is particularly significant. As will be pointed out subsequently, the basic properties of an ion diminish with increasing potential. Whereas there is, in general, an increase in basic character with increasing atomic weight in comparing ions of the same valence, this order is reversed in the rare earths, so that luteciurn is even less basic than yttrium. These relations are accurately shown by the ionic potentials, and it is strikingly indicated that yttrium falls in the rare-earth elements in the neighborhood of dysprosium and holmium (which accords with its experimental behavior) while scandium is less basic (higher potential) than lutecium. The relation of the rare earths to the bivalent ions is shown in the near equality of the potentials of lanthanum and magnesium.

It will be convenient to speak of ions having very nearly equal potentials as *equipotes*.

The Periodic Families of Ions

Although it will be shown in the succeeding paper that the ionic potentials are a reliable index to the variation of numerous properties, it is necessary to remember that the ionic structure must also be taken into account in comparing the chemical and physical character of ions and their compounds. There is a close connection between the chemical relationships of the different families and series of ions and the character of their outer electronic shells, *particularly with respect to the completeness or incompleteness of these shells.* This observation has suggested a modification of the division into families as made by Mendelejeff. The successive shells are complete when they contain, respectively, 2, 8, 18, 32, and 50 (?) electrons, so that the *ionic types* to be distinguished on this basis are as shown in Table II.

In this representation A or B is used only if the simplest ion of the series has two or more electronic groups. A is used if the outer shell is either a simple 8-shell or a partial development of one, as $K^+ = 2,8,8$; $Mn^{7+} = 2,8,8$; $Mn^{++} = 2,8,13$. B is used for an outer shell of 18 or a

TABLE II

PERIODIC SERIES AND FAMILIES OF IONS

Series designation	Outer shell	Next underlying shell	**Examples**
I	*0*	..	H^+ only
11	*2*	..	H^-, N^{5+}
III *A*	8 (complete)	2 (complete)	C^{4-}, Cl^{7+}
IV *A'*	8 (incomplete)	8 (complete)	Si^{4-}, Mn^{7+}
IV *B*	18 (complete)	8 (complete)	Cu^+, Se^{6+}
V *A'*	8 (incomplete)	18 (complete)	Ge^{4-}, Ru^{8+}
V *B'*	18 (incomplete)	18 (complete)	Ag^+, I^{7+}
VI *A''*	8 (incomplete)	18 (incomplete)	Sn^{4-}, Ce^{4+}
VI *A'*	8 (incomplete)	32 (complete)	Lu^{3+}, Os^{8+}
VI *B'*	18 (incomplete)	32 (complete)	Au^+, Po^{e+}
VII *A''*	8 (incomplete)	18 (incomplete)	Ra^{++}, U^{6+}

development of one, as $As^{5+} = 2,8,18$; $As^{3+} = 2,8,18,2$. The prime marks are used to indicate the incompleteness of the two outer 8 or 18 shells; a single prime mark signifies that only the outer 8 or 18 shell is incomplete; a double prime denotes that the two outermost 8 or 18 shells are incomplete.

Inspection of Fig. 1 reveals the close relationships indicated by the brackets in the upper portion of the figure. This method of defining the periodic families brings out clearly the effects associated with the "lanthanide contraction,"[13] such as the association in nature of zirconium with hafnium, of columbium with tantalum, and so forth. The classification also serves to indicate the unique character of the ions of series I (H^+) and II ($Li^+ - N^{5+}$), as well as the double relationship of the ions of series III A, which are most like A' members in the first two groups but more like B ions in groups III to VII.

This definition of the periodic families taken in connection with Fig. 1 serves to bring out the differences among the members of a given family in the Mendelejeff arrangement. In the alkali family, for example, the relatively large divergence in properties between lithium and sodium and also between sodium and potassium is clearly shown. Potassium and rubidium have very nearly equal potentials (and properties) while the differences between rubidium and cesium are somewhat larger (less marked isomorphism, for example). Even in Group IV, in which family differences are less pronounced than in other groups, the variations in properties are significantly shown. Titanium, zirconium and hafnium are thrown together, the last two having equal potentials and very similar properties, while cerium and thorium are in another family with somewhat different potentials. The near equality of the potentials of both A and B families in Group IV corresponds to the extensive isomorphism which occurs in many of their compounds.

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[13] Goldschmidt, Barth and Lunde, *Skrifter Norske Videnskaps.-Akad. Oslo., I, Matemat. Natur. Klasse,* **1925**, *No. 7;* v. Hevesy, *Z. anorg. allgem. Chem.,* **147**, 217 **(1925).**

The relation of the ionic potential to certain properties of compounds will be shown in subsequent papers, in which it will appear that the numerical values of the potentials may be used to indicate the order of variation of numerous effects.

Summary

1. A periodic classification of ions has been developed, with provision for all valence forms of all the elements. It is shown that no single atomic characteristic is an adequate basis for a periodic classification, and the new arrangement takes account of the charge, structure and radius of the ions. For this purpose a new function, the ionic potential, is introduced and used as a quantitative basis for the classification.

2. It is shown that the ionic potential is related to many of the characteristics of ions and their compounds, and that the new arrangement satisfactorily represents the behavior of hydrogen, the eighth group elements and the rare earths.

3. It is also shown that the properties of the ions are definitely related to the structure of their outermost electronic shells, with respect to the completeness or incompleteness of these shells. On this basis a new definition of the periodic families is given.

BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

STUDIES ON THE PERIODIC SYSTEM. II. THE IONIC POTENTIAL AND RELATED PROPERTIES[1]

BY G. H. CARTLEDGE

RECEIVED APRIL 7, 1928 PUBLISHED NOVEMBER 6, 1928

In the preceding paper[2] it has been shown that the ratio of charge to radius is an important periodic property of the ions and may be made the basis of a quantitative classification. This function has been called the ionic potential. In the present paper the relation between the ionic potential and several related properties of substances will be developed, and it will be shown that the periodic classification presented in the preceding paper is able to indicate the order of variation of many properties which may not readily be related to the older forms of representation.

Ionic Hydration and Associated Effects

When a polar crystal is placed in water the lattice becomes disrupted under the influence of the attraction between the ions and the polarized water molecules. Following Fajans,[3] the measured heat of solution, Q,,

[1] In memory of Ira Remsen.

[2] Cartledge, THIS JOURNAL, **50, 2855** (1928).

[3] Fajans, *Ber. physik. Ges.*, ***20,*** 712 (1918); *ibid.*, 21, 549, 714 (1919).

plus the lattice energy, U, is equal to the sum of the heats of hydration of the ions. According to Born[4] the molal heat of hydration of an ion (W_h) is equal to the decrease in its electrostatic energy when the gaseous ion is placed in water; that is

$$W_h = \frac{\overline{N}Z^2e^2}{2r}\left(1 - \frac{1}{D}\right) \tag{1}$$

in which $\overline{N}$ is Avogadro's number, e the electronic charge, Z the ionic valence, r the radius of the ion and D the dielectric constant of water.

The situation is more complicated than this relation assumes in equating the decrease in electrostatic energy to the heat of hydration, since a portion of this energy goes into an increased intramolecular energy of the water molecules as a consequence of their distortion. In the case of cations an additional heat *evolution* is also undoubtedly caused by the effect of the outer electronic region of the ion in attracting the hydrogen ends of the water molecules. If the Born relationship were correct, the heat of hydration per *equivalent* should be linearly proportional to the ionic potential, ϕ, since from (1)

$$\phi = \frac{Z}{r} \propto \frac{W_h}{Z} \tag{2}$$

For the ions of the alkalies the linear relation is found to hold, although the equation is of the form

$$\frac{W_h}{Z} = a\phi + b \tag{3}$$

and the constant a does not correspond to that given by Born's equation when the crystal radii of Pauling are used for the calculation.[5] The ionic potential may be used in general, therefore, only to indicate the order of *variation* of the heats of hydration. For the alkali ions the equation $W_h = 60\phi + 30$ (kg. cal. per equivalent) represents the values of Fajans quite closely.

Since the heat of hydration of the ions of a salt is equal to the lattice energy plus the heat of solution and since, for salts with a common anion, the electrostatic energy of the cation varies inversely as the cation radius r_c, while the lattice energy varies inversely as the interionic distance $r_c + r_a$, the electrostatic energy increases more rapidly than the lattice energy as the radius is decreased. As a consequence, in a series of salts such as the alkali or alkaline earth chlorides, the heat of solution (evolution) of the anhydrous salt in sufficiently dilute solution should vary in the same order as the varying ionic potential. Table I includes data from the Landolt-Bornstein "Tabellen" which show that this conclusion is in accordance with the facts. The only exceptions to the rule are in cases in which the ions are very unlike in size, mutual repulsion of the larger ions

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[4] Born, *Ber. physik.* Ges., 21, 679 (1919).

[5] Pauling, THIS JOURNAL, 49, 765 (1927).

then becoming a complication. With lithium fluoride the lattice energy is large and decreases very rapidly as either ion is changed in the alkali or halogen series. The decrease in the lattice energy more than compensates the decrease in the heat of hydration of the varying ions, and an increase in the heat of solution is observed (LiF to LiI or LiF to CsF). In the alkaline earth group this effect is more marked as the anion is varied. The solid arrows in Table I show the order of increasing potential and heat of solution in accordance with the rule. The broken arrows indicate increasing heat evolution with decreasing potential. The data give the heat evolution (lower figure) attending the addition of I mole of the anhydrous salt to the number of moles of water given by the upper figure."

TABLE I

HEAT OF SOLUTION (KG. CAL. PEK MOLE)

	Li	Na	K	Rb	Cs	Be	Mg	Ca	Sr	Ba
	—	400	—	—	—			—	—	—
F	⇢	⇢	⇢	⇢	⇢			⇠	⇢	⇢
	−1.04	−0.6	+3.6	5.8	8 37			2.70	−2.10	−1.90
	⇣	↑	↖ ↑	↑	↑			⇣	⇣	⇣
	230	100	200	100	—	--	800	300	400	400
Cl	←	←	←	←	←	←	←	←	←	←
	8.37	−1.2	−4.4	−4.4	−4.75	44.5	35.92	17.41	11.14	2.07
	⇣	⇣	↑	↖ ↑	↑		⇣	⇣	⇣	⇣
	—	200	200	—	—		—	400	400	400
Br	←	←	←	←	←		←	←	←	←
	11.25	−0.19	−5.08	−5.96	−6.73		**43.3**	24.51	16.11	4.98
	⇣	⇣	↑	↑	↖ ↑		⇣	⇣	⇣	⇣
	—	200	200	—	—		—	—	—	—
I	←	←	←	←	←		←	←	←	←
	14.76	1.22	−5.11	−6.5	−8.25		49.8	28.12	20.12	10.3

	Ca^{++}	Cr^{++}	Mn^{++}	Fe^{++}	Co^{++}	Ni^{++}	Cu^{++}	Zn^{++}
	300	—	350	350	400	400	600	300
Cl	→	→ ←	← →	→	→	→	—	—
	17.41	18.6	16.01	17.85	18.34	19.17	11.08	15.63

The development of acidic properties is obviously closely associated with an increase in the ionic potential. If the potential is sufficiently high, not only is the hydration greatly increased but the increase in the intramolecular energy of the bound water molecules may exceed the heat of ionization of water into hydrogen and hydroxyl ions. In such a case the change may be expressed,

$$M^{m+} + nH_2O \longrightarrow M(H_2O)_n^{m+} \longrightarrow M(H_2O)_{n-1}\,(OH)^{(m-1)+} + H^+$$

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[6] The effect of the *relative* size of the ions in a crystal in producing "abnormal" variations in properties in a series of compounds has been quantitatively treated for certain cases since the completion of the present paper. See Pauling, THIS **JOURNAL**. SO, 1036 (1928).

This corresponds to the hydrolysis of chlorides of non-metals, such as PCl_5, or to the acid character of hydrated ions, such as the cation of hexa-aquo-chromic chloride, $Cr(H_2O)_6^{3+}$, the ionization of which according to the scheme

$$Cr(H_2O)_6^{3+} \rightleftarrows Cr(H_2O)_5OH^{++} + H^+$$

has been recently studied by Bronsted and King.[7]

As a matter of fact, according to Fig. 1 of the preceding paper, *the exclusively basic ions have values of $\sqrt{\phi}$ falling below 2.2; between 2.2 and 3.2 the ions are amphoteric, and above 3.2 all ions are acidic in character.*[8] The similarity of Be^{++}, Al^{3+} and Ti^{4+} from this point of view is strikingly suggested, corresponding to the well-known diagonal relationship of the Mendelejeff system. The relative positions of B^{3+}, Si^{4+} and P^{5+} are also apt.[9]

Another aspect of the view of hydration effects here presented is in connection with the existence of oxy-ions, such as UO_2^{++}. Compounds derived from ions of this type are stable in acid solution only if the potential of the simple cation U^{6+}, for example, exceeds the minimum value requisite for the ionization of a bound water molecule. If the potential is sufficiently high, complete hydrolysis to an acid occurs. The occurrence of ions which form such stable oxy-salts is, therefore, limited to the amphoteric region of potentials.

Ionic Potentials and Electrochemical Behavior

While the ionic potentials are obviously most closely related to the ionizing potentials of the atoms in the gaseous state, there is a qualitative connection also with the electrode potentials in electrolysis. In the alkali element family lithium has the highest ionization potential, corresponding to the order of increase in the ionic potentials. In aqueous solutions, however, lithium has also the highest electrode potential, which may be due to the existence of a smaller concentration of unhydrated ions, since the

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[7] Bronsted and King, *Z. physik. Chem.*, *130,* 699 (1927).

[8] An apparent exception is zinc, which is in the basic region of potentials. As a matter of fact, zinc is not certainly amphoteric [Hantzsch, *Z. anorg.* Chem., *30,* 289 (1902); Britton, J. *Chem. Soc.*, *127,* 2120 (1925)], and seems to be more basic than magnesium in the extent of hydrolysis of its chloride in solution and in the readiness with which the chloride may be dehydrated by heating. Zinc and mercuric salts are, however, anomalous in other respects also (see p. 2869).

[9] The theoretical potentials of the ions of series II (B^{3+} – N^{5+}) are somewhat higher than corresponds to their observed acidic character. This is no doubt due to the fact that these ions are very small and in their hydroxyl compounds the oxygen ions are very close together. Mutual repulsion of these hydroxide ions would be equivalent to a decrease in the potential of the positive central ion and a weakening of the acidic character would result. To this cause may be ascribed the low coördination number of these ions (4) and the corresponding instability of higher hydrates (H_3NO_4 $C(OH)_4$, $R_2C(OH)_2$ compounds, etc.).

extent of the ionic hydration is, in general, greater the stronger the field of force about the ion. In comparing elements of the alkali and alkaline earth families, the ionic potential increases with the valence, corresponding to a decrease in the electrode potentials. The increase in the heat of hydration is not sufficient in these cases to counteract the increase in the ionization potential.

Even more striking results are obtained by considering the discharge potentials of the cations from fused electrolytes. Data for a number of ions are given by Neumann and Richter.[10] The discharge potential should be greater the lower the ionic potential. That this is true is strikingly shown in Fig. 1, in which univalent, bivalent and tervalent ions are included. It is obvious that lithium has a normal discharge potential in fused salts.

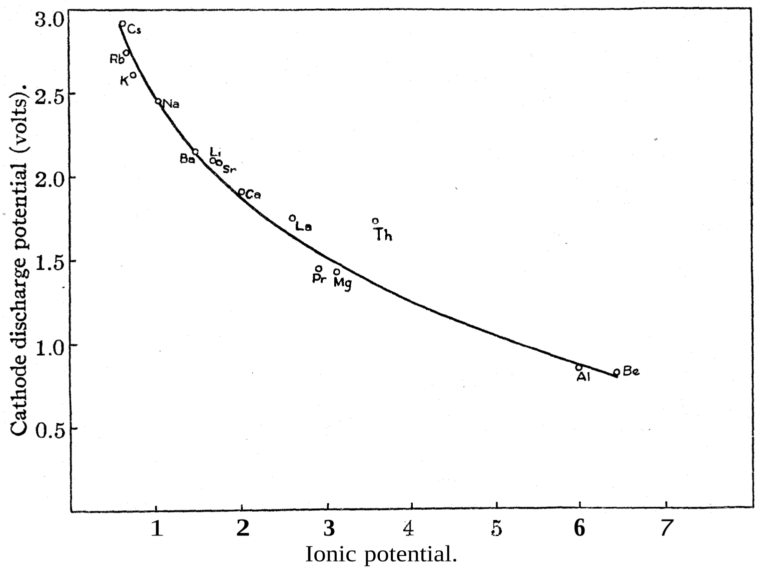

Fig. 1.—Ionic potentials and cathode potentials in the fused chlorides.

The roughly estimated ionic potential of the H^+ ion is in satisfactory agreement with the electrode potential of hydrogen. Considering only cations with inert gas structures, it will be seen from Pig. 1 of the preceding paper that all ions having lower ionic potentials than H^+ may be formed by displacement of hydrogen from acids or superheated steam. This is not the case with those having potentials greater than that of Hf, and in the ease of equipotes of H+, solution of the metal generally takes place sluggishly and oftentimes only with hydrofluoric acid, which forms a complex fluo-ion giving very low concentrations of the simple cation, as in the case of vanadium, columbium and tantalum.

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[10] Neumann and Richter, *Z. Elektrochem.*, 31, 287,296 (1925).

Biltz and Klemm[11] have shown that there is a sharp decrease in the electrical conductance of the fused chlorides in passing from left to right in the several periodic series, and have pointed out that where the conductance becomes very low there is also an abrupt decrease in the melting point. This break in properties has been ascribed to a progressive deformation of the anion with increasing charge or decreasing radius of the cation,[12] as revealed by the decrease in the molal refraction of the anions in such a series as CaO–MgO–BeO. The deformation is regarded as finally reaching such a value that there is a transition from a polar, ionic lattice to a non-polar, molecular lattice.[13]

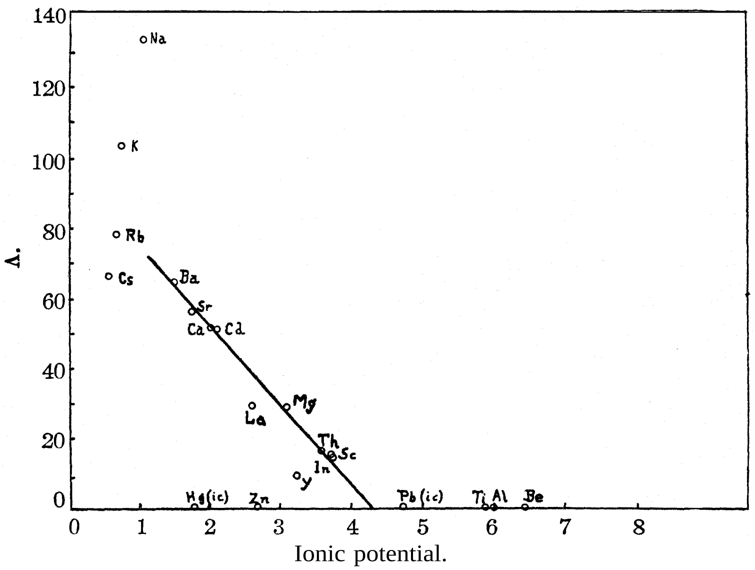

Fig. 2.—Ionic potential in relation to the equivalent conductance of fused chlorides at the melting point.

The deformation of the anion is closely related to the ionic potential of the cation, and it is found that *the zigzag line of Biltz and Klemm dividing the high melting, conducting chlorides from the volatile, non-conducting chlorides corresponds to an equipotential line* drawn at $\sqrt{\phi} = 2.2$. At lower ionic potentials the melting point of the chloride is high (generally $> 600°$); the equivalent conductance of the fused chloride increases rapidly as the cation potential becomes less than 4.2, according to the relation $\Lambda = 98 - 23\phi$ in the case of the chlorides of Mg^{++}, Ca^{++}, Sr^{++}, Ba^{++}, Cd^{++}, Th^{4+}, Sc^{3+} and In^{3+}; La^{3+} and Y^{3+} have a distinctly lower conductance

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[11] Biltz and Klemm, *Z. physik. Chem.*, 110, *318* (1924); *Z. anorg. allgem. Chem.*, **152**, 225, 267 (1926); Klemm, *ibid.*, **152**, 235, 252, 295 (1926).

[12] Fajans and Joos, *Z. Physik*, **23**, *1* (1924).

[13] Fajans, *Naturwissenschaften*, **11**, 165 (1923).

than this relation would indicate and the conductances of the alkali chlorides increase in the reverse order (Fig. 2). As suggested by Biltz, in the case of the alkali chlorides the variation is no doubt to be ascribed to the variation in ionic mobility rather than to any incompleteness of ionization as a result of the electrostatic effects, whereas in the other cases the ionic field of force is the important factor. The low conductance and melting point of mercuric and zinc chlorides are striking exceptions to the general rule.

Considering only the quadrivalent ions, the melting points of the chlorides of both A and B families increase in the same order as the ionic potential decreases, excepting carbon and zirconium

Element	Si^{4+}	Ge^{4+}	Ti^{4+}	Sn^{4+}	Zr^{4+}	Pb^{4+}	Th^{4+}
M. p., °C.	−70	−49.5	−30	−30.2	..	−15	820
$\sqrt{\phi}$	3.13	2.74	2.43	2.30	2.24	2.18	1.90

The volatility and non-conductance of liquid hydrogen chloride are in accordance with the estimated potential of H^+, and the sharp contrast between the high melting, conducting thorium chloride and the chlorides of other quadrivalent ions is particularly striking.

Cation Potentials and the Deformation of Anions

The varying deformation of anions such as CO_3^{--} and NO_3^- is associated with numerous properties of compounds containing such ions. In a crystalline carbonate the C–O valences are presumably non-polar, the carbonate ion as a whole acting as one of the crystal units in a polar lattice. The firmness of the binding *within* the carbonate ion is less the stronger the electrostatic action of the cation. This effect has been called *a contrapolarization* by Goldschmidt;[14] for a series of salts with a common anion the effect obviously increases with increasing cation potential.

In respect to crystallo-chemical relationships, Goldschmidt has shown that an increase in temperature quite generally acts in the same direction as the substitution of a smaller cation of the same valence, that is, in the same direction as an increase in the cation potential. Thus, in the rare earth oxides the cubic modification is the high temperature form of the cerite earths, while in the yttrium earths (higher potential) it is the low temperature form.

In similar manner, the deformation of the anion may increase to the point of complete dissociation of the compound. It is found, for example, that the ionic potentials indicate the order of increasing dissociability of the carbonates and nitrates. Cations with $\sqrt{\phi} > 2$ do not form stable normal carbonates or nitrates; in cases in which $2 < \sqrt{\phi} < 2.5$, basic carbonates may be precipitated in solution which we generally soluble

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[14] **Goldschmidt,** *Skrifter Norske Videnskaps-akad., Oslo., I, Matemat.-Natur.-Klasse, 1926, No.* **2.**

in excess of ammonium or alkali carbonate. The greater stability of nitrates as compared with carbonates at not too high temperatures may be associated with the higher potential of N^{5+} as compared with C^{4+}, the result being a greater deformability of the carbonate ion.[15] The instability of bicarbonates in the solid state may in like manner be related to the high value of $\sqrt{\phi_{H^+}}$, only the low potential alkali ions forming stable bicarbonates.

Other properties which have been associated with the deformation of ions may in like manner be related to ionic potentials, such as color[15] and the photoelectric conductance of salts.[16]

Ionic Potentials and the Hardness of Compounds

Goldschmidt[14] has pointed out that the hardness of inorganic compounds of similar composition increases as the inter-ionic distance decreases. In Table II Goldschmidt's data on the hardness of previously fused or sintered compounds are given on Moh's scale, together with the corresponding ionic potential.

TABLE II

HARDNESS AND IONIC POTENTIALS

	$\sqrt{\phi}$	2.54	1.76	1.64	1.44	1.42	1.35	1.33	121
$\sqrt{\phi}$	Ion	Be^{++}	Mg^{++}	Zn^{++}	Cd^{++}	Ca^{++}	Hg^{++}	Sr^{++}	Ba^{++}
1.19	O^{--}	9	6.5	5	...	4.5	...	3.5	3.3
1.04	S^{--}	7.5	4.5–5	4	3.2	4.0	3	ca. 3.3	ca. 3
1.00	Se^{--}	5.5	3.5	3 4	3.0	3.2	2.8	ca. 2.9	ca. 2.7
0.95	Te^{--}	3.8	..	3.0	2.8	2.9	2.6	ca. 2.8	ca. 2.6

	NaF	MgO	ScN	TiC
Hardness	3.2	6.5	7–8	8–9
$\sqrt{\phi}$ (cation)	1.02	1.76	1.92	2.43
$\sqrt{\phi}$ (anion)	0.86	1.19	1.32	1.24

It is clear that in a general way there is a parallel increase in hardness and potential.

In a recent paper[17] Noyes and Beckman have presented the results of a study of the ionization potentials for the different valence states of the elements as far as atomic number 26; these authors reach the conclusion that there is no definite relation between the ionization potential for the formation of a particular ion and the tendency of the element to assume that ionic form. While the work described in the present paper was in progress the ionization potential was considered as a possible basis of classification, but was rejected both because of the limitations in the data that are available and because it was realized that the ionic potential as

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[15] Fajans and Scott, *Naturwissenschaften*, 11, 165 (1923), give the anion refraction per oxygen octet as 3.66 for NO_3^- and 4.08 for $^1/_2$ CO_3^{--}.

[16] Gudden and Pohl, *Z. Physik*, 16, 42 (1923).

[17] Noyes and Beckman, *Proc. Nat. Acad. Sci.*, 13, 737 (1927).

here defined is a closer index to the behavior of an ion in compounds than is the ionization potential.

The thermochemistry of chemical combination is, in general, too complex to be simply related to the periodic system.[18] In analyzing the heat of formation of polar compounds having a common anion, the ionization potential of the cation and the lattice energy of the compound have opposite signs. They vary in magnitude in the same direction when the cation radius is varied, both quantities increasing as the ionic potential increases. In general, however, the ionization potential increases more rapidly than the ionic potential, while the lattice energy increases less rapidly, being inversely proportional to $r_c + r_a$. In so far as the heat of formation of a compound is determined chiefly by the difference between these two quantities, it will be expected that in a series of compounds with one ion in common the heat of formation (per *equivalent*) will decrease with increasing potential of the varying constituent. This is true in many instances, as seen in the following data for the oxides (kg. cal. per equivalent)

$^1/_2$ MgO	$^1/_6$ Al_2O_3	$^1/_4$ SiO_2	$^1/_{10}$ P_2O_5	$^1/_6$ SO_3
72	63.4	48.7	37.0	17.2

This relationship is not uniform throughout the periodic system, however, but it will be shown in a subsequent paper that the ionic potential may be used to indicate the order of variation in thermochemical effects in the entire periodic classification.

It is proposed in subsequent publications to develop still other relationships between ionic potentials and the properties of matter.

Summary

The following generalizations may be given as a summary of the results of this paper.

1. The heat of hydration of gaseous ions increases with the ionic potential.

2. The heat of solution (evolution) of salts having a common anion increases with the ionic potential of the cation, except in the case of fluorides, with which the order is reversed.

3. Cations having $\sqrt{\phi} < 2.2$ are basic, those between 2.2 and 3.2 are amphoteric and those above 3.2 are acidic in aqueous media.

4. The discharge potentials of cations in fused electrolytes decrease regularly with increasing ionic potentials.

5. Cations having $\sqrt{\phi} > 2.2$ form volatile chlorides which are nonconductors in the liquid state. The conductance increases rapidly as $\sqrt{\phi}$ falls below 2.2, except in the case of the alkali ions, which vary in the reverse order.

6. High temperature and increase in the ionic potential of the cation

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[18] Compare Grimm, "Handbuch der Physik," Springer, Berlin, Vol. 24, pp. 568 ff.

have similar effects in the polymorphic and stability relations of compounds with a common anion.

7. Binary crystals increase in hardness as the ionic potentials of their constituents increase.

BALTIMORE, MARYLAND

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

THE CATALYTIC ACTIVITY OF METALLIZED SILICA GELS. V. THE OXIDATION OF ETHYLENE[1]

BY L. H. REYERSON AND L. E. SWEARINGEN

RECEIVED MAY 31, 1928 PUBLISHED NOVEMBER 6, 1928

Previous investigations of the authors[2] have shown that metallized silica gels exhibit considerable activity in certain oxidation reactions. The following investigation is an extension of this work to the oxidation of ethylene. Willstatter and Bommer[3] in their quantitative study of the conditions for the formation of formaldehyde from ethylene showed that, unless dilute, both ethylene and formaldehyde are unstable at temperatures much above 300°. They found that the use of catalysts accelerated the oxidation of ethylene but no formaldehyde was detected when catalysts were used. An osmium catalyst was found to initiate the oxidation of ethylene at about 130°, while copper proved to be effective at 250°. Blair and Wheeler[4] continued these investigations and found that, with a platinum catalyst, formaldehyde was formed at 405° when the gases were streamed through the catalyst very rapidly. As a result of these investigations, it was hoped that the use of metallized silica gels as catalysts would so lower the temperature at which reaction occurred that partial oxidation of ethylene could be effected and a mechanism for its catalytic oxidation obtained.

The experimental procedure was similar to that used by the authors in the study of the oxidation of methane.[5] Samples of the same catalysts were used as in the preceding investigations. Mixtures of ethylene, oxygen and nitrogen were passed over the catalysts at temperatures ranging from about 100 to 310° at varying rates of flow. In no case did the sum of oxygen and ethylene in the mixture exceed 50% of the gas volume. Preliminary experiments showed that the products of oxidation were carbon dioxide and water, so that the gases after passing through the catalyst were analyzed for ethylene, oxygen and carbon dioxide. In no case did tests show the presence of intermediate products of oxidation.

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[1] In memory of Ira Remsen.

[2] Swearingen and Reyerson, *J. Phys. Chem.*, **32**, 113, 192 (1928).

[3] Willstätter and Bommer, *Ann.*, 422, 36 (1921).

[4] Blair and Wheeler, *J. Soc. Chem. Ind.*, **41**, 303T (1922).

[5] Ref. 2, p. 192.

Experimental Results

The results of the experiments are given in Tables I to IV and Figs. 1 and 2 graphically represent typical experiments. The symbols used in the tables have the following significance.

A = the percentage of ethylene in the original mixture
A' = the percentage of ethylene found in the exit gas
A'' = the percentage of ethylene calculated to be present
O_2 = the amount of oxygen present in the original mixture
O_2' = the amount of oxygen found in the exit gas
O_2'' = the amount of oxygen calculated to be present
f = the fraction of carbon dioxide in the final mixture
F = the percentage of carbon dioxide in the final mixtures ($F = 100f$)
x = the fraction of the ethylene oxidized
X = the percentage of ethylene oxidized ($X = 100x$)
B = temperature of bath surrounding catalyst tube
C = temperature of catalyst during reaction

TABLE I

SILVER CATALYST

Gas mixture: (A) Ethylene, 27.00%; (O_2) Oxygen, 18.00%

Temperature B C	Rate, cc. per min.	Final gas analysis A'	O_2'	F	Calcd. X	A''	O_2''
310–313	30	25.90	12.89	3.79	6.63	26.13	12.99
310–311	50	25.85	14.82	2.87	5.17	26.34	14.21
310–312	60	26.25	15.05	2.51	4.55	26.42	14.68
310–313	180	26.10	17.86	1.32	2.41	26.70	16.32
200–201	30	26.50	18.20	0.66	1.22	26.85	17.13
200–201	60	26.42	18.28	.66	1.22	26.85	17.13
200–200	180	26.85	18.62	.44	0.87	26.80	17.42
Gas mixture:		(A) Ethylene, 19.00%; (O_2) Oxygen, 26.50%					
300-302	30	17.30	19.25	4.24	10.72	17.69	20.76
300-301	60	18.20	21.06	3.56	9.01	17.90	22.12
300–301	100	18.41	23.51	2.33	6.00	18.28	23.62
300–302	140	18.73	24.30	1.94	5.00	18.40	24.10
300–304	180	18.96	22.48	1.52	3.94	18.53	24.64

TABLE II

COPPER CATALYST

Gas mixture: (A) Ethylene, 30.00%; (O_2) Oxygen, 18.00%

Temperature B C	Rate, cc. per min.	Final gas analysis A'	O_2'	F	Calcd. X	A''	O_2''
310–310	30	29.80	1.87	11.02	16.65	27.80	3.48
310-312	60	28.80	6.16	8.80	13.50	28.24	6.40
310-324	100	29.50	8.80	6.64	10.37	28.68	9.25
310-327	180	29.45	12.55	4.26	6.84	29.15	12.37
Gas mixture:		(A) Ethylene, 24.00%; (O_2) Oxygen, 19.20%					
200-200	30	23.50	16.38	2.09	4.26	23.46	16.47
200-200	95	24.20	18.04	0.98	2.03	23.75	17.92
200-200	180	24.61	17.08	0.76	1.57	23.80	18.21

TABLE II (*Concluded*)

Gas mixture: **(A) Ethylene,** 19.50%; **(O_2) Oxygen,** 27.50%

Temperature B C	Rate, cc. per min.	Final gas analysis			Calcd.		
		A'	O_2'	F	*X*	*A''*	O_2''
300-306	30	14.45	5.58	17.76	38.70	14.09	5.75
300-317	60	15.72	6.50	14.42	32.30	15.10	9.82
300–330	140	16.88	13.68	10.62	24.65	16.26	14.48
300-320	180	17.25	16.40	8.84	20.85	16.80	16.65
200-200	30	19.00	24.65	2.13	5.36	18.85	24.89
200-200	60	19.23	25.02	1.85	4.64	18.94	25.55
200–205	180	19.43	26.10	0.96	2.45	19.20	26.32
300	30	27.80	3.87	11.02	16.65	27.80	3.48
260	30	29.55	12.25	4.52	7.19	29.10	12.08
200	30	23.50	16.38	2.09	4.26	23.46	16.47
150	30	29.20	20.18	1.18	2.00	28.75	19.78
106	30	23.75	18.73	0.54	1.14	23.86	18.49

TABLE III

PLATINUM CATALYST

Gas mixture: **(A) ethylene,** 20.00%; **(O_2) Oxygen,** 18.00%

Temperature B C	Rate, cc. per min.	Final gas analysis			Calcd.		
		A'	O_2'	*F*	*X*	*A''*	O_2''
210–227	60	17.08	7.93	7.62	17.65	17.72	7.97
203–212	60	17.78	9.00	7.02	16.38	17.90	8.76
198–212	60	18.00	10.37	6.13	14.45	18.16	9.90
170-175	60	18.60	13.14	3.94	9.45	18.82	12.80
160–165	60	18.85	14.72	2.60	6.33	19.22	14.56
130–125	60	19.50	16.78	1.31	3.23	19.61	16.27
115–115	60	19.95	17.30	0.64	1.59	19.81	17.15
90– 90	60	19.85	18.07	0.22	0.55	19.95	17.71
Gas mixture:		**(A) Ethylene,** 29.00%; **(O_2) Oxygen,** 21.30%					
200-215	30	26.45	4.40	12.53	19.22	26.48	5.18
200–215	60	27.30	8.80	10.10	15.90	27.88	8.30
200–220	100	27.06	10.63	7.98	13.00	27.32	11.02
200–225	140	27.50	13.09	6.15	10.08	27.71	13.38
200–235	180	27.99	14.10	5.50	8.97	27.85	14.22
130–130	30	28.43	18.59	2.18	3.67	28.44	18.49
130–130	60	28.68	20.42	0.76	1.30	28.84	20.32
130–130	180	28.70	20.65	0.54	0.93	28.89	20.30
Gas mixture:		**(A) Ethylene,** 21.50%; **(O_2) Oxygen,** 26.50%					
300-300	30	15.50	1.18	21.00	40.40	15.50	0.55
300–308	60	16.00	2.24	20.08	38.00	15.80	1.75
300329	120	16.40	5.18	17.06	33.95	11.64	5.45
300–335	180	17.78	7.35	15.35	31.00	17.31	7.55
200–200	30	15.53	4.23	18.35	36.10	16.26	3.80
200–217	60	16.50	5.03	18.06	35.60	16.36	4.25
200–223	180	17.75	11.41	12.80	26.40	17.85	10.68
110–110	30	21.00	25.80	0.76	1.75	21.29	25.56
95– 95	30	21.78	25.90	0.66	1.64	21.31	25.68
90- 90	39	21.00	25.95	0.55	1.36	21.34	25.82

TABLE III *(Concluded)*

Gas mixture: (A) **Ethylene,** 21.30%; (O_2) **Oxygen,** 16.85%

Temperature *B* C	Rate, cc. per min.	Final gas analysis *A'*	O_2'	*F*	Calcd. *X*	*A''*	O_2''
300–304	60	17.68	1.34	12.13	26.45	17.93	0.75
300–306	60	17.96	1.54	12.00	25.15	17.84	0.87
250–255	60	18.63	6.02	8.33	18.00	18.91	5.75
200–203	60	19.95	10.85	5.76	12.77	19.65	9.19
150–150	60	20.39	12.36	3.57	8.10	20.28	12.08
100–100	60	20.56	14.29	1.75	4.02	20.80	14.52
Gas mixture: (A) **Ethylene,** 22.65%; (O_2) **Oxygen,** 17.50%							
310–315	60	19.20	2.07	11.65	23.08	19.46	2.07
280–285	60	19.00	4.83	10.00	20.10	19.92	4.25
260–262	60	20.25	7.67	7.80	16.00	20.51	7.17
220–222	60	20.85	11.13	5.18	10.85	21.83	10.64
134–135	60	22.50	15.70	1.53	3.33	22.23	15.47
120–120	60	22.50	16.64	1.08	2.36	22.35	16.07
95– 95	60	22.62	16.73	0.86	1 8 8	22.41	16.36

TABLE IV

PALLADIUM CATALYST

Gas mixture: (A) **Ethylene,** 24.00%; (O_2) **Oxygen,** 20.50%

Temperature A *C*	Rate, cc. per min.	Final gas analysis *A'*	O_2'	*F*	Calcd. X	A''	O_2''
300–304	30	20.52	2.15	14.42	26.28	20.25	1.80
300–309	60	21 63	5.17	12.12	22.54	20.85	4.81
300–312	100	21.56	7.00	10.60	20.00	21.24	6.75
300–315	140	21.95	9.08	9.11	17.40	21.63	8.70
300–330	180	22.21	10.12	8.25	15.88	21.85	9.82
200-205	30	22.58	13.75	6.49	12.73	22.31	12.09
200–205	60	23.55	14.65	4.74	9 4 5	22.86	13.36
200–210	100	23.60	16.40	2.86	5.80	23.26	16.80
200–210	180	24.20	19.30	0.58	1.20	23.85	19.75
250–254	30	21.80	5.80	11.02	20.70	21.13	6.20
250–255	60	21.88	9.10	9.05	17.28	21.63	8.78
250–255	100	22.06	8.96	7.98	15.40	21.92	9.15
250–259	140	22.05	10.98	7.21	14.00	22.13	11.15
250–262	180	22.40	12.06	6.71	13.10	22.25	11.80
Gas mixture: (A) **Ethylene,** 21.00%; (O_2) **Oxygen,** 25.00%							
300–304	30	16.28	0.96	19.70	39.18	15.29	0.40
300–309	60	16.38	2.73	17.60	35.70	15.90	3.00
300–310	100	16.58	5.15	16.05	33.00	16.35	4.98
300–313	140	17.08	7.20	14.42	30.00	16.80	6.90
300–319	180	16.50	8.17	13.18	27.90	17.08	8.50
200–204	30	16.08	3.29	18.15	36.70	15.74	2.30
200–205	60	15.85	4.81	16.55	33.85	16.20	4.32
200–208	100	17.15	7.15	14.42	30.00	16.80	6.90
200–214	140	17.85	14.77	12.72	26.90	17.32	14.10
200-215	180	17.84	11.94	11.42	24.60	16.28	11.75
110–110	30	21.00	24.70	0.83	2.00	20.85	24.34
110–110	30	20.53	23.30	0.98	2.30	20.72	23.77

In the tables under the headings A', O_2' and F are given the results of the quantitative analysis of the gases after reaction. The column headed X gives the percentage of ethylene oxidized provided the reaction proceeds according to the following reaction: $C_2H_4 + 3O_2 \longrightarrow 2CO_2 + 2H_2O$. The fraction of ethylene oxidized is given by $x = 100\,f/(2A + 2Af)$, so that $100\,x = X$. From the amount of carbon dioxide formed it is also possible to calculate the amount of ethylene and oxygen which should be present with this carbon dioxide provided the oxidation of ethylene is complete. The calculated percentage of ethylene in the products of reaction is given by $A'' = A + f(A - 50)$, while for oxygen we have $O_2'' = O_2 + f(O_2 - 150)$. The values calculated for ethylene and oxygen check the experimental values very well and probably within the limits of the experimental error in the gas analysis.

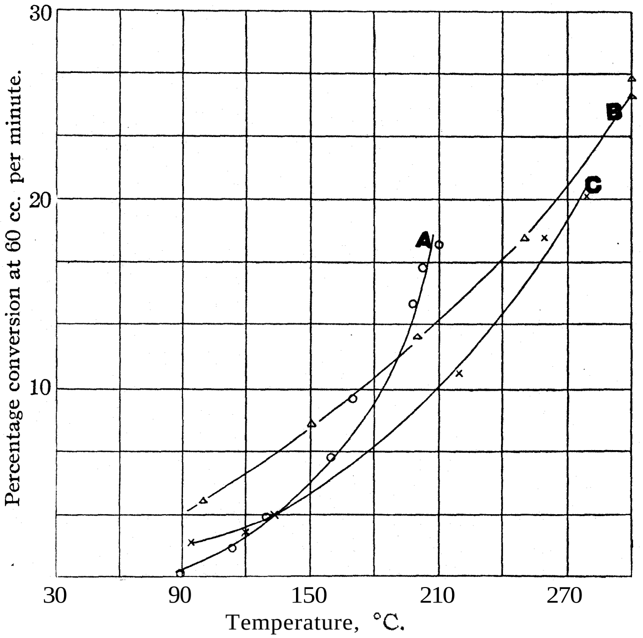

Fig. 1.—Composition of gas mixture: A = C_2H_4, 20%; O_2, 18%. B = C_2H_4, 21.3%; O_2, 16.85%. C = C_2H_4, 22.65%; O_2, 17.5%.

Discussion and Results

It is evident from these results that the catalysts used were effective in promoting the oxidation of ethylene at lower temperatures than previously reported. The copper, platinum and palladium catalysts began to be effective at about 100°. Fig. 1 shows the effect of temperature on the oxidation of ethylene for three different gas mixtures with platinized silica gel as the catalyst. The effect of increased rate of streaming on the conversion is shown graphically in Fig. 2. The silver catalyst is shown to be less effective than the other catalysts. The catalysts all speeded up the successive oxidation reactions so that no intermediate products were detected. This confirms the previous work on the oxidation of ethylene.

The experimental results here given indicate that the reaction is directly proportional to the oxygen concentration and inversely proportional to the ethylene concentration. For example, when the ratio of ethylene to oxygen is changed from 1.36 to 0.81, the amount of ethylene oxidized by the platinum catalyst at 200° increases from 19.22 to 36.10%. Thus the amount oxidized is nearly doubled. Similar results were obtained with the other catalysts. The simplest explanation for these results would seem to be that collisions of ethylene molecules with oxygen molecules which are adsorbed and activated by the effective catalyst centers resulted in reaction, whereas collisions of oxygen molecules with adsorbed ethylene molecules were ineffective. The adsorption studies of the authors[6] indicate specific adsorption of both ethylene and oxygen by these catalysts. Therefore, when the ethylene molecules are adsorbed by the active catalyst centers, then these centers, are no longer effective. The double bond of ethylene is no doubt directed toward the catalyst. When,

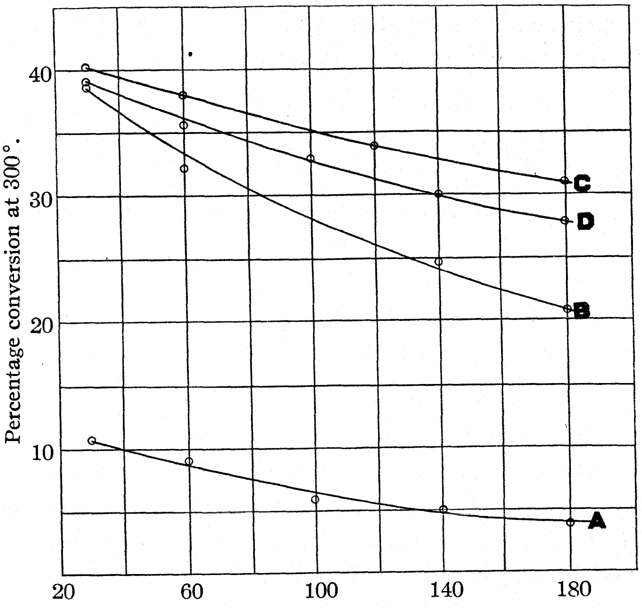

Fig. 2.—Catalysts: A, Silver; B, Copper; C, Platinum; D, Palladium.

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[6] Reyerson and Swearingen, J. *Phys.* Chem., **31, 88** (1927).

however, an oxygen molecule reaches an active center and is adsorbed, it is activated so that it is able to react with the ethylene which reaches it. Mere adsorption is not sufficient, otherwise the silica gel itself would be an active catalyst. Because of their higher energy content the primary products of oxidation are likely to be very reactive whether they are dihydroxyethylene or formaldehyde. Furthermore, as indicated in the tables, the temperature of the catalysts is often higher than that of the bath in which they are immersed. This indicates that the temperature at which the reaction takes place may be very much higher than that indicated, so that successive collisions with oxygen molecules result in complete oxidation. Otherwise intermediate products of oxidation should be detected when the rate of streaming through the catalyst was increased.

Conclusion

1. Metallized silica gels actively promote the oxidation of ethylene, beginning to be effective at about 100".

2. The catalysts are so active that no intermediate products of oxidation are detected.

MINNEAPOLIS, MINNESOTA

[CONTRIBUTION FROM THE GAYLEY CHEMICAL LABORATORY, LAFAYETTE COLLEGE]

THE FLUIDITY OF MERCURY[1,2]

BY EUGENE C. BINGHAM AND THEODORE R. THOMPSON

RECEIVED JUNE 25, 1928 PUBLISHED NOVEMBER 6, 1928

Tammann and Hinnüber[3] have raised the question whether the viscosity of a liquid is trustworthy when it is measured in a tube that is not thoroughly wetted by the liquid. They claim to have found the viscosity of mercury in an amalgamated copper capillary to be 4.931 ± 78 *cp* at 13.5" instead of 1.609 *cp* for mercury in glass. Whether one accepts their explanation of the phenomenon based on "slippage," or not, the discrepancy of over 200% is quite beyond experimental error and demands investigation.

1. The hypothesis of slippage is, of course, not new. It has often been offered to account for results which at the time seemed inexplicable, but on further investigation it has always been found that some factor has been overlooked which has made this explanation unnecessary. On the other hand, the fair agreement among the results of different investigators using widely different forms of viscometers and shearing stresses constitutes what may be fairly regarded as proof that slippage is certainly not

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[1] In memory of Ira Remsen.

[2] Part of Master's Degree "Thesis" of Theodore R. Thompson.

[3] Tammann and Hinniiber, *Z. anorg. Chem.*, 167,230 (1927).

a very important factor in the flow of mercury over glass. As the subject has been discussed elsewhere,[4] repetition here is unnecessary. We propose to inquire whether there is not some other explanation for the phenomenon other than the one suggested by Tammann and Hinnuber.

2. S. Erk[5] has already suggested as an alternative explanation that the walls of metal capillaries are perhaps not as smooth as those of glass capillaries, so that the flow is not perfectly linear. Erk has shown that in the steel capillary used by Tammann and Hinniiber the velocity of flow was so high that according to the Reynold's criterion turbulence should have been expected. The weak points in this explanation are, first, that the decrease in fluidity was not marked in the steel capillary and not very marked in the copper capillary until after thorough amalgamation; and, second, that the apparent fluidity in the amalgamated copper capillary steadily decreased for several days. It is not obvious why thorough amalgamation should increase the turbulence nor why the turbulence should not reach its maximum value at once.

3. The most obvious explanation is that the copper or something derived from the copper has decreased the fluidity of the mercury. This hypothesis has been considered by Tammann and Hinnuber and rejected because copper is only soluble to 0.0032% at 15° and at this dilution the fluidity is lowered not over 0.3%. We have confirmed this, finding that the fluidity at 20° of a saturated solution of copper was 63.9 rhes,[6] as compared with 64.2 for pure mercury. The method of preparation was intentionally such that the solution would contain the impurities derived from the copper but the solution was passed through chamois skin before measurement in order to remove any suspended particles. The difference obtained is only a little more than experimental error.

4. E. von Schweidler[7] claimed to have prepared a solution of copper in mercury containing 0.5% of copper with the low fluidity of 61.7. This may have been a suspension of colloidal copper, mercury or oxide, but whatever its nature it is worth considering whether suspended material could have caused the actual reduction in apparent fluidity noted by Tammann and Hinniiber. This difficulty can be largely overcome by the cleaning out of the viscometer and the use of clean mercury, but we have proved that the fluidity is not restored to that obtained in a glass capillary, so that this explanation is inadequate.

5. Even if the copper does not dissolve to any extent in the mercury, it is possible that the mercury diffusesinto the copper and causes it to expand, thus partially filling the capillary. However, the measurements

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[4] Bingham, "Fluidity and Plasticity," pp. 29-35.

[5] S. Erk, *Z. Physik*, 47, 886 (1928).

[6] Reciprocal *poises.*

[7] E. von Schweidler, *Wied-Sitzb.*, [2A] 104, 273 (1895).

of the diameter of the amalgamated tube made by Tammann and Hinnuber give no evidence of a decrease in diameter.

6. Copper is slightly soluble in mercury and the solution is very fluid, as already pointed out. In a saturated solution it is to be expected that the small crystals of copper would be dissolved to promote the growth of large crystals. It is therefore possible that after amalgamation there is a progressive alteration in the surface which would in time result in a pronounced change in the *effective* radius of the capillary. Since the copper taken away at one place is deposited at another, the average radius measured by Tammann and Hinnüber would not be affected, but the "constant" of the capillary should change. We have found as a matter of fact that after removing the mercury from the amalgamated capillary of a viscometer by heating in a stream of hydrogen, the constant of the viscometer as determined with pure water decreased from 4.94 to 4.79×10^{-7}, which is roughly 3.0%.

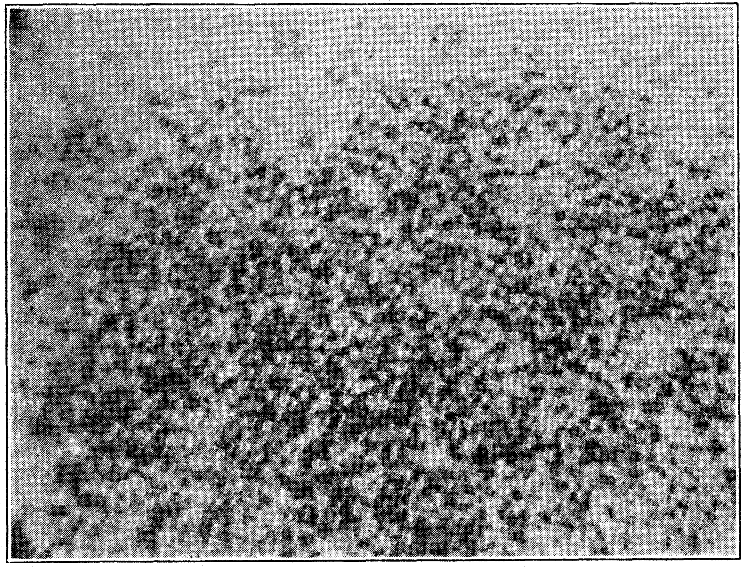


Fig. 1.—Surface after fifteen minutes.

Before amalgamation the apparent fluidity of the mercury as measured at different pressures in the copper capillary at 20° was 62.2 rhes and after twenty-four hours 62.1 rhes. We obtained in a glass capillary at 20° the fluidity of 64.3 rhes. The apparent fluidity in the copper capillary is therefore 3.3% lower than when measured in a glass capillary but it does not change rapidly with the time. Tammann and Hinnüber obtained a value 22.3% lower than the value as measured in glass. Perhaps the difference is due to partial but unequal amalgamation.

After thorough amalgamation the apparent fluidity decreased steadily but there was no evidence that it was tending toward a constant value until after ten hours it had fallen to 20% of its original value, when the experiment was discontinued. Repeating the experiment with a smaller capillary, the flow after a time ceased altogether. Tammann and Hinnüber observed that the time of flow increased for a period of five days, but on somewhat scanty evidence they assumed that the time of flow will reach a constant value. However, even if the time of flow does become constant, this fact would not prove that the fluidity of the mercury was tending toward a constant value, for it might be the capillary and not the mercury which is changing. Slippage is supposed to help the flow so that the final value of Tammann and Hinnüber should be a minimum, but our value of about 12.5 rhes is considerably lower than their value of 20.3 rhes, and it is not the minimum value.

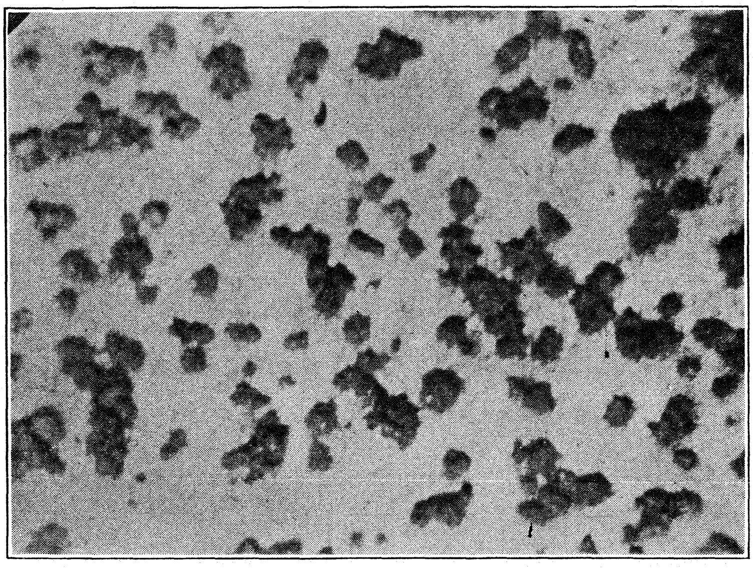
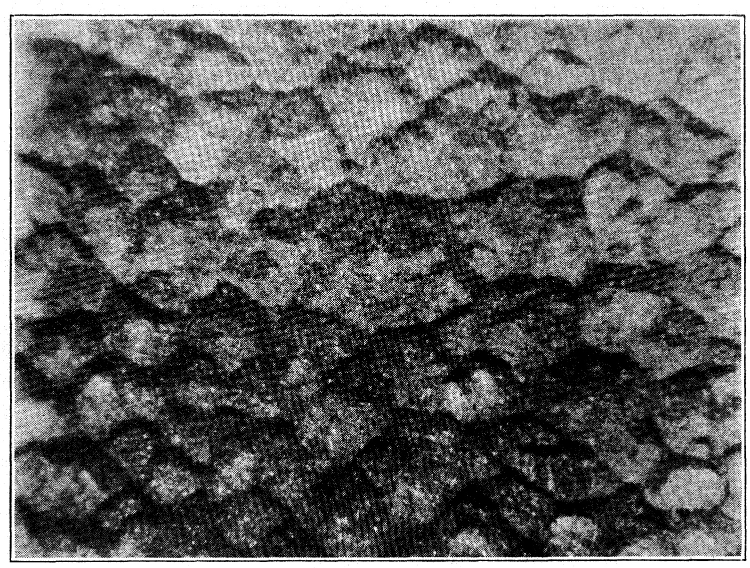


Fig. 2.—Surface after forty-two hours.

It appeared possible to prove quite conclusively that recrystallization of the copper does take place on the walls of the capillary and that it is sufficient to explain any decrease in apparent fluidity. To do this, pieces of copper were smoothly polished, amalgamated for a few seconds with mercurous nitrate and then bathed in metallic mercury for different periods of time, after which the mercury was driven off by heat in an atmosphere of hydrogen. It will be seen from Fig. 1 that the etching of the surface is quite marked after only fifteen minutes, large isolated crystals stand out prominently from the surface at the end of two days, Fig. 2, and at the end of two weeks, Fig. 3, large crystals appear to cover the entire surface. Some of the crystals were as much as 0.5 mm. above the surface, which is about twice the diameter of one of the capillaries which we used. A section made at right angles to the surface showed the irregular surface very well.

It is not necessary, however, to use any elaborate technique to show the effect, for a smooth piece of copper amalgamated for more than a few hours shows to the unaided eye a rough sandy appearance. We assume that this recrystallization has been noticed repeatedly heretofore but we are unable as yet to give any references.



Pig. 3.—Surface after two weeks.

We therefore reaffirm the earlier conclusion that there is no positive evidence of slippage of mercury in a glass tube, and we reach the new conclusion that the fluidity of mercury measured in a copper tube is unreliable, particularly when the copper is wetted by the mercury.

TABLE I

THE FLUIDITY OF MERCURY MEASURED IN A GLASS CAPILLARY

Capillary No. 1.23; $C = 1.994 \times 10^{-7}$; $C' = 0.018$; $h' = 0.15$ cm.

Temp., °C.	Time of efflux	Fluidity rhes	Av. earlier 'fluidity, Erk
0	254.5	59.4	59.3
10	244.0	62.1	61.9
20	237.0	64.3	64.8
30	228.9	66.8	66.7
40	223.4	686	69.0
50	216.9	71.0	71.1
60	211.8	72.9	73.2
70	207.3	74.9	75.1
80	203.2	76.7	77.0
90	199.3	78.5	78.9
100	196.0	80.0	80.6

The fluidity of mercury from 0 to 100° was determined as an incidental part of this investigation, using glass capillary No. 1.23. The values are a little higher at low temperatures than the mean values of earlier experimenters given by Erk,[5] and our values are somewhat lower than theirs at 40° and above. This slight change does not alter the conclusion that mercury is different from all other liquids yet studied in that its fluidity temperature curve is concave toward the temperature axis.

Summary

1. The suspicion that mercury exhibits slippage while flowing over unwet surfaces such as glass appears to be unfounded.

2. The fluidity of mercury from 0 to 100°, measured in a glass capillary viscometer with attention to recent corrections, was found to be not inconsistent with earlier determinations.

3. The rate of flow of mercury through a narrow copper capillary is irregular but decreases with time, particularly when the tube is well amalgamated. The values of the fluidity are quite untrustworthy. The effect is the indirect result of the very slight solubility of copper in mercury. Differential solubility of the crystals causes large crystals to build up on the surface of the capillary which interfere with the flow.

EASTON, PENNSYLVANIA

[CONTRIBUTION FROM HILLSIDE LABORATORY]

THE COLOR OF IODINE SOLUTIONS[1]

BY FREDERICK H. GETMAN

RECEIVED JULY 2, 1928 PUBLISHED NOVEMBER 6, 1928

The dependence of the color of solutions of free iodine upon the nature of the solvent has been the subject of numerous investigations, but notwithstanding the thoroughness of these studies the problem of the exact composition of iodine solutions yet remains to be solved completely.

As a result of their study of colors of iodine solutions, Gauthier and Charpy[2] concluded that four different colors may be distinguished, depending upon the nature of the solvent, as follows: (1) violet, as in chloroform; (2) red, as in ethylene bromide; (3) reddish-brown, as in toluene; (4) brown, as in ethyl alcohol. Although a number of solvents were found to conform to this classification, no satisfactory relation between the properties of the solvents and the colors of the solutions was discovered. Subsequent investigations by Rigollot[3] and by Krüss and Thiele[4] failed to establish any satisfactory connection between the chemical

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[1] In memory of Ira Remsen.

[2] Gauthier and Charpy, Compt. *rend.*, **110,1890; 111,645** (1890).

[3] Rigollot, *ibid.*, 112, 38 (1891).

[4] Krüss and Thiele, *Z. anorg.* Chzm., **7, 25 (1894).**

behavior of the solvent and the color of the solutions. In 1903, Lachman,[5] after examining solutions of iodine in more than sixty carefully purified solvents, representative of twelve different types of organic compounds, was unable to distinguish more than two colors, namely, violet and brown. Furthermore, he formulated the following generalization between the color of the solution and the character of the solvent: saturated solvents give violet solutions, whereas solvents having an unsaturated character yield brown solutions. The differences in the colors of iodine solutions have been attributed by Krüss and Thiele,[4] Wiedemann and Ebert,[6] Loeb,[7] Beckmann[8] and others to differences in the molecular condition of the solute. Subsequent investigations, notably by Hildebrand and Glascock[9] Waentig,[10] Ley and Engelhardt,[11] and Dolezalek,[12] have confirmed this view and have furnished abundant experimental evidence to show that in the brown solutions the solute is more or less solvated, whereas in the violet solutions the solute consists solely of diatomic molecules of iodine. The compound, PyI_2, has actually been isolated by Waentig from a pyridine solution of iodine.

It has long been known that brown solutions of iodine tend to become violet when heated, while violet solutions become brown when sufficiently cooled. This change of color with temperature may be satisfactorily explained by assuming a displacement of the equilibrium between solvated and unsolvated iodine.

More recently, Amann[13] has put forward the view that while in some instances iodine, either free or solvated, may form true solutions, yet in other cases it forms colloidal solutions. He states that brown solutions of iodine contain ultramicroscopic particles, while violet solutions contain none.

Notwithstanding Lachman's statement that iodine solutions are either violet or brown, and that intermediate colors are never observed unless the solvents contain minute amounts of impurities, one finds repeated statements throughout the literature that solutions of iodine in certain solvents exhibit various colors such as blue-violet, red-violet, red and red-brown.

With the exception of the work of Coblentz[14] on solutions of iodine in carbon disulfide and ethyl alcohol, relatively few spectrophotometric

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[5] Lachman, THIS JOURNAL, **25**, 50 (1903).

[6] Wiedemann and Ebert, *Wied. Ann.*, 41,299 (1890).

[7] Loeb, *Z. physik. Chem.*, 2, 606 (1888).

[8] Beckmann, *ibid.*, 17,107 (1895); 58, 543 (1907).

[9] Hildebrand and Glascock, THIS JOURNAL, **31**, 26 (1909).

[10] Waentig, *Z. physik. Chem.*, 68, 513 (1909).

[11] Ley and Engelhardt, *ibid.*, 72, 55 (1911).

[12] Dolezalek, *ibid.*, 64, 727 (1908).

[13] Amann, *Z Kolloid*, 6, 235 (1910); *Kolloid Beihefte*, **3**, 337 (1912).

[14] Coblentz, *Phys. Rev.*, 16, **35**, *72* (1903); 17, 61 (1904).

measurements of iodine solutions in the visible range of the spectrum have been recorded. It has seemed of interest, therefore, to undertake a series of spectrophotometric measurements of iodine solutions in typical solvents with a view to testing the validity of Lachman's statement relative to the colors of iodine solutions,

Apparatus.—The spectrophotometric measurements have been made with a Nutting photometer in conjunction with a Hilger wave length spectrometer. As a source of light a 13-watt Mazda lamp operating on the 110-volt a. c. circuit was employed. Absorption tubes of 10-cm. length were used throughout the entire series of measurements.

Materials.—Alerck's resublimed iodine served as the solute in each of the solutions. Solvents of a high degree of purity were subjected to thorough dehydration and subsequent fractionation before being used in the preparation of the solutions. The following solvents were employed: ethyl alcohol, b. p. 78.4°, 760 mm.; *iso*propyl alcohol, b. p. 80.2–81.2°, 750 mm.; acetone, b. p. 56.6°, 755 mm.; chloroform, b. p. 61.0–62.0°, 757 mm.; carbon tetrachloride, b. p. 77.0°, 763.4 mm.; carbon disulfide, b. p. 46.0–46.2°, 752 mm.; n-hexane, b. p. 68.0°, 760 mm.; benzene, b. p. 80.0–80.2°, 757 mm.; toluene, b. p. 110.2–110.8°, 758 mm.; pyridine, b. p. 114.8–115.6°, 751.6 mm.; nitrobenzene, b. p. 209.2–209.4°, 753.5 mm.; acetophenone, b. p. 202–203°, 756 mm. The aqueous solutions of potassium iodide were prepared from a high grade of salt dissolved in conductivity water.

Results.—The values of the extinction coefficients,[15] ϵ, for the different solutions, as measured at intervals of 10 mμ throughout the visible spectrum from 680 mμ to 430 mμ, are given in Table I. Inspection of the data of the table shows that, if solutions in nitrobenzene be disregarded, the solutions may be grouped in two distinct classes as follows: (1) solutions resembling that of iodine in n-hexane (violet solutions), and (2) solutions resembling that of iodine in ethyl alcohol (brown solutions). Solutions in n-hexane, benzene, toluene, carbon disulfide, carbon tetrachloride and chloroform have absorption maxima ranging between 520 mμ and 540 mp. On the other hand, solutions in ethyl alcohol, *iso*propyl alcohol, acetone, acetophenone and pyridine have absorption maxima ranging between 460 mμ and 480 mp. All of the solvents belonging to the first group are saturated in character, whereas all of those belonging to the second group are unsaturated. While not differing essentially in the spectral character of their absorption, solutions of iodine in both acetone and pyridine are found to differ markedly from the other solutions belonging to the second group in the intensity of their absorptions. With the exception of these two solutions, and that of iodine in nitrobenzene already mentioned, very little difference is found to exist between the absorptive powers of the solutions within each group. The absorption

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[15] The extinction coefficient, ϵ, is defined by the equation $\epsilon = 1/d \log I/I_0$, where I_0 is the intensity of the light entering the solution and I is the intensity of the emergent light after having traversed d cm. of solution.

TABLE I

ABSORPTION OF LIGHT BY 0.0005 *M* IODINE SOLUTIONS

Wave length λ(mμ)	Extinction Coefficients													
	n-Hexane	Benzene	Toluene	Carbon disulfide	Carbon tetrachloride	Chloroform	Ethyl alcohol	*Iso*propyl alcohol	Acetone	Acetophenone	Nitrobenzene	Pyridine	0.01*M* KI	0.1*M* KI
680	0.048	0.049	0.043	0.069	..	0.055	0.044	0.022	0.022	0.040	..	0.037	0.027	..
670	..	.051	.044	.071	..	.057	.038	..	.024	..	..	.038	.030	..
660	..	.053	.045	.076	..	.060	.036	..	.027	..	..	.039	.033	..
650	.049	.058	.047	.083	0.065	.064	.037	.031	.029	.043	0.038	.041	.035	0.043
640	.054	.061	.048	.088	.070	.068	.041	.032	.030	.045	.045	.043	.037	.045
630	.064	.066	.050	.103	.079	.075	.044	.033	.031	.048	.048	.045	.038	.048
620	.083	.075	.055	.120	.094	.087	.046	.034	.033	.050	.050	.047	.039	.051
610	.103	.082	.066	.150	.110	.101	.052	.036	.034	.053	.056	.050	.043	.054
600	.132	.104	.083	.190	.143	.119	.055	.038	.035	.056	.068	.053	.048	.058
590	.175	.132	.105	.24	.180	.150	.061	.042	.037	.059	.084	.057	.051	.062
580	.23	.156	.134	.29	.23	.190	.066	.046	.038	.062	.108	.061	.056	.067
570	.29	.21	.180	.34	.28	.25	.072	.053	.040	.065	.142	.064	.064	.073
560	.36	.28	.24	.38	.37	.30	.082	.062	.042	.070	.180	.070	.073	.076
550	.40	.32	.28	.40	.40	.40	.094	.071	.044	.076	.22	.075	.081	.083
540	.42	.38	.33	.41	.41	.41	.105	.087	.047	.083	.26	.084	.090	.088
530	.42	.40	.40	.40	.40	.41	.126	.106	.050	.090	.33	.095	.099	.093
520	.40	.38	.42	.38	.38	.40	.15	.127	.054	.099	.37	.110	.115	.105
510	.36	.36	.37	.35	.35	.38	.18	.165	.064	.116	.40	.130	.129	.120
500	.32	.34	.33	.31	.31	.35	.23	.20	.083	.140	.42	.165	.150	.147
490	.25	.31	.29	.26	.26	.30	.27	.26	.116	.183	.38	.21	.20	.190
480	.18	.28	.26	.22	.22	.25	.30	.27	.155	.25	.32	.24	.28	.26
470	.12	.23	.23	.17	.18	.22	.27	.26	.195	.29	.25	.22	.29	.32
460	.07	.19	.18	.12	.12	.15	.21	.22	.23	.24	.17	.19	.23	.26
450	.04	.14	.15	.09	.08	.10	.17	.18	.17	.18	.07	.15	.19	.23
440	.03	.09	.09	.06	.06	.07	.13	.16	.13	.13	..	.13	.14	.19
430	..	05	..	..	.04	..	.09	..	..	..	..	.08	.09	.15

curves for solutions of iodine in n-hexane, ethyl alcohol, acetone and pyridine, as plotted from the data of Table I, are shown in Fig. 1.

The intensity of absorption is seen to be decidedly different in the two groups of solvents. The maximum intensity is found with the solvents of the first group, that is, with saturated solvents. Furthermore, the intensity of the absorption with saturated solvents is nearly identical. On the other hand, the intensity of absorption with solvents of the second group is markedly less than that with solvents of the first group. While the intensity of absorption with saturated solvents is practically constant, it varies widely amongst the different unsaturated solvents studied. These facts are clearly brought out by the data of Table II, showing the absorption maxima of the solutions examined.

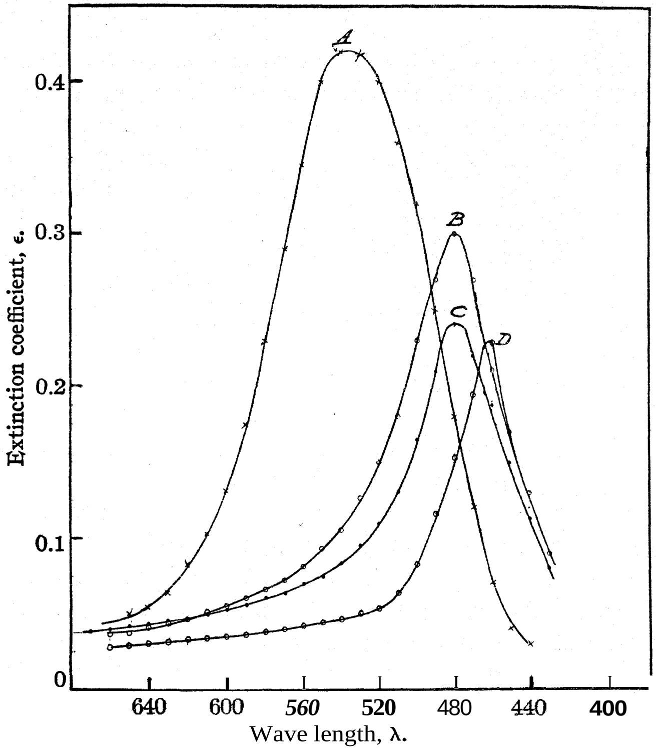

Fig. 1.—A, 0.0005 M I_2 in n-hexane; B, in ethyl alcohol; C, in pyridine; D, in acetone.

In this table λ_m denotes the wave length corresponding to the absorption maxima as determined from large scale plots of the data of Table I, while ϵ_m denotes the corresponding values of the extinction coefficients. The last column of the table gives the number of the group to which each solvent belongs.

TABLE II

ABSORPTION MAXIMA OF SOLUTIONS

Solvent	$\lambda_{m\mu}$	ϵ_m	Group	Solvent	$\lambda_{m\mu}$	ϵ_m	Group
n-Hexane	535	0.42	I	Ethyl alcohol	480	0.30	II
Benzene	530	.40	I	*Iso*propyl alcohol	480	.27	II
Toluene	520	.42	I	Acetone	460	.23	II
Carbon disulfide	540	.41	I	Acetophenone	470	.29	II
Carbon tetrachloride	540	.41	I	Pyridine	480	.24	II
Chloroform	535	.41	I	Water	470	.29	II
Nitrobenzene	50	.42					

The foregoing facts appear to substantiate Lachman's generalization that when iodine is dissolved in a saturated solvent the resulting solution is violet in color, whereas when it is dissolved in an unsaturated solvent the solution is brown in color. While in the case of saturated solvents iodine may be fairly assumed to form true solutions, its behavior with unsaturated solvents is by no means as clear. Although in the presence of an unsaturated solvent it is possible that the iodine molecule may undergo solvation, with equal probability it may be assumed to undergo association and give rise to a solution possessing a distinctly colloidal character. This latter possibility is in agreement with the view put forward by Amann[13] that brown solutions of iodine contain ultramicroscopic particles, whereas violet solutions are optically void.

It was pointed out by Ley and Engelhardt[11] that the absorption spectrum of iodine solutions changes with time, and that the differences between their results and those of Waentig[10] and of Crymble, Stewart and White[16] were to be traced to the failure of the latter observers to examine their solutions immediately after preparation. While the alteration in the character of the absorption spectrum of an iodine solution which occurs on standing is more pronounced in the ultraviolet than in the visible region of the spectrum, care has been taken throughout the present investigation to measure each solution immediately after it was prepared. The most pronounced example of the change in color with time which we have observed was furnished by solutions of iodine in isopropyl alcohol and acetone. Within a few hours after the solutions were prepared, the original brown color had faded to a light amber, and within a few days the solutions became absolutely colorless. This is undoubtedly due to a chemical reaction between the components of the solutions.

It is well known that solutions of iodine in aqueous potassium iodide darken on exposure to light. Recently the increase in the ultraviolet absorption of aqueous solutions of potassium iodide on exposure to light has been measured by Brode[17] and shown to be due to the presence of free iodine in the solutions. When a fixed weight of iodine is dissolved

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[16] Crymble, Stewart and White, *Ber.*, 43, 1183 (1910).

[17] Brode, THIS JOURNAL, 48,1877 (1926).

in aqueous solutions of potassium iodide of increasing concentration, it has been found that the ultraviolet absorption increases with the concentration of the potassium iodide. In order to determine whether a similar increase in absorption occurs in the visible portion of the spectrum, 0.0005 *M* solutions of iodine in 0.01 *M* and 0.1 *M* potassium iodide have been measured. As will be seen from the last two columns of Table I, the more concentrated solution possesses slightly greater absorbing power.

The photochemical decomposition of iodine solutions has been studied by Stobbe and Schmidt.[18] They point out that solutions of iodine in alcohols slowly undergo transformation into solutions of periodides, such as hydrogen tri-iodide or other addition compounds. This reaction is accelerated by spongy platinum as well as by light. While the absorption spectrum of true solutions of iodine reveals but a single band in the visible portion of the spectrum, the ultraviolet absorption spectra of periodide solutions are found to resemble each other and to he characterized by two bands having wave lengths of 357 mμ and 290 mμ. Stobbe and Schmidt state that during the change of an iodine solution into a solution containing periodides, solutions of mixtures are formed which exhibit three absorption bands. In the solutions of iodine whose absorption spectra have hitherto been described by earlier observers, Stobbe and Schmidt have estimated that from 5 to 100% of the iodine present had undergone transformation into periodides. Furthermore, Stobbe and Schmidt found upon irradiating solutions of iodine in chloroform or benzene for twenty-four hours with a quartz mercury lamp, that the solutions became yellow on diluting with the respective solvents instead of acquiring the reddish color which unilluminated solutions of iodine assume when similarly diluted.

It seemed of interest, therefore, to carry out a few qualitative experiments on the stability of some of our solutions in ultraviolet light. To this end, 0.0005 *M* solutions of iodine in ethyl alcohol, *n*-hexane and carbon disulfide were irradiated in quartz flasks with ultraviolet light from a quartz mercury lamp for a period of six hours, after which their absorption curves were again determined spectrophotometrically. On comparing the resulting curves with those of the freshly prepared solutions, it was found that some change had occurred, the alcohol solution showing the most and the hexane solution the least photolysis. This is what might be expected with solvents containing oxygen which are known to decompose when exposed to ultraviolet radiation. Carbon disulfide on exposure to ultraviolet radiation has likewise been found by both Berthelot[19] and Bruhat and Pauthenier[20] to undergo partial decomposition, the walls of the containing vessel becoming coated with a

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[18] Stobbe and Schmidt, *Z. wiss. Photochem.*, **20**, 57 (1920).

[19] Berthelot, *Ann. chim. phys.*, (VII) 19, 150 (1900).

[20] Bruhat and Pauthenier, Comfit. rend., 178, 1536 (1924); 180, 1018 (1925).

brown deposit. A similar deposit was observed in the present series of experiments. Hexane appears to be quite stable when exposed to ultraviolet radiation and the solution of iodine in this solvent was found to be equally stable. The behavior of iodine solutions on exposure to ultraviolet radiation, as far as our few experiments have been carried, appears to confirm the view put forward by Lachman that unsaturation in the solvent is a factor of considerable importance in determining not only the color but other properties of iodine solutions.

Summary

1. The extinction coefficients of iodine solutions in a series of carefully purified solvents have been measured at intervals of 10 mμ throughout the visible spectrum.

2. The solutions may be divided into two distinct groups, as follows: *(a)* solutions in n-hexane, benzene, toluene, carbon disulfide, carbon tetrachloride and chloroform give violet solutions with absorption maxima ranging from 520 mμ to 540 mμ; (b) solutions in ethyl alcohol, *iso*propyl alcohol, acetone, acetophenone and pyridine give brown solutions with absorption maxima ranging from 460 mμ to 480 mμ.

3. The first group of solvents are saturated compounds, while the second group of solvents are unsaturated compounds.

4. The intensity of absorption differs markedly in the two groups. The maximum intensity of absorption is found with the saturated solvents of the first group, and is practically constant throughout the group. The intensity of absorption varies appreciably between the unsaturated solvents of the second group and is in every case less than with saturated solvents.

5. Solutions of iodine tend to undergo change on standing, this change being accompanied by a corresponding change in their absorption spectra.

6. The color and stability of iodine solutions on exposure to ultraviolet radiation appear to be more or less dependent upon the degree of saturation of the solvent.

STAMFORD, CONNECTICUT

[CONTRIBUTION FROM THE PHYSICO-CHEMICAL LABORATORY OF THE POLYTECHNICAL INSTITUTE OF COPENHAGEN]

CATALYSIS IN THE HYDRATION OF ACETIC ANHYDRIDE[1]

BY MARTIN KILPATRICK, JR.

RECEIVED JULY 12, 1928 PUBLISHED NOVEMBER 6, 1928

In a general paper on reaction velocity, Skrabal[2] has regarded the hydrolysis of the organic oxides as made up of *(a)* a hydrogen-ion catalyzed reaction, (b) a hydroxyl-ion catalyzed reaction, (c) an uncatalyzed or water reaction. This classification was first made by Hudson, who applied it to the case of the mutarotation of glucose. Bronsted and Guggenheim[3] studied the effect on the mutarotation of glucose of other acid molecules than hydrogen ion, and of other basic molecules than hydroxyl ion; they showed that water may be considered to act catalytically both as an acid and as a base. Similarly, in the decomposition of nitramide, water may be classed as a basic catalyst,[4] since the constant for the decomposition of nitramide in acidified water lies on the straight line obtained when one plots the logarithm of the basic catalytic constant against the logarithm of the constant of basic strength. In all cases where catalytic effects of other acid molecules than hydrogen ion and other basic molecules than hydroxyl ion have been detectable, a water reaction has also been found to occur.[5] Conversely, it should be interesting to investigate from the point of view of acid and basic catalysis, a substance showing a particularly fast water reaction relative to the hydrogen- and hydroxyl-ion catalyzed reactions.

Acetic anhydride is such a substance. As Skrabal points out, the accurate determination of the catalytic effects of hydrogen and hydroxyl ion has not been possible because the minimum reaction rate already lies close to the limit of measurability. Skrabal[6] followed the hydration of acetic anhydride by coupling it with the iodide–iodate reaction; he assigns to the constant of hydroxyl ion catalysis the value $k_{OH^-} \leqq 4.4 \times 10^6$ at 25°. More recently Szabó[7] has studied the hydration of acetic and succinic anhydrides at 14 and 18° in the presence of electrolytes and non-electrolytes, using an interferometer to measure the change in refractive index which accompanies the reaction. Szabó reports catalysis by hydrogen

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[1] In memory of Ira Remsen.

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

[3] Bronsted and Guggenheim, THIS JOURNAL, 49, 2554 (1927).

[4] Brönsted and Pedersen, *Z. physik. Chem.*, **113**, 389 (1924).

[5] In the case of the acetone–iodine reaction, a water reaction has not been detected experimentally, but it has been inferred from calculations (Dawson and Key, *J. Chem. Soc.*, **1928**, p. 543).

[6] Skrabal, *Monatsh.*, **43**, 493 (1922).

[7] Szabó, *Z. physik. Chem.*, **122**, *405* (1926).

and acetate ions in the case of acetic anhydride and by hydrogen and succinate ions in the case of succinic anhydride. Practically all her experiments, however, were carried out in solutions of high electrolyte concentration and no proportionality between catalyst concentration and reaction rate is shown. Orton and Jones[8] studied the reaction in acetic acid, in acetic anhydride, in acetone, and in various mixtures of these solvents with water. From their experiments with different acids, they conclude that the non-ionized acids are effective catalysts in a solvent of over 90% acetic acid. They also notice the catalytic effect of sodium acetate in aqueous solutions but do not distinguish it from the effect of hydroxyl ion. The reaction has also been studied by Verkade,[9] who measured the change in the conductivity, and by Benrath,[10] who determined the change in the density of the solution as the reaction proceeded.[11]

It was thought that a dilatometric method might be convenient. Preliminary experiments showed that there was a considerable heat of reaction, a fact which appears often to have been overlooked and which is of the utmost importance in dilatometric work. A dilatometer was designed to take care of the heat of reaction and experiments were carried out at 0°. Here the half time of the reaction is twenty-six minutes. It was found possible to measure accurately the rate of reaction where the half time is as little as ten minutes.

Experimental Method

The apparatus as shown in Fig. 1 consists of a mixing chamber A connected by means of capillary tubing through the stopcock E to the two arms of the dilatometer F,F' and so to the calibrated capillary G. F and F' have a capacity of approximately 25 cc. each and the bore of the capillary G is 0.4 mm. In addition, the mercury filled chamber, J, is connected at D. A steel cap is sealed into the chamber J and the steel screw H turning through this cap acts as a plunger. By turning the screw the mercury can be raised through D and through E to K and K'. The whole apparatus is mounted and set in the Dewar P. Since the apparatus is packed in ice, and since it is necessary to observe the mercury levels at D and N, the tubes M and N extending to the walls of the Dewar are affixed with suitable supports. The stopcock E is encased; in addition it is fitted with a spring to hold the cock tightly in the barrel and with a mechanical arrangement for turning the cock.

A description of the procedure will further explain the apparatus. The glass rod B with a ground tip is set in place and 50 cc. of the solution run into the chamber A. A is then closed by a rubber stopper. The apparatus is packed tightly in snow ice and sufficient ice water added to fill the Dewar. After an hour a platinum stirrer and thermometer are placed in A. The stopcock E is opened and the level of the mercury adjusted to D by means of the screw H; this could be observed through M. When the solution has come to 0.0° ± 0.01°, the thermometer is removed and 0.35 cc.

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[8] Orton and Jones, J. *Chem. Soc.*, *101*, 1708 (1912).

[9] Verkade, *Rec. trav. chim.*, *35*, 79, 299 (1915).

[10] Benrath, *Z. physik. Chem.*, *67*, *501* (1909).

[11] A more complete list of references is given by Verkade (ref. 9) and Skrabal (ref. 6).

of acetic anhydride is added from a small weight pipet, After mixing, the rod B is removed and a rubber stopper with glass tube inserted in the top of the mixing chamber. The tube is connected to a suitable pressure system and the solution is forced over through the cotton plug C into the dilatometer and up into the capillary G. The rubber stopper is then removed from A and the rod B replaced. By turning H mercury is forced up to K and K′. Any excess of solution is taken up with filter paper and by turning H the liquid is brought to a suitable level in the capillary, E is closed and B removed. The rubber stopper is replaced in A, the Dewar wrapped in an insulating jacket and at *a* convenient time the first reading is taken. The manipulation occupies from six to ten minutes from the time of mixing. If, as occasionally happens, an air bubble is trapped between D and E it appears on the surface of the mercury when the mercury is forced up to N and is easily seen. It is a simple matter to draw the mercury back, remove B, and after inserting a rubber stopper in the top of L remove the bubble by gentle suction at R. Very little trouble was experienced with air bubbles; on the whole the method of filling a dilatometer by pressure is superior to filling by suction.

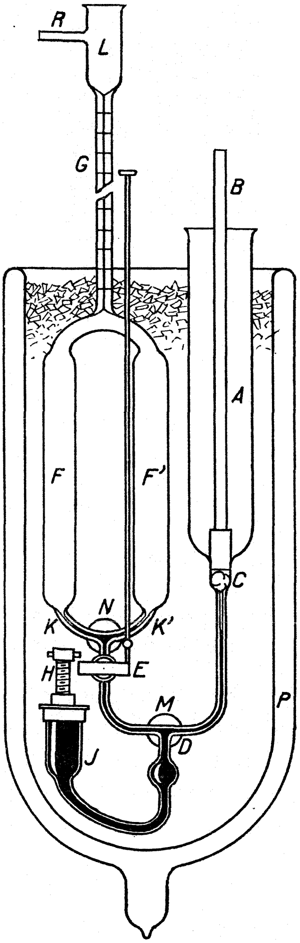

Fig. 1.—Apparatus.

Readings were taken at minute intervals for thirty minutes and at two minute intervals for another thirty minutes. One-half hour later a second set of readings was made, at the same intervals, and the velocity constant was calculated by the method of Guggenheim.[12] In those cases where the infinity reading was observed, the velocity constant was also calculated from the usual monomolecular formula. The observed infinity reading and that calculated from the velocity constant of Guggenheim's method usually agreed within 0.05 cm. for a total contraction of 6 cm. in the capillary. Since it is difficult to reproduce briefly an experiment calculated by the plotting method, Table I gives, for a typical experiment, the constant obtained from the observed infinity value and the formula $k = 1/t \ln (V_0 - V_\infty)/(V_t - V_\infty)$.

In no case was there a trend of more than 2% in the value of k during the course of an experiment. The change in k[13] with change in concentration of anhydride was not investigated, the initial concentration being 0 07 M ± 10% in **all** cases. The medium effect of acetic acid was investigated and will be discussed later. The anhydride used was a fraction of Kahlbaum's "für analytische

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[12] Guggenheim, *Phil. Mag.*, [7] 2, **538** (1926).

[13] Rivett and Sidgwick, J. *Chem. Soc.*, **97**, 732 (**1910**).

TABLE I

EXPERIMENT IN DISTILLED WATER

First reading after ten minutes. (Anhydride) = 0.07 *M*, T = 0° C.

Time, min.	Dilato-meter reading	$V - V_\infty$	log $V - V_\infty$	0.434 k min.$^{-1}$	Time, min.	Dilato-meter reading	$V - V_\infty$	log $V - V_\infty$	0.434 k min.$^{-1}$
0	18.27	5.99	0.777	....	25	15.34	3.06	0.486	0.0117
1	18.10	5.82	.765	0.0120	26	15.27	2.99	.476	.0116
2	17.94	5.66	.753	.0120	27	15.19	2.91	.464	.0116
3	17.80	5.52	.742	.0117	28	15.10	2.82	.450	.0117
4	17.66	5.38	.731	.0115	29	15.02	2.74	.438	.0117
5	17.50	5.22	.718	.0118	30	14.96	2.68	.428	.0118
6	17.37	5.09	.707	.0117	32	14.82	2.54	.405	.0116
7	17.23	4.95	.695	.0117	34	14.68	2.40	.380	.0117
8	17.10	4.82	.683	.0118	36	14.55	2.27	.356	.0116
9	16.99	4.71	.673	.0116	38	14.41	2.13	.328	.0118
10	16.87	4.59	.662	.0115	40	14.30	2.02	.305	.0118
11	16.74	4.46	.649	.0116	42	14.20	1.92	.283	.0118
12	16.62	4.34	.637	.0117	44	14.09	1.81	.258	.0118
13	16.51	4.23	.626	.0117	46	13.98	1.70	.230	.0119
14	16.40	4.12	.615	.0116	48	13.91	1.61	.207	.0119
15	16.29	4.01	.603	.0116	50	13.80	1.52	.182	.0119
16	16.19	3.91	.592	.0116	52	13.73	1.45	.161	.0118
17	16.09	3.81	.581	.0116	54	13.65	1.37	.137	.0119
18	15.99	3.71	.569	.0116	56	13.57	1.29	.111	.0118
19	15.89	3.61	.557	.0116					———
20	15.79	3.51	.545	.0116	∞	12.28			0.0117
21	15.70	3.42	.534	.0116	∞ calcd.	12.26		k =	0.0269
22	15.60	3.32	.521	.0116					
23	15.51	3.23	.509	.0117					
24	15.42	3.14	.497	.0117					

The constant[a] calculated by Guggenheim's method is 0.434 k min.$^{-1}$ = 0.0118 or k = 0.0271.

[a] All the remaining constants in this paper are given in terms of natural logarithms.

Zwecke" distilling between 137 and 138° at 753 mm. Other samples of anhydride gave constants not differing by more than 2% from 0.0269.[14]

On account of the high constant of the spontaneous or water reaction, the effects of H_3O^+ and OH^- ions are practically negligible over a wide range. Taking[15] k_{OH^-} as 4×10^5, $k_{H_3O^+}$ as 3×10^{-2} and k_0 as 3×10^{-2} at 0°, for a hydroxyl-ion concentration of 1×10^{-8} M, the effect of hydroxyl ion is only 1% of the total reaction and for a hydrogen-ion concentration of 1×10^{-2} M the effect of the hydrogen ion is 1% of the whole. As will be shown later, k_{Ac^-} is of the same order of magnitude as $k_{H_3O^+}$; any catalysis by the acetate is therefore negligible in the experiments carried out to determine k_0.

Table II shows the influence on k_0 of small amounts of hydrochloric acid and of neutral salts present in concentrations up to 0.2 N.

The salt effect is negative and varies with the individual salt. The

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[14] Szabó, ref. 7, p. 411.

[15] k_0 is used for the water reaction in distinction from k_{H_2O} which is $k_0/55$.

TABLE II

EFFECT OF NEUTRAL SALTS

Acid–salt	Acid, moles per liter	Salt, moles per liter	Velocity constant, k_0	Acid–salt	Acid, moles per liter	Salt, moles per liter	Velocity constant, k_0
HCl	0.002–		0.0269[a]	HNO_3–KNO_3	0.0008	0.099	0.0261
	.0004	0	.0267				
HCl–NaCl	.0008	0.059	.0263	CCl_3COOH–CCl_3COONa	.0008	.198	.0260
HCl–NaCl	.001	.099	.0262	HCl–NH_4Cl	.0008	.198	.0259
HCl–NaCl	.0008	.138	.0260	$HClO_4$–$NaClO_4$	.0015	.087	.0261
HCl–NaCl	.0008	.198	.0258	$HClO_4$–$NaClO_4$	.0015	.174	.0251
HCl–NaCl	.002	.198	.0255				
HCl–KCl	.0008	.198	.0253	$HO_3SC_6H_5$–$NaO_3SC_6H_5$	.0015	.079	.0254
HCl–KCl	.0008	.198	.0250				
HNO_3–KNO_3	.0008	.198		$HO_3SC_6H_5$–$NaO_3SC_6H_5$	.0015	.0108	.0248

[a] Average values.

results for sodium chloride are plotted in Fig. 2; these results can also be expressed by the equation $k_0 = 0.0268 - 0.0052\,c$ (where c is the concentration of sodium chloride).

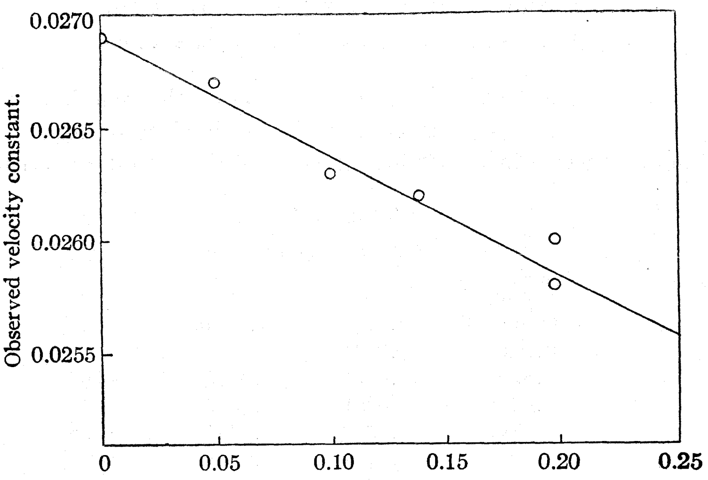
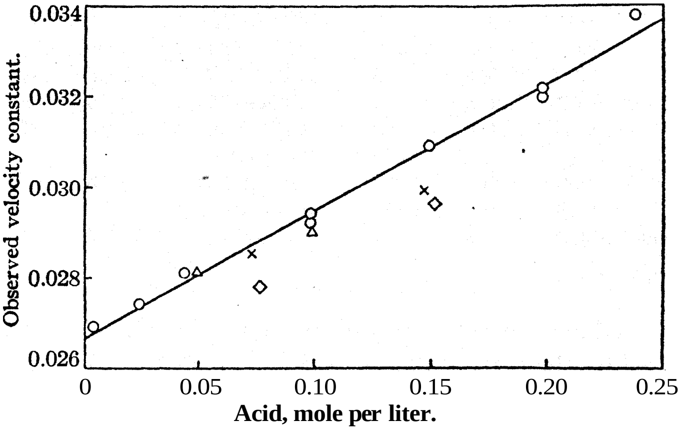


Fig. 2.—Effect of sodium chloride on reaction rate.

Figure 3 and Table III give the results of experiments carried out to determine $K_{H_3O^+}$. In Fig. 3 the observed velocity constants are plotted against the acid concentrations.

The plot shows approximate proportionality between acid concentration and increase in velocity constant; however, the correction for salt effect on the velocity constant remains to be made. In Table III the correction is made and $K_{H_3O^+}$ is computed.

The third column of Table III gives the observed velocity constant. The fourth gives k_0 corrected for salt effect, the effect for each acid being taken equal to the value shown in Table II for the corresponding salt. In the case of hydrochloric acid the effect is taken to be the same as that of sodium chloride. Col. 5 shows the portion of the reaction due to the hydrogen ion and $K_{H_3O^+}$ (sixth column) is obtained by dividing $k_{obs.} - k_0$ by the acid concentration. When it is considered that an error of 1%



⊙, HCl; △, HNO_3; X $HClO_4$; ◇, $HO_3SC_6H_5$.

Fig. 3.—Effect of hydrogen ion on reaction rate.

TABLE III

EFFECT OF HYDROGEN IONS

Add	Concn.. moles per liter	$k_{obs.}$	ko	$k_{obs} - k_0$	$k_{H_3O^+}$
HCl	0.00040.002	0.0269	Av. value	....	...
HCl	0.004	.0269	....	....	...
HCl	.0240	.0274	0.0267	0.0007	0.027
HCl	.0443	.0281	.0267	.0014	$.031^5$
HCl	.0985	.0292	.0264	.0028	$.028^5$
HCl	.0984	.0294	.0264	.0030	$.030^5$
HCl	.149	.0309	$.0261^5$	.0049	.032
HCl	.198	.0320	$.0258^5$	$.0061^5$	.031
HCl	.198	.0322	$.0258^5$	$.0063^5$	.032
HCl	.248	.0338	.0256	.0082	.033
HNO_3	.0495	.0281	.0265	.0016	$.032^5$
HNO_3	.099	.0290	.0261	.0029	.029
$HClO_4$	.0738	.0285	.0261	.0024	$.032^5$
$HClO_4$	.148	.0299	.0252	.0047	.032
$HO_3SH_5C_6$	.0757	.0278	.0254	,0024	.032
$HO_3SH_5C_6$	.152	.0297	.0248	.0049	.032

Av. = 0.031

Average deviation = 5%

in the observed velocity constant means an error of 7% in $K_{H_3O^+}$ as determined from an experiment in 0.1 N acid, and an even greater error in the case of experiments in more dilute acid, the agreement in the values of $K_{H_3O^+}$ is very good.

In order to measure the acetate ion catalysis it is necessary to work in a sodium acetate–acetic acid buffer solution. Here the medium effect of k_0 of the non-electrolyte acetic acid and the salt effect of the sodium acetate must be known. Since 0.2 M sodium trichloro-acetate has the same effect as 0.2 M sodium chloride, we may assume the salt effect of sodium acetate to be the same as that of sodium chloride. Table IV and Fig. 4 show the medium effect of acetic acid upon the velocity constant.

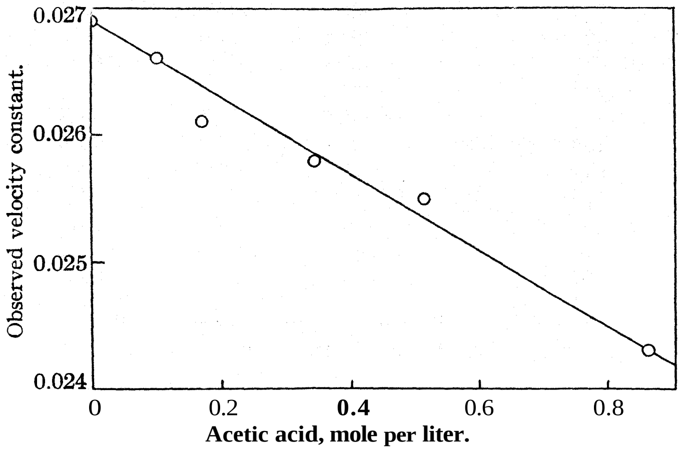


Fig. 4.—Effect of acetic acid.

TABLE IV

EFFECT OF ACETIC ACID

Init. concn. HAc, m./l.	0.000	0.100	0.170	0.343	0.514	0.860
k	.0269	.0266	.0261	.0258	.0255	.0243

These results may also be expressed by the equation $k_0 = 0.0269 - 0.0030\,m$, where m is the molarity of the acetic acid.

In Table V the results with sodium acetate–acetic acid buffers are given and K_{Ac} is calculated.

Here k'_0 (Col. 5) is k_0 corrected for the medium effect of the acetic acid and for the salt effect of the sodium acetate, upon the assumption that the two effects are additive. The corrected k_0 or k'_0 is then subtracted from the observed velocity constant, and the difference, divided by the acetate concentration, gives the constant of acetate ion catalysis. The concentration of acetate may be taken as equal to that of the sodium ion, since the hydrogen-ion concentration is less than 0.0002 M in all cases. An inspection of the acid–salt ratios in Table V shows that K_{Ac^-} is independent of the hydrogen-ion concentration. K_{Ac^-} is some 20% greater than $K_{H_3O^+}$.

TABLE V

EPRECT OF ACETATE:

$NaOOCCH_3$, moles per liter	$HOOCCH_3$ moles per liter	NaCl, moles per liter	$k_{obs.}$	k'_0	$k - k'_0$	$k_{acetate}$
0.0495	0.236	0	0.0281	0.0261	0.0020	0.042
.0590	.112	0.139	.0281	.0256^5	.0024^5	.041^5
.0990	.025	0	.0306	.0264	.0042	.042
.0990	.115	0	.0294	.0262	.0032	.032
.0990	.233	0	.0291	.0257	.0034	.034
.0990	.117	.0990	.0294	.0256^5	.0037^5	.038
.0990	.188	.0990	.0292	.0252^5	0039^5	.040
.0990	.044	.0990	.0297	.0257^5	.0039^5	.040
.119	.225	.0790	.0294	.0251^5	.0042^5	.035^5
.198	.232	0	.0327	.0250	.0077	.039
.198	.477	0	.0315	.0243	.0072	.036^5
.198	.232	0	.0331	.0251^5	.0079^5	.040
.198	.089	0	.0338	.256^5	.0081^5	.041^5
.198	.375	0	.0326	.0247	.0079	.040

Av. = 0.0385

Average deviation = 5%

Early experiments showed the formate ion to be a remarkably good catalyst, so good, in fact, that it was necessary to work at much lower concentrations of formate than of acetate and hydrogen ion. In studying the effect of formate ion the formic acid concentration must be sufficiently high so that the formateformic acid buffer equilibrium is not appreciably displaced by the acetic acid which is formed during the course of the reaction. The results of the experiments in formate–formic acid buffer solution are summarized in Table VI.

TABLE VI

EFFECT OF FORMATE

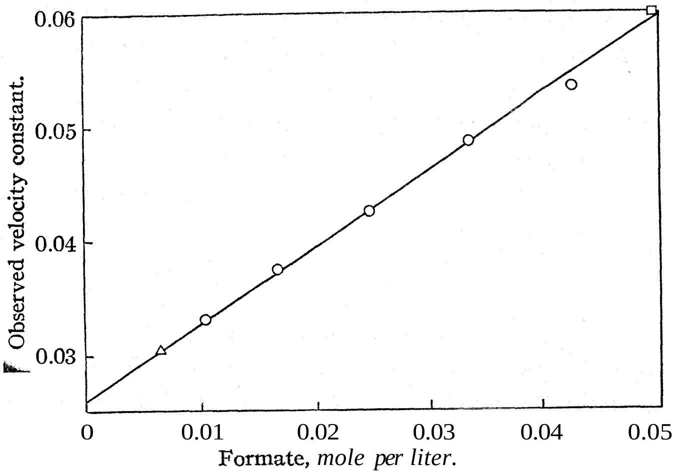
Composition of buffer							
Acid, moles/liter	Sodium salt, moles/liter	H^+, moles/liter	Pormate, moles/liter	$k_{obs.}$	k	$k - k'$	$k_{formate}$
0.495	0	0.0104	0.0104	0.0331	0.0257	0.0074	0.712
.495	0.0099	.0067	.0166	.0375	.0256	.0119	.717
.495	.0198	.0049	.0247	.0426	.0255	.0171	.692
.495	.0297	.0038	.0335	.0488	.0255	.0233	.696
.495	.0396	.0031	.0427	.0536	.0254	.0282	.660
.198	0	.0063	.0063	.0304	.0263	.0041	.651
.024	.0495	.0003	.0498	.0591	.0266	.0325	.653
.120	.198	.0020	.200	.1564	.0255	.1309	.655

The formate-ion concentration (Col. 4) was calculated from the dissociation constant of formic acid, K_c, account being taken of the change in K_c with change in electrolyte concentration. For this purpose an equation given by Brönsted[16]

$$K_c = K_0\frac{f_0}{f_1^2} = 1.8\,(1 + 2.36\,\sqrt{m})\,10^{-4}$$

was used; in this equation m represents the molarity of a monomonovalent solvent salt. k', given in Col. 6, is k_0 corrected for the medium effect of formic acid (assumed to be equal to that of acetic acid, see Table IV) and for salt effect, and to this is added $K_{H_3O^+}[H_3O^+]$, or the amount of reaction due to the hydrogen-ion catalysis. The maximum total correction is 4%. In the last three experiments the concentration of formic acid was low and the observed velocity constant was obtained from the first part of the reaction.

In Fig. 5, $k_{obs.}$ is plotted against the formate-ion concentration.



Formic acid: ○, 0.495 mole/liter; △, 0.198 mole/liter; □, 0.024 mole/liter.

Fig. 5.—*Effect of* formate.

From the figure it is evident that the increase in rate of hydration or $k_{obs.} - k'$ is proportional to the formate-ion concentration. In other words, the acetic anhydride is disappearing by two paths as in the cases of hydrogen-ion and acetate-ion catalysis. The intercept on the axis of velocity constants is 0.0260, which represents the constant in a 0.495 *M* formic acid solution, the hydrogen-ion catalysis being included and the formate-ion catalysis excluded. The value chosen for k' on the assumption that the medium effect was the same as that of acetic acid was 0.0257.

It is to be noted that Szabó[7] does not report any-catalytic effect of formate ion. She did no experiments, however, in sodium formate–formic acid buffer solution where the effect is very apparent.

[16] Brönsted *and* Volquartz, *Z. physik. Chem.*, 134, 109 (1928).

At 14° her velocity constants are: in water alone, **133.5** $\times 10^5$ (time in seconds); in 2.07 M acetic acid, 85.9 X 10^5; in 2.07 M formic acid, 126.8 $\times$ 109 The medium effect of two molar acetic acid on k_0 is therefore 35% at 14°. Assuming the medium effect of acetic or formic acid on k_0 at 0° to be linear up to 2 *M* acid, the decrease amounts to 22%. In **2.1** M formic acid the formate-ion concentration is approximately 0.023 M. Since k_{formate} is 0.7, the formate-ion catalysis is 0.016, corresponding to a 60% increase in the velocity constant. Therefore, at 0° the rate of hydration in **2** M formic acid would be greater than that in water alone. Szabó found the opposite to be the case at 14°. Two explanations may be suggested: first, that the medium effect of formic acid on k_0 is greater at 14° than at 0° (which Szabó's figures indicate); and, second, that the temperature coefficient of the hydration in water alone is greater than the temperature coefficient of the formate-ion catalysis, that is

$$\frac{k_0^{14°}}{k_0^{0°}} > \frac{k_{F^-}^{14°}}{k_F^{0°}}$$

Szabó's few experiments in acetate buffer solution were made at such high salt concentrations that only an approximate value can be calculated for k_{Ac^-} at 18°. Expressing Szabo's constants in minutes^{-1}, and using her salt effects, one gets $k_{Ac} = 0.10$ at 18° and $k_0 = 0.096$ at 18°, whence

$$\frac{k_0^{18°}}{k_0^{0°}} = \frac{0.096}{0.027} = 3.6 \text{ and } \frac{k_{Ac}^{18°}}{k_{Ac}^{0°}} = \frac{0.10}{0.039} = 2.6$$

When one considers the magnitude of k_{F^-} it is evident that there is no simple relationship between basic strength and catalytic efficiency as there is in the cases of the mutarotation of glucose and the decomposition of nitramide which will include both the formate and acetate ions. Since formate is a weaker base than acetate, k_{F^-} should be less than k_{Ac^-}; the value found is over fifteen times greater.

Experiments were also carried out in sodium propionate–propionic acid and sodium butyrate–butyric acid buffer solutions. In these solutions the reaction rate is slower than in water alone, as is shown by the results summarized in Tables VII and VIII.

TABLE VII

EXPERIMENTS IN PROPIONATE–PROPIONIC ACID BUFFER

Composition of Buffer			Composition of Buffer		
Acid moles/liter	Sodium salt, moles/liter	$k_{\text{approx.}}$	Acid, moles/liter	Sodium salt, moles/liter	$k_{\text{approx.}}$
0.304	0	0.0257^5	0.500	0.150	0.0184
.304	0	.0246[a]	.500	.200	.0174
.530	0	.0246	.250	.200	.0200
.500	0.0500	.0232	.125	.100	.0244
.500	.100	.0214	.150	.120	.0223

[a] In 0.2 *M* NaCl.

TABLE VIII

EXPERIMENTS IN BUTYRIC ACID–BUTYRATE BUFFER

Acid, mole/l.	0.50	0.50	0.50	0.50	0.50
Na salt, mole/l.	0	.050	.100	.150	.200
$k_{\text{approx.}}$	.0244	.0226	.0186	.0158	.0156

The reaction no longer exactly follows the monomolecular law and the constants have therefore been recorded as "approximate" in the tables. In addition, the contraction is much smaller.

From these results one may conclude that the acetic anhydride is no longer present wholly as such in the solution, but has combined with the propionate or butyrate to form an intermediate compound. The intermediate compound may be the mixed anhydride, for the rates of hydration are approximately the same as those calculated for the mixed anhydrides from the following considerations. Verkade has found 0.434 k for acetic anhydride at 25° to be 0.0713, the propionic anhydride 0.0372 and for the mixed anhydride 0.0524. The arithmetical mean of the constants for the simple anhydrides is 0.0542, which is approximately the constant determined for the mixed. Verkade's 0.434 k for propionic anhydride at 0° is 0.00700, and taking my value for acetic anhydride at 0° as 0.0117, the mean is 0.00935, or in terms of natural logarithms, 0.0215. In the absence of any actual determinations, 0.0215 may be taken as the approximate value of the constant for the mixed anhydride at 0°. In the fifth experiment of Table VII, that experiment in which there was a slight excess of propionate ion over acetic anhydride, the initial concentrations being 0.10 and 0.07 M, respectively, the constant found is 0.0214. According to a similar calculation for butyric acetic anhydride, k at 0° is 0.0189, while the value found in the third experiment of Table VIII is 0.0186. It must be mentioned, however, that before the kinetics of the hydration in solutions containing propionate or butyrate can be worked out, it will be necessary to know k_0, $k_{\text{H}_3\text{O}^+}$ k_{Ac^-} and possibly $k_{\text{propionate}}$ and k_{butyrate} for propionic and butyric anhydrides as well as for the mixed anhydrides, propionic–acetic and butyric–acetic.

There is considerable evidence[17] in the literature of organic chemistry for the formation of compounds between acetic anhydride and the carboxylic acids and their anions. Such compounds, however, have been formed under conditions quite different from those of the present experiments. The results of the experiments in formate–formic acid buffer solution do not preclude the formation of an unstable intermediate compound between the acetic anhydride and the formate ion.

The author wishes to thank the Rask-Ørsted Foundation, Copenhagen, for the grant which has made this work possible.

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[17] For discussion and further references see Autenrieth and Thomae, Ber., 57B, 423 (1924); Van der Haar, *Rec. trav. chim.*, 47, 321 (1927); Verkade, *ibid.*, 37, 331 (1918).

Summary

1. The velocity of hydration of acetic anhydride has been measured by a dilatometric method at 0°.

2. The salt effect on k_0 has been determined for a number of neutral salts in dilute solution. The medium effect of acetic acid has been measured.

3. The constants of hydrogen, acetate and formate-ion catalysis have been determined. The formate ion is a remarkably good catalyst.

4. In propionate–propionic acid and in butyrate–butyric acid buffer solutions the hydration is slower than in water alone. It is hoped to make a further study of this effect.

COPENHAGEN, DENMARK

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

THE INTERACTION BETWEEN NITROGEN TRICHLORIDE AND NITRIC OXIDE. REACTIONS OF COMPOUNDS WITH ODD ELECTRONS[1]

BY WILLIAM ALBERT NOYES

RECEIVED JULY 25, 1928 PUBLISHED NOVEMBER 6, 1928

In papers recently published,[2] the point of view has been presented that valence is a ***unitary*** atomic phenomenon. This is closely in accord with the original ideas of Frankland, Couper and Kekulé.

The endeavor has been made to show that for any given molecule, at any particular instant, the distinction between polar (or ionic) valences and covalences is sharp and definite. In the interest of clarity it has been proposed[3] to confine the term "polar valence" to the designation of valences which are actually ionic because of the complete transfer of an electron. The "semipolar" valences of oxygen in the sulfate radical, the amine oxides, etc., are, of course, half polar and half covalence.[4]

It has also been proposed to call those valences which have an electrical moment and which permit atoms held by a covalence to separate readily in the ionic form, "potentially polar," because the distinction between a covalence and an ionic valence is, theoretically, sharp and definite, while there may be all degrees of "potentially" polar valences.

This discussion seems to be a simple and logical development of the

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[1] In memory of Ira Remsen.

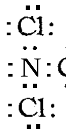
[2] (a) Noyes, *Z. physik. Chem.*, 130, 325 (1927); (b) *Proc. Am. Phil. Soc.*, *66*, 299 (1927).

[3] Noyes, ref. 2a, pp. 329; 26, **300**.

[4] T. M. Lowry, *Trans. Faraday Soc.*, 19, 486 (1923); J. *Chem. Soc.*, 123, 822 (1923); Sugden, *ibid.*, 125, 1186 (1924); 127, 1527 (1925); Harrison, Kenyon and Phillips, *ibid.*, 129, 2079 (1926); Noyes, THIS JOURNAL, **47**, 3027, footnote (1925); *Z. physik. Chem.*, 130,327 (1927).

positive and negative valences proposed, in part erroneously and vaguely in 1901[5] and 1904[6] and advocated by Professor Stieglitz,[7] Falk and Nelson,[8] Fry,[9] L. W. Jones[10] and others. It also furnishes an almost complete and satisfactory reconciliation with the octet theory of G. N. Lewis[11] and its exposition by Langmuir.[12]

If the hypothesis that a covalence is due to a pair of electrons which include the kernels of the two atoms which they unite in their orbits and that a polar valence is due to a pair rotating about the kernel of some negative atom or a deficiency of one electron in some positive atom[13] should receive further support and come to be generally accepted, the distinction between covalences and polar valences will become still more sharp than it is at present; but the distinction made in this and other papers is not dependent on that hypothesis.

Nearly all reactions of elements of low atomic weights occurring at ordinary temperatures seem to be, in reality ionic in character but we are compelled to assume odd electrons and reactions of a different type for a few compounds. For this reason, the interaction of nitric oxide, which has an odd electron, $\cdot\overset{\cdot\cdot}{N}::\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}$,[14] and nitrogen tri-chloride,  $\begin{array}{c}:\overset{\cdot\cdot}{Cl}:\\ :\underset{\cdot\cdot}{N}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}:\\ :\underset{\cdot\cdot}{Cl}:\end{array}$, an endothermic compound[15] with potentially positive[16] chlorine atoms, has proved to be of exceptional interest. Nearly all of the experiments with these compounds were carried out with a solution of the trichloride in a mixture of chloroform with enough carbon tetrachloride to prevent the mixture

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[5] Noyes and Lyon, THIS JOURNAL, 23, 463 (1901).

[6] Noyes, *Chem. News*, 90, 228 (1904).

[7] Stieglitz, THIS JOURNAL, 23, 796 (1901).

[8] Falk and Nelson, *ibid.*, 32, 1637 (1910).

[9] Fry, *Z. physik. Chem.*, 76, 385, 398, 591 (1911); THIS JOURNAL, 34, 664 (1912).

[10] L. W. Jones, *ibid.*, 36, 1268 (1914).

[11] G. N. Lewis, THIS JOURNAL, 38, 762 (1916).

[12] Langmuir, *ibid.*, 41, 868, 1543 (1919).

[13] Noyes, THIS JOURNAL, 39, 879 (1917); C. A. Knorr, *Z. anorg. allgem. Chem.*, 129, 109 (1923); Sidgwick, *Trans. Faraday Soc.*, *19*,*469* (1923); Paulus, THIS JOURNAL, 48, 1132 (1926); Grimm and Sommerfeld, Z. *Physik*, 36, 52 (1926); Glockler, THIS JOURNAL, 48, 202 (1926); Noyes, *Proc. Nat. Acad. Sci.*, 13, 377 (1927).

[14] This might also be written $\cdot\overset{\cdot\cdot}{N}^{+}:\overset{\cdot\cdot}{O}:^{-}$, with a semipolar union between the oxygen and nitrogen, but Sugden, J. *Chem. Soc.*, 125, 1187 (1924), has given good evidence, based on the parachor, that nitrosyl chloride, $:\overset{\cdot\cdot}{O}::\overset{\cdot\cdot}{N}:\overset{\cdot\cdot}{Cl}:$, has a double covalence between the oxygen and nitrogen and it would seem quite probable that there is a similar structure in nitric oxide.

[15] Noyes and Tuley, THIS JOURNAL, 47, 1336 (1925).

[16] Seliwanow, *Ber.*, 27, 1017 (1894); Noyes and Haw, *Ber.*, 42, 2167; Noyes, *Ber.*, 42, 2173 (1920).

from freezing at −80°. A few were tried at 0°, one at −20° and two in petroleum ether at −130 to −140°.

About a hundred experiments have been performed in the endeavor to develop a satisfactory technique for separating the products formed and analyzing them to establish the course of the reaction at the different temperatures and in the different media. One hundred samples of mixed gases have been analyzed by the methods described in a previous paper,[17] $N/10$ potassium hydroxide instead of water being used to absorb the gases, which were sometimes nearly pure chlorine.

Experimental Part

Nitrogen **Trichloride.**—The chlorine generated by dropping 300 cc. of concd. hydrochloric acid on 60 g. of potassium permanganate was passed into 225 g. of a mixture of chloroform and carbon tetrachloride containing 10 to 20% of the latter. The mixture was in a one-liter, round-bottomed flask and had above it 600 cc. of a 10% solution of ammonium sulfate. The flask was closed with a cork stopper carrying the wide delivery tube for the chlorine and a second glass tube connected with rubber tubing to the bottom of a 2.5-liter bottle to collect a slight amount of chlorine which might escape absorption. The chloroform and ammonium sulfate solution were shaken vigorously during the half hour required to generate the gas. The solution warms somewhat but if it is cool at the beginning this does no harm. The ammonium sulfate solution was poured off and the chloroform solution transferred to a 500cc. bottle and shaken for five minutes with a 5% solution of ammonium sulfate. After separating, this was repeated. The solution was then separated sharply, dried with a few grams of powdered calcium chloride and filtered on a dry filter.

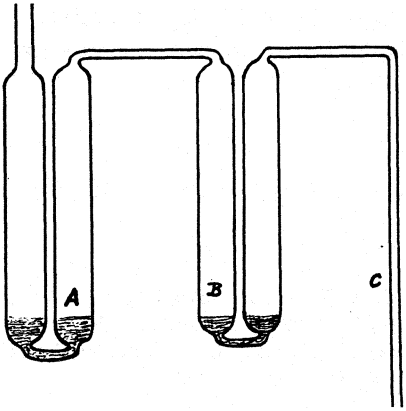

Fig. 1.

The solution prepared in this manner contains about 12% of the nitrogen trichloride, or one millimole per gram. If any unused portion is kept in the dark and in contact with a 5% solution of ammonium sulfate, there is little loss in strength for some days. It should be shaken vigorously with the sulfate solution before use.

Solutions as concentrated as 18% have been prepared and Hentschel's[18] statements seem to indicate that there is no danger of explosion in working with such concentrations.

Analysis.—Three to five-tenths of a gram of the solution was weighed in a U-tube having a capacity of less than 1 cc. and drawn out at right angles, on one side, to a small, thin capillary. The contents of the tube was transferred to A of the double U-tube shown in Fig. 1. A contained 2 cc. of concentrated hydrochloric acid and B, 0.5 cc. of water. The tube C dipped beneath the surface of 15 to 20 cc. of a 10% solution of potassium iodide. A slow current of air was passed through the apparatus until the chloroform was all evaporated and the liberated chlorine was swept out into the iodide solution.

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[17] Noyes, This Journal, 47, 2162 (1925).

[18] Hentschel, *Ber.*, 30, 1434 (1897).

The iodine was titrated with $N/10$ sodium thiosulfate, the hydrochloric acid solution was neutralized with 10 cc. of 30% potassium hydroxide and the ammonia distilled over into $N/10$ hydrochloric acid. The equation for the reaction is

$$NCl_3 + 4HCl = NH_4Cl + 3Cl_2$$

If the nitrogen trichloride is pure and free from chlorine, the volume of thiosulfate used will be 6 times the volume of the $N/10$ hydrochloric acid. Any excess of thiosulfate furnishes a determination of the free chlorine present.

Nitric oxide was prepared by dropping sulfuric acid (1:1) into a 25% solution of sodium nitrite[19] and the gas was kept in an aspirator bottle having a capacity of 3.5 liters.

Technique of the Experiments.—A weighed quantity of the nitrogen trichloride solution, containing in different experiments from 28 to 82 millimoles, was introduced through D (Fig. 2) into the bulb F. B was connected with an aspirator bottle containing nitrogen purified by passing it through an acid solution of chromous chloride to remove a trace of oxygen, through a tower containing soda lime and through an effective wash bottle containing concd. sulfuric acid.

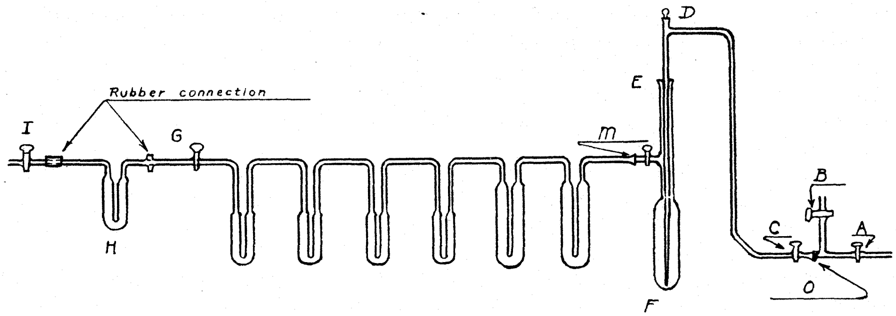

Fig. 2.—Ground glass joints at O, E and M.

After immersing F in a Dewar cylinder containing carbon dioxide-snow and acetone, the apparatus was evacuated with a good mechanical pump connected with I. By closing C and opening B, the T-tube was filled with nitrogen and after closing B and opening C this was pumped out. A few repetitions removed the small amount of oxygen remaining in the apparatus. The stopcocks m, G and I were then closed and nitric oxide was admitted through A. In many of the experiments nearly 3 liters of nitric oxide was admitted and the products absorbed without opening the stopcock m. The bottle containing the nitric oxide had been calibrated and the amount used was determined with an accuracy of 1 to 2%.

After introducing the gas, the apparatus was allowed to stand for an hour or more to permit the last of the nitric oxide to react with the nitrogen trichloride or chlorine present in the bulb. After this a variety of methods was used for separating and analyzing the products. The best of these is now thought to be the following.

The U-tube nearest to the bulb and U-tube H were immersed in liquid air, the U-tubes having all been evacuated. With the stopcocks I and G closed and m open, the nitrous oxide formed and some of the nitrosyl chloride and chlorine began to distil into the first U-tube. With the mechanical pump connected beyond I continually working, the stopcock G was opened and after closing it I was opened momentarily to allow nitrogen which had passed into U-tube H to escape. By this method a good

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[19] Noyes, This Journal, 47, 2170 (1925).

vacuum was maintained with only a very slight loss of nitrous oxide. The solution in F was allowed to warm up to $-20°$ and a very slow current of nitrogen admitted through B. After the nitrous oxide and some of the chlorine and nitrosyl chloride had condensed in the first U-tube, the liquid air was transferred to the second and a carbon dioxideacetone cylinder placed around the first. When a considerable part of the chlorine and nitrosyl chloride had been distilled, the stopcock m was closed and the bulb F was cooled again to $-80°$.

In many of the earlier experiments the condensed gases were distilled and analyzed without contact with air in the endeavor to get evidence for the possible presence of nitrogen dichloride or monochloride. After many analyses had demonstrated that these compounds are absent or present in very small amounts, the manipulation was changed at this point and in subsequent experiments air was admitted to the U-tubes through I and G, the liquid air was transferred from the second to the third U-tube and the carbon dioxide–acetone to the second and a freezing mixture of ice and hydrochloric acid, giving a temperature of $-20°$, was placed around the first. By judicious use of these temperatures, it was possible to fraction the mixture through the tubes and finally secure all the nitrous oxide in U-tube H with comparatively little chlorine or nitrosyl chloride. The U-tube was disconnected, weighed quickly to about 0.01 g. (corresponding to about $^1/_4$ millimole of nitrous oxide) and the condensed gases were allowed to evaporate through an efficient wash bottle containing potassium hydroxide. The chlorine and nitrogen (from the nitrosyl chloride) were determined and by subtracting these from the weight of the contents of the U-tube the weight of the nitrous oxide was known.

The chlorine and nitrosyl chloride remaining in the U-tubes were sometimes allowed to evaporate and condense in U-tube H, weighed and then permitted to evaporate through a solution of potassium hydroxide and in other cases allowed to evaporate directly through the solution.

After this, liquid air was placed about the last of the U-tubes and the air in the tubes was removed by the pump. By opening m the remaining chlorine, nitrosyl chloride and chloroform were distilled back into bulb F. The contents of F was then hydrolyzed with ice water, the aqueous solution was analyzed for nitrogen and chlorine and the chloroform–carbon tetrachloride solution for chlorine and unchanged nitrogen trichloride. The results were calculated in milligram moles of the nitrogen trichloride which reacted or decomposed, of the nitric oxide used and in millimoles of the nitrous oxide and nitrosyl chloride and miligram atoms of the chlorine formed. In the table the results have been recalculated in ratios to one mole of nitrogen trichloride reacting or decomposed. From nearly 100 experiments, **23** performed after the technique and the methods of analysis had been pretty well developed are recorded.

The nitrous oxide, which had previously been found in a former investigation, from the action of phosphorus pentoxide on nitric oxide,[19] was identified by its effect on a glowing splinter, by condensation with liquid air and evaporation at $-80°$ and by its molecular weight, 44.4.

The experiments with petroleum ether suggest that either an intermediate compound, $NCl_3{\cdot}NO$, is formed, which decomposes directly to nitrous oxide and chlorine, or that hydrochloric acid formed by the action of nitrogen trichloride on petroleum ether[20] catalyzes the reaction

$$NCl_3 + NOCl = N_2O + 2Cl_2$$

That the second explanation is true was demonstrated by passing nitric

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[20] Coleman and Noyes, THIS JOURNAL, 43, 2211 (1921).

TABLE I

MOLECULAR RATIOS

Solvent, $CHCl_3 + CCl_4$

NCl_3 recovered	NCl_3 reacting	NO	N_2O	NOCl	Cl	Temp., °C.
0	1	0.59	0.06	0.44	2.45	0
0	1	0.97	.09	.79	1.91	0
0	1	1.26	.11	.63	2.05	0
0	1	0.81	.28	.11	2.30	−20
0.43	1	1.01	.38	.35	2.05	−80
.37	1	1.36	.51	.75	2.29	−80
.46	1	1.69	.54	.67	2.39	−80
.19	1	1.84	.55	.71	2.32	−80
.04	1	2.05	.82	.86	1.97	−80
.27	1	2.37	.89	1.19	1.66	−80
.06	1	2.09	.90	0.93	1.86	−80
.11	1	2.13	.83	1.06	1.90	−80
.06	1	2.32	.85	1.28	1.74	−80
.38	1	2.46	.89	1.13	1.53	−80
.14	1	2.73	.91	1.28	1.00	−80
.05	1	2.94	1.06	1.54	1.01	−80
.09	1	2.96	0.94	1.50	0.98	−80
0	1	3.26	1.09	1.86	1.00	−80
0	1	3 37	1.01	1.49	1.45	−80
0	1	3.41	1.04	2.12	0.96	−80
		Solvent, petroleum ether				
0.99	1	0.66	0.77	0	0.90	−130
.71	1	1.44	1.03	0.01	2.15	−140
.16	1	1.03	0.98	.01	2.11	−80

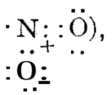
oxide into a chloroform–carbon tetrachloride solution of the trichloride until the trichloride present was exhausted and removing the nitrous oxide formed. More of the trichloride solution was then added and the mixture was allowed to stand for twenty hours at −80°; 5.5 milligram moles of nitrous oxide was formed. Three-tenths g. of hydrochloric acid was now added. After eighteen hours at −80°, 10.5 milligram moles of nitrous oxide was found and the trichloride was all exhausted, demonstrating that the acid catalyzes the reaction, as had been suspected.

Discussion

A rational explanation of the results is based on the following considerations.

1. Nitrogen trichloride is an endothermic compound which decomposes readily to nitrogen and chlorine. This means that the affinities of nitrogen for nitrogen and of chlorine for chlorine are much greater than the affinity of nitrogen for chlorine. Thermodynamically, it may be stated that the energy liberated when two isolated nitrogen atoms unite to form molecular nitrogen and six isolated atoms of chlorine unite to

form three molecules of chlorine is very much greater than the energy liberated when two isolated atoms of nitrogen combine with six isolated atoms of chlorine to form two molecules of nitrogen trichloride. It may be worth while to notice that our ignorance of the reason for these relations and, indeed, of the source of the energy liberated when atoms unite is still very profound.

2. Nitrogen readily forms compounds containing odd electrons, which are stable at ordinary and even at high temperatures but which react readily at low temperatures. Nitric oxide, $\cdot\ddot{N}::\underset{\cdot\cdot}{\ddot{O}}$, is an endothermic compound and even at 3000' the equilibrium is far on the side toward its decomposition; but nitric oxide will combine with oxygen to form nitrous anhydride even at the temperature of liquid air. The decomposition of nitrogen tetroxide, N_2O_4, to nitrogen dioxide, NO_2 (probably  $\begin{array}{l}\cdot N\underset{\cdot\cdot\,+}{:}:\ddot{O} \\ \;:\underset{\cdot\cdot}{O}\underline{:}\end{array}$), begins at ordinary temperatures.

3. At **0°,** 90% of the nitrogen trichloride decomposes to nitrogen and chlorine. The reaction is evidently catalyzed by the nitric oxide or the nitrosyl chloride.

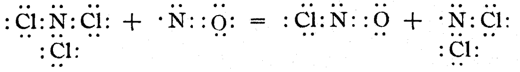
4. At −20° the reaction $NOCl + NCl_3 = N_2O + 2Cl_2$, which occurs slowly at −80° (see above), increases the amount of nitrous oxide and decreases the nitrosyl chloride present at the end.

5. At −80°, in chloroform–carbon tetrachloride, the results indicate that the normal course of the reaction corresponds to the equation $NCl_3 + 2NO = N_2O + NOCl + Cl_2$. This equation represents a trimolecular reaction and it seems much more probable that the action takes place in two stages. An intermediate stage in which nitrosyl chloride reacts with nitrogen trichloride is excluded by the slowness of that reaction at −80°, by the fact that two moles of nitric oxide are required before the trichloride is exhausted and because more than one mole of nitrosyl chloride is formed for each mole of nitrous oxide in every case except one. The excess must be due to the union of nitric oxide with chlorine.

The most probable steps seem to be the following: $NCl_3 + NO = NOCl + NCl_2$; $NCl_2 + NO = N_2O + Cl_2$.

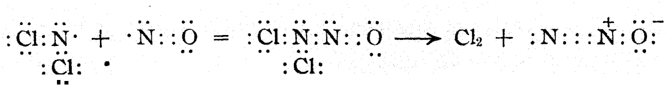
As already stated, many attempts have been made to isolate the nitrogen dichloride. The speed of the reaction between the dichloride and nitric oxide is evidently very great, as might be expected for two compounds with odd electrons.

In the primary reaction an atom of chlorine with an odd electron must separate from the nitrogen trichloride



$$:\underset{\cdot\cdot}{\ddot{Cl}}:\underset{:\underset{\cdot\cdot}{Cl}:}{\underset{\cdot\cdot}{\ddot{N}}}:\underset{\cdot\cdot}{\ddot{Cl}}: + \cdot\ddot{N}::\underset{\cdot\cdot}{\ddot{O}}: = :\underset{\cdot\cdot}{\ddot{Cl}}:\ddot{N}::\underset{\cdot\cdot}{\ddot{O}} + \cdot\underset{:\underset{\cdot\cdot}{Cl}:}{\underset{\cdot\cdot}{\ddot{N}}}:\underset{\cdot\cdot}{\ddot{Cl}}:$$

The second reaction may be represented electronically



$$:\underset{..}{\overset{..}{\mathrm{Cl}}}:\underset{:\underset{..}{\mathrm{Cl}}:}{\overset{..}{\mathrm{N}}}\cdot + \cdot\overset{..}{\mathrm{N}}::\underset{..}{\overset{..}{\mathrm{O}}} = :\underset{..}{\overset{..}{\mathrm{Cl}}}:\underset{:\mathrm{Cl}:}{\overset{..}{\mathrm{N}}}:\overset{..}{\mathrm{N}}::\underset{..}{\overset{..}{\mathrm{O}}} \longrightarrow \mathrm{Cl_2} + :\mathrm{N}:::\overset{+}{\mathrm{N}}:\underset{..}{\overset{..}{\mathrm{O}}}:^{-}$$

The formula for nitrous oxide is supported by the following facts and considerations.

The parachors of nitric acid and nitro compounds indicate a semipolar union in these compounds;[21] the parachor of alkyl cyanides and also the hydrolysis of these cyanides to organic acids and ammonia indicate a triple covalence between carbon and nitrogen and that such a triple covalence is a stable form of combination for nitrogen; the extreme unreactivity of molecular nitrogen points to a very stable tripe covalence, $:\mathrm{N}:::\mathrm{N}:$. The ease with which nitrous oxide gives its oxygen to a glowing splinter indicates that the oxygen is in a reactive form and also that the molecule already approaches the structure of the nitrogen molecule; the decomposition of an alicyclic diazo compound to form nitrogen **and** an azo compound[22] and the ready decomposition of all diazo compounds, $\mathrm{R_2}\underset{-}{\mathrm{C}}:\underset{+}{\mathrm{N}}:::\mathrm{N}:$ or $\mathrm{R}:\underset{+}{\mathrm{N}}:::\mathrm{N}:$, show that compounds whose structure approaches that of molecular nitrogen readily go over to that.

Summary

1. At 0° the interaction of nitric oxide and nitrogen trichloride results, chiefly, in the catalytic decomposition of the trichloride to nitrogen and chlorine.

2. At −20°, about one-fourth of the nitrogen trichloride is converted to nitrous oxide and chlorine. The comparatively small amount of nitrosyl chloride found at this temperature is probably due to the interaction of nitrogen trichloride with the nitrosyl chloride formed in the primary reaction, giving nitrous oxide and chlorine.

3. At −80° the reaction proceeds chiefly in accordance with the equation $\mathrm{NCl_3} + 2\mathrm{NO} = \mathrm{N_2O} + \mathrm{NOCl} + \mathrm{Cl_2}$.

4. Reasons are given for believing that this reaction occurs in two steps with the intermediate formation of nitrogen dichloride, although attempts to isolate this compound have not been successful.

5. The structure of nitrous oxide is probably $:\underset{..}{\overset{-\,..}{\mathrm{O}}}:\overset{+}{\mathrm{N}}::\mathrm{N}:$, with a semipolar union between the oxygen and nitrogen atoms. Facts and considerations are given in support of this formula.

6. In petroleum ether at −130 to −140° the reaction follows the course $\mathrm{NCl_3} + \mathrm{NO} = \mathrm{N_2O} + 3/2\mathrm{Cl_2}$.

The hydrochloric acid formed by the action of the trichloride on the

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[21] Sugden, *J. Chem. Soc.*, **125**, 186 (1924).

[22] Noyes and Coss, THIS JOURNAL, **42**, 1280 (1920); Noyes and Kendall, *ibid.*, **48**, 2406 (1926).

petroleum ether catalyzes the reaction between nitrogen trichloride and nitrosyl chloride referred to in 2.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE GEOPHYSICAL LABORATORY, CARNEGIE INSTITUTION OF WASHINGTON]

RADIUM AND GEOLOGY[1]

BY CHARLES SNOWDEN PIGGOT

RECEIVED JULY 26, 1928 PUBLISHED NOVEMBER 6, 1928

This article is a brief account of the general problem of the relation of radioactivity to geologic phenomena and of some of the experimental results so far obtained by the author in this field of investigation.

As soon as the experiments of Strutt (Lord Rayleigh) and Joly had revealed the apparently universal distribution of radium and its associated disintegration products throughout the lithosphere and perhaps throughout the entire earth, and when the work of Rutherford, Curie and others had demonstrated the extraordinary properties of these substances, it immediately became a subject of speculation as to the significance of so universal and so powerful an agent on the great earth phenomena which were known to have taken place.

The general problem has three main subdivisions:

1. The determination of the radium content of, and its distribution throughout, the lithosphere, and possibly an estimation of the amount and distribution throughout the earth.
2. The heat energy made available for the melting of the sub-crustal structure and its role in mountain building.
3. The radioactive disintegration of uranium into lead and its application to the determination of geologic time.

Since the problem was taken up by this Laboratory, there has not been time for the accumulation of any great quantity of data, but a satisfactory apparatus and technique have been developed and a number of measurements made in each of the above subdivisions.

Determination of Radium in **Rocks.**—For measuring the radium in ordinary rocks, where the quantity is of the order of 10^{-12} grams per gram of rock, the determination was made by decomposing the rock by fusing with a flux, collecting the radium emanation thereby liberated, and determining it by means of an electroscope.[2]

Calibration was accomplished by making a number of runs on a rock alone, and then another series, identical in every respect except that a

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[1] In memory of Ira Remsen.

[2] A detailed description of the apparatus and technique, including drawings, dimensions, etc., will appear shortly in the *American Journal of Science.*

known amount of radium, in equilibrium with its disintegration products, was added. This added radium was secured by pipetting a standard radium solution[3] containing 32.2×10^{-12} grams of radium element per cubic centimeter into small thin-walled glass bulbs, evaporating slowly to dryness, and then sealing the bulbs. These were kept for more than thirty days to permit the radium to come into equilibrium with its emanation. Bulbs containing 1 and **3** cc. of solution, respectively, were used. A bulb would be embedded in the mix and the fusion carried out in the usual way.

The flux alone showed some radioactivity; 100 g. gave an electroscope reading of 0.0014 division per second[4] and a 200-g. sample of the same material gave a reading of 0.0020 division per second.

A sample of granite from Stone Mountain, Georgia, was used to calibrate the apparatus and procedure. Sixteen measurements on this rock gave an average of 0.01089 division per second; this less 0.0014 for the effect of 100 g. of flux, gave 0.0095 division per second for the rock alone.

On adding bulbs containing **1** cc. and **3** cc. of standard radium the results were, in divisions per second

	1 *cc*,	3 *cc*.
		0.0179
		.0179
	0.0137	.0197
	.0137	.0197
	.0131	.0179
Average	0.01350	0.01856
Less effect of flux and rock	.01089	.01089
		3) .00767
1 cc. of standard Ra solution	0.00261	0.00256

The average of the two series is therefore 0.00259.

Since 1 cc. of radium solution is equivalent to 32.2×10^{-12} grams of radium element, 0.00259 div./sec. is equivalent to 32.2×10^{-12}, or

$$1 \text{ div./sec.} = \frac{32.2 \times 10^{-12}}{0.00259} = 12702 \times 10^{-12} \text{ g. of Ra}$$

So that

$$\frac{(E - F) \cdot 12702}{W} = \text{grams} \times 10^{-12} \text{ of Ra per gram of rock}$$

where E = electroscope reading (corrected for natural leak), F = effect of flux alone and W = weight in grams of rock sample used.

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[3] Tested and certified by the U. S. Bureau of Standards.

[4] The gold leaf of the electroscope is observed to pass across the field of a low-powered microscope in the image plane of which is a scale of 100 divisions. The rate across the same ten divisions is determined with a stopwatch.

Experimental

Using the above calibration and formula, the radium content of seven representative granites of the eastern seaboard of the United States, from Georgia to Maine, has been determined.

TABLE I

DETERMINATION OR THE RADIUM CONTENT OF SEVEN REPRESENTATIVE GRANITES OF THE EASTERN SEABOARD OR THE UNITED STATES

Locality	Description	G. of Ra per g. of rock
Stone Mountain, Georgia	Fine-grained, gray, biotite-muscovite granite	4.826×10^{-12}
Mt. Airy, North Carolina	Light-gray, coarse-grained biotite granite	0.655×10^{-12}
Woodstock, Maryland	Gray biotite granite with considerable allanite and epidote	1.448×10^{-12}
Ilchester, Maryland	Gray biotite diorite with accessory epidote	1.935×10^{-12}
Milford, Massachusetts	Very light pink, mottled, biotite granite	0.378×10^{-12}
Rockport, Cape Ann, Massachusetts	Hornblende-biotite granite	0.955×10^{-12}
Hurricane Island, Maine	Pinkish-buff, gray, coarse-grained biotite granite	3.65×10^{-12}

Complete chemical analyses and petrographic examinations were made on each rock studied.

The granite from Stone Mountain, Georgia, was separated into its constituent minerals by Kline's solution (aqueous solution of cadmium borotungstate) and each of these minerals examined separately for radium, with the following results in grams of radium per gram: quartz, 0.019×10^{-12}; potash feldspar, 1.129×10^{-12}; plagioclase, 1.657×10^{-12}; muscovite, 3.832×10^{-12}; biotite, 8.637×10^{-12}; from which it is apparent that in this rock, and presumably in others, the radium is associated more with those minerals having a high specific gravity rather than with those that have a low specific gravity, and that it is particularly associated with the micas.

Radioactive Heat.—Although the concentration of radium in the rocks of the lithosphere is very small, it seems to be universally distributed, and when one considers the masses involved there is a considerable amount of radium to be reckoned with. Since radium, in equilibrium with its disintegration products, produces 100 cal. per curie per hour, and since the heat conductivity of rocks is low and geologic time is long, there is good reason to believe that the accumulation of heat is sufficient to have a very real effect upon the earth's thermal gradient, and it is possible, as Joly believes, that there is quite enough heat from this source to furnish the heat of fusion of the subcrustal basaltic layer.[5]

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[5] See J. M. Joly, "The Movements of the Earth's Crust," *Phil. Mag.*, [6] 45, 1167 (1923).

Also Holmes[6] has shown that potassium must be considered; that although its radioactivity is slight, its relative amount makes it of considerable importance.

Geologic Time.[7]—Of the various methods which have been used or suggested for obtaining a more or less accurate estimate in terms of years of geologic time, that one which uses the uranium–lead ratio is by far the most promising and the most definite.[8]

Theoretically a chemical analysis of a mineral containing uranium or thorium or both, together with their corresponding lead, should give all the data necessary for a calculation of the age of the mineral and presumably of the rock with which it was associated. However, the estimates made in this way vary greatly, due to a number of factors. The necessary separations are difficult and tedious, and the amounts of the significant elements are so small that legitimate analytical errors produce disproportionately great effects upon the ultimate results. The extrapolation in terms of years over vast geologic ages is so great that these analytical errors may cause, a difference of hundreds of thousands of years in the indicated age.

But the chemical analysis alone cannot show whether or not the lead obtained is all of radioactive origin, or whether it came partly from uranium, partly from thorium or partly from some other source. The possibility of enrichment by lead from some non-radioactive source must be considered, and also the partial removal of the lead already radioactively produced. However, these are problems for the geologist at the time of selecting the sample and are not part of the mechanism of age determination being considered here.

What is emphasized here is that the uranium–lead ratio method, as now applied, has two inherent uncertainties associated with it. They are

(1) The uncertainty associated with the disintegration of the thorium series—the time required and the amount and origin of the lead produced. The thorium series of radioactive disintegrations has not yielded to experimental examination as readily as the uranium series has. Consequently there is considerable uncertainty associated with the time required for a given amount of thorium to form its corresponding amount of lead. Also, the quantity of lead produced by a given quantity of thorium is not known with satisfactory accuracy. Therefore the presence of thorium in a mineral to be used for an age determination injects an element of uncertainty into the result, and as some thorium is always present this

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[6] Arthur Holmes, *Phil. Mag.*, [7] *2,* 1218 (1926).

[7] For a general discussion of the problem and methods used, see Arthur Holmes, *Phil. Mag.*, [7] *1,* 1055 (1926).

[8] See "Factors Involved in the Calculation of the Ages of Radioactive Minerals," Arthur Holmes, *Am. J. Sci.*, [5] 13, 327 (1927).

cannot be avoided. The formula now used contains a corrective factor to take care of the thorium content, but it is admittedly unsatisfactory.

(2) The fact that there is no actual measure of that proportion of the total lead which is known to have been produced from the uranium alone.

If this latter could be determined by actual experimental measurement, the thorium uncertainty could be disregarded and the only other uncertainty which would remain inherent and unmeasured in this method would be the existence of possible isotopes of uranium which might have disintegrated more rapidly in the past than the uranium which we know today.

If the lead in any given mineral being studied could be obtained in sufficient quantity and converted into some compound capable of giving lines in the mass-spectrograph, and if the intensity of these lines could be accurately measured, we would then have a direct experimental method for determining the actual amount of uranium lead present. The position of the line would identify it with the uranium lead isotope and its relative intensity would furnish a measure of its relative amount, and since the actual weights of uranium and lead would be known from the chemical analysis, we should then have all the information necessary for a direct comparison of the amounts of uranium and uranium-derived lead. Other isotopes of lead could be disregarded and no reliance need be placed upon assumed proportions figured from atomic weight determinations of lead associated with uranium and thorium, while any enrichment by ordinary lead would probably be revealed by an abnormally intense "207 line."

With these considerations in mind the author secured the cooperation of Dr. F. W. Aston in a proposed plan to convert samples of lead into some volatile compound such as lead tetramethyl and to endeavor to secure with it the identification and determination of any isotopes by means of his mass-spectrograph. In July, 1927, the author took a sample of lead tetramethyl[9] prepared from ordinary laboratory lead to Dr. Aston, who shortly thereafter carried out several experiments with this material. The results were most satisfactory and were first published by Dr. Aston in a brief note to Nature dated July 30, 1927.[10]

The experiments demonstrated very clearly the existence of the three anticipated isotopes, namely, those of masses 206, 207 and 208 in the approximate ratios of 4, 3 and 7, respectively, and also revealed the existence of other isotopes of lead, present in very small proportions, of which 203, 204 and 205 were indicated and 209 was reasonably certain.

The isotopes having been thus definitely separated and identified, the

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[9] Prepared for him by Mr. S. C. Witherspoon of the U. S. Chemical Warfare Service.

[10] Aston, *Nature*, 120, 224 (1927).

next step was to do the same for "radioactive lead," that is, lead which had been formed mostly or entirely by the radioactive disintegration of uranium and thorium.

For this purpose the author secured some very pure Norwegian bröggerite, a mineral containing considerable proportions of uranium and lead but a very small proportion of thorium. This material was carefully analyzed[11] for uranium, thorium and lead and a sufficient quantity "worked up" to yield about 15 g. of "radioactive lead" chloride.

Five grams of this material has been converted into lead tetramethyl[8] and sent to Dr. Aston, and he proposes to test this in the mass-spectrograph this autumn.

Meanwhile Dr. Aston has been developing an instrument for accurately measuring the relative intensities of the lines on the photographic plates from his mass-spectrograph. This will eliminate the personal equation from this determination and render it capable of exact repetition and comparison.

Since there is very little thorium, relative to uranium, in this broggerite, it is anticipated that these next experiments will show a very heavy line at 206, a very light one at 203, and possibly none at all at 207. It will be interesting to see whether any of the other isotopes show up stronger from this radioactive lead than they did with the ordinary lead.

From the data obtained from these two series of lead isotope measurements and from the determinations of the uranium, thorium and total lead of the broggerite, we hope to be able to determine directly the uranium: uranium lead ratio for this sample of broggerite and thereby secure a reliable estimate of its age, to determine definitely the thorium: thorium lead relationships with time, and possibly to throw some light on the other isotopes of lead and their origin. Experiments are now under way with the object of identifying and determining the isotopes of uranium. If these are successful the amounts involved at both ends of a radioactive series will be experimentally determined.

Summary

1. The significance of radioactivity in geologic problems is outlined.

2. A method for the determination of the radium in ordinary rocks is outlined and the radium content of seven representative granites of the eastern seaboard of the United States is given.

3. The geologic significance of the heat-producing power of radium is mentioned but the discussion of this should await the accumulation of more data.

4. A direct experimental means of determining the uranium and uranium-derived lead involved in an age determination is given.

[11] By Dr. C. N. Fenner of the Geophysical Laboratory.

5. The circumstances of the first determination of the isotopes of lead are given.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE JOHNS HOPKINS UNIVERSITY, H. A. METZ LABORATORIES, INC., AND THE U. S. BUREAU OF STANDARDS]

III. THE REVERSIBLE ADDITION OF ETHYL ALCOHOL TO PARA-BROMOBENZONITRILE CATALYZED BY SODIUM, POTASSIUM AND LITHIUM ETHYLATES[1]

BY C. N. MYERS AND S. F. ACREE

RECEIVED JULY 26, 1928 PUBLISHED NOVEMBER 6, 1928

Introduction

In earlier papers of this series it was shown that the quantitative data available in sixty-two examples of different types of chemical changes can apparently be coordinated on the theory of the activity of both the ions and the non-ionized forms of electrolytes. This hypothesis was advanced in 1907 by Acree[2] and by Senter,[3] who did not have the good fortune to put it on a firm experimental basis supplied later by the co-workers[8] of Acree, Lapworth, Arrhenius, Goldschmidt, Bredig, Dawson and more recently Bronsted.

In the study of many of these reactions the solutions were fairly concentrated and varied from $N/1$ to $N/32$. Certain physical properties were therefore different from those in very low concentrations and were partly the cause of those deviations from the mass law which are called changes in activity, abnormal salt effects, etc. In the more concentrated solutions the ionic mobilities, viscosities and other physical factors can neither be considered the same as in the dilute solutions nor used without proper modifications in calculating the percentage of ionization of the ethylate or other electrolyte present.

In view of these facts it seemed desirable to investigate the catalytic activities of sodium, potassium and lithium ethylates in very dilute solu-

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[1] In memory of Ira Remsen.

[2] (a) Acree, *Am. Chem. J.*, 37, 410 (1907); (b) 38, 258 (1907); (c) 43, 505 (1910); (d) 48, 352, 368, 378 (1912); (e) 49, 116, 127, 345, 369, 474 (1913); (f) THIS JOURNAL, 37, 1902, 1909 (1915); (g) 38, 2145 (1916); (h) 39, 376 (1917); (i) *J. Phys. Chem.*, 19, 381, 589 (1915); (j) 20, 118, 353 (1916).

[3] (a) Senter, *J. Chem. Soc.*, 94, 472 (1907); (b) Taylor and Arrhenius, *Mem. Nobelinst.*, 2, Nos. 34, 35, 37; (c) Goldschmidt, *Z. Elektrochem.*, 15, 6 (1909); (d) *Z. physik. Chem.*, 70, 627 (1910); (e) Bredig, *Z. Elektrochem.*, 18, 535, 543 (1912); (f) *Z. physik. Chem.*, 80, 129, 170, 211 (1913); (g) Stieglitz, THIS JOURNAL, 34, 1687, 1688, 1689, 1690, 1694 (1912); (h) 35, 1774 (1913); (i) Dawson, *J. Chem. Soc.*, 103, 2135 (1913); (j) 107, 1426 (1915); (k) 130, 2282 (1926); (1) Brönsted, THIS JOURNAL, 49, 2554 (1927).

tions ($N/32$ to $N/2048$) having practically constant viscosities, ionic mobilities, etc., in order to see whether a simple relation exists between the reaction velocities and the conductivities of the ethylates and harmonizes with the idea of the possible activity of both the ethylate ions and the non-ionized ethylate molecules. The reaction chosen was the reversible addition of ethyl alcohol to *p*-bromobenzonitrile to form p-bromobenzimido ethyl ester in which the concentrations of the catalyzing sodium, potassium and lithium ethylates are not appreciably altered with time. Since this work was finished[4] a similar quantitative study by Gruse and Acree[5] has been interpreted on the basis that $N/32$ to $N/512$ solutions of sodium, potassium, and lithium ethylates may cause the inversion of *l*- to *d*-menthone.

Let us now examine the reaction velocities and conductivities of the different ethylates to see whether one possible interpretation of this reaction is that both the ethylate ions and the non-ionized ethylate molecules are catalytically active. Let α represent the ionized fraction, $(1 - \alpha)$ the un-ionized portion of the ethylate present in the concentration of one gram molecule in V liters. Let K'_i and K''_i be the velocity constants for unit concentrations of ethylate ions in the two opposing reactions and K'_m and K''_m be the corresponding constants for un-ionized ethylates. Let A be the original concentration (0.15 N in all cases) of the nitrile and X be that concentration of the imido ester formed in t minutes. Let $K_i = K'_i + K''_i$ and $K_m = K'_m + K''_m$. Let K_V be the velocity constant of the reaction when the ethylate is α ionized in N/V concentrations and call K_N the value of VK_V. Let $K = X/(A - X)$ at equilibrium or at infinite values of t. Then the correct differential equation for expressing the reaction is

$$\frac{dx}{dt} = [K'_i\alpha + K'_m(1 - \alpha)](A - X)(1/V) - [K''_i\alpha + K''_m(1 - \alpha)][X/V] \qquad (1)$$

On integration and collection of terms, this equation becomes

$$\begin{aligned} K_N/V = K_V &= [K_i\,\alpha + K_m(1 - \alpha)]/V \\ &= (1/t)\log\frac{KA}{KA - (K + 1)X} \end{aligned} \qquad (2)$$

in which the constants are really complex, as shown earlier.[6] But the use of Equation (2) should really give constant values[2b,e,5] for K_V and K_N for any given concentration of ethylate when proper data for t, K, A and X are inserted. From *(2)* we readily get

$$K_N = K_i\alpha + K_m(1 - \alpha) \qquad (3)$$

for any ethylate. Our problem is to learn whether the value of K_i is

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[4] Acree, *Am. Chem. J.*, 49, 127, 369 (1913).

[5] Gruse and Acree, THIS JOURNAL, 39, 376 (1917).

[6] Acree, *Am. Chem. J.*, *38*, 1 (1907); Birge and Acree, THIS JOURNAL, 41, 1031 (1919).

constant for the ethylate ions, coming alike from all ethylates, and whether the values for K_m for the three unlike ethylate molecules are positive and of about the same order of magnitude as K_i, and perhaps differ among themselves because of the influence of the different metals sodium, potassium and lithium within such molecules. But even though we are testing this theory, as have Bronsted and Dawson,[7,3e,i,j,k] again, recently, we have also suggested other mechanisms[2e,5] and have scrutinized[Zb] various intermediate steps, the inter-relations of α, K_i, K_m and K_N,[8] and the possible activities of the cations and anions together.

Experimental Work

The *p*-bromobenzonitrile was prepared by treating cold diazotized pure *p*-bromoaniline slowly with a solution of solid cuprous cyanide dissolved in potassium cyanide. When distilled twice with steam, extracted in ether solution with dilute acid to remove any *p*-bromo-aniline and recrystallized from alcohol, a very white product is obtained with the melting point of 112.5° corrected. The ethyl alcohol was distilled twice from ignited calcium oxide as in earlier work[9,2i] and was 99.98% pure. Special experiments showed that the water need not be thoroughly removed as it does not here exhibit the marked influence shown in acid catalysis.

The concentration of the *p*-bromobenzonitrile was 0.15 *N* in all experiments. Sodium, potassium, lithium and thallium were dissolved in the pure cold alcohol and the ethylate solutions were made in duplicate and standardized as in the earlier work against hydrochloric acid accurately adjusted by gravimetric and volumetric methods. All volumetric glassware was accurately calibrated by the Bureau of Standards and by us. The very dilute ethylate solutions were made from the more concentrated ones by proper dilution with the pure alcohol while excluding the air. All ethylate solutions were rechecked just before use and were added to the nitrile solutions by means of a machine described earlier[10] for mixing solutions in proper amounts in flasks at the constant temperature of the reaction bath, 25°. When the desired reaction period had elapsed, the contents of the flasks were poured and washed into a slight excess of ice-cold standard hydrochloric acid in Erlenmeyer flasks and titrated back with standard alkali in the presence of methyl orange. By subtracting the known equivalent of the ethylate, the remaining acid used corresponded in cc. to the amount of imido ester, X, formed in t minutes or at equilibrium when A = 30.00 cc. expressed as possible complete transformation of the nitrile. The ester formed at equilibrium was about 27% of the maximum possible. The reaction velocity constants, K_V, were calculated by the special monomolecular formula in Equation (2), eliminating the equilibrium constants, and were then multiplied by V, the volume containing one gram mole of ethylate, to get K_N for a normal solution of ethylate having the α-ionization found for the $1/V$ concentration. Four tables, I, II, III and IV, are given here to show some of the representative data taken from the 75 tables marked out with sodium, potassium, lithium, thallium and tetramethylammonium ethylates. K_N and Kv are constant in all the tables. Data on the last two salts will be published when the conductivity and ionization measurements are completed. Tables V, VI, VII and VIII give the calculations of K_i and K_m and their relations to a and K_N for these three ethylates.

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[7] Brönsted and Dawson, *Z. physik. Chem.*, 108, 185 (1924); 117, 299 (1925).

[8] Ref. 2 e, p. 481, and above.

[9] Ref. 2 e, p. 493.

[10] Ref. 2 e, p. 490; 2 f, p. 1902.

Discussion and Interpretation of the Results

Tables V, VI, VII and VIII give a résumé of all the results obtained with sodium, potassium and lithium ethylates in concentrations varying from $N/32$ to $N/2048$. Similar results for much more concentrated solutions showing a salt effect will be given in another paper, together with data on added neutral salts. Each table gives the essential facts regarding V, a, $(1 - a)$, the duplicate and average values for K_N calculated for all the different time periods used with each concentration of ethylate, the "K_N calculated" from $K_N = \alpha K_i + K, (1 - a)$ by substituting therein the values found for K_i and K_m for each ethylate in Table VIII, the experimental "Error in Per Cent," the percentage of the reaction $a K_i$ due to the ethylate ions and the percentage of the reaction $(1 - a) K_m$ due to the non-ionized ethylate molecules. Table VIII gives the individual and average values for the K_i and K, calculated by solving all the pairs of simultaneous equations obtained by substituting the proper data for K_N and a in the equation $K_N = K_i a + K, (1 - a)$. A study of all the tables will bring out a number of points bearing on the theory and discussed briefly in the summary.

TABLE I

0.15 N p-BROMOBENZONITRILE AND $N/64$ POTASSIUM ETHYLATE AT 25°. $A = 30.00$

T	x	K_V
29.5	1.21	0.00241
43.5	1.73	,00241
58.0	2.23	.00241
71.0	2.66	.00242
85.0	3.08	.00242
103.0	3.57	.00243
	Av. K_V	.00242
	K_N =	.1549

TABLE II

0.15 N p-BROMOBENZONITRILE AND $N/512$ POTASSIUM ETHYLATE AT 25°. $A = 30.00$

T	x	K_V
244	1.33	0.000309
289	1.55	.000308
325	1.73	.000308
372	1.93	.000307
428	2.20	.000309
489	2.45	.000309
	Av. K_V	.000308
	K_N =	.1577

TABLE III

0.15 N p-BROMOBENZONITRILE AND $N/32$ SODIUM ETHYLATE AT 25°. A = 30.00

T	x	K_V
15	1.08	0.00499
19	1.35	.00501
29	1.95	.00502
35	2.29	.00499
42	2.63	.00500
49.5	3.00	.00501
55	3.23	.00500
	Av. K_V	.00500
	K_N =	.1600

TABLE IV

0.15 N p-BROMOBENZONITRILE AND $N/2048$ LITHIUM ETHYLATE AT 25°. $A = 30.00$

T	x	K_V
1303	1.12	0.000076
1363	1.16	.000076
1500	1.29	.000077
1571	1.35	.000078
1707	1.45	.000078
2807	2.14	.000076
4320	2.89	.000076
	Av. Kv	.000077
	K_N =	.1577

Table V

Experimental Values of K_N for Sodium Ethylate and p-Bromobenzonitrile and for the Ionization of Sodium Ethylate in absolute Alcohol at 25°

V	α	$1 - \alpha$	K_N	K_N, av.	K_N, calcd.	Error, %	Reaction due to a K_i, %	Reaction due to $(1 - a)$ K_m, %
32	0.5771	0.4229	0.1600, 0.1600	0.1600	0.1596	+0.20	58.07	41.91
64	.6777	.3223	0.1598, 0.1594, .1604, 0.1600	.1599	.1598	.00	68.10	31.90
128	.7723	.2277	.1600, 0.1600	.1600	.1601	.00	77.47	22.53
256	.8714	.1286	.1643, 0.1620	.1632	.1603	+1.81	87.30	12.70
512	.9449	.0551	.1602, 0.1597, .1603	.1600	.1604	−0.25	94.61	5.39
1024	.9819	.0181	.1604, 0.1608, .1603	.1605	.1605	.00	98.25	1.75
2048	.9819	.0021	.1577, 0.1556	.1567	.1606	−2.43	99.79	0.21

Table VI

Experimental Values of K_N for Potassium Ethylate and p-Bromobenzonitrile and for the Ionization of Potassium Ethylate in Absolute Alcohol at 25°

V	a	$I - a$	K_N	K_N, av.	K_N, calcd.	Error, %	Reaction due to α K_i, %	Reaction due to $(1 - a)$ K_m, %
32	0.5790	0.4210	0.1449, 0.1449, .1456	0.1451	0.1548	−6.27	60.93	39.07
64	.6739	.3261	.1549, 0.1555, .1542, 0.1555	.1550	.1566	−0.89	70.10	29.90
128	.7675	.2325	.1626, 0.1651	.1629	.1584	+3.03	78.93	21.07
256	.8546	.1454	.1687, 0.1697, .1702	.1695	.1601	+5.87	88.95	11.05
512	.9234	.0766	.1587, 0.1577	.1582	.1614	−1.98	93.19	6.81
1024	.9745	.0255	.1556, 0.1587	.1571	.1624	−3.28	97.75	2.25
2048	.9993	.0007	.1556	.1536	.1629	−4.48	99.93	0.07

Table VII

Experimental Values of K_N for Lithium Ethylate and p-Bromobenzonitrile and for the Ionization of Lithium Ethylate in Absolute Alcohol at 25°

V	α	$1 - \alpha$	K_N	K_N, av.	K_N, calcd.	Error, %	Reaction due to α K_i, %	Reaction due to $(1 - a)$ K_m, %
32	0.4553	0.5447	0.1187, 0.1184	0.1188	0.1232	−3.72	58.71	41.29
64	.5624	.4376	.1293, 0.1286	.1290	.1303	−1.00	68.58	31.42
128	.6775	.3225	.1382, 0.1357	.1370	.1390	−1.44	77.45	22.55
256	.7865	.2135	.1439, 0.1439	.1439	.1449	−0.65	86.21	13.79
512	.8855	.1145	.1562, 0.1567	.1564	.1514	+3.30	92.94	7.06
1024	.9579	.0421	.1505, 0.1516	.1511	.1561	−3.30	97.51	2.49
2048	1.0000	.0000	.1577	.1577	.1589	−0.76	100.00	0.00

TABLE VIII

EXPERIMENTAL VALUES OF K_i AND K_m FOUND FOR SODIUM ETHYLATE, POTASSIUM ETHYLATE AND LITHIUM ETHYLATE AND 0.15 N *p*-BROMOBENZONITRILE AT 25°

V	Sodium ethylate		Potassium ethylate		Lithium ethylate	
	K_i	K_m	K_i	K_m	K_i	K_m
V = 32 : V = 64	0.1596	0.1606	0.1889*	0.08347*	0.1715*	0.07439*
V = 32 : V = 128	.1600	.1600	.1848	.09042	.1637	.08090
V = 32 : V = 256	.1646	.1537	.1823	09383	.1602	.08382
V = 32 : V = 512	.1600	.1600	.1611	.12300	.1665	.07859
V = 32 : V = 1024	.1603	.1593	.1578	.12750	.1538	.08916
V = 32 : V = 2048	.1567	.1645	.1556	.13060	.1577	.08592
V = 64 : V = 128	.1602	.1592	.1825*	.09595*	.1594*	.08991*
V = 64 : V = 256	.1654	.1484	.1810	.10180	.1581	.09161
V = 64 : V = 512	.1600	.1596	.1591	.14700	.1661	.08131
V = 64 : V = 1024	.1605	.1586	.1572	.15090*	,1535	.09757
V = 64 : V = 2048	.1567	.1667	.1556	.15430	.1577	,09212
V = 128 : V = 256	.1674	.1851	.1805*	.10590*	.1574*	.09411*
V = 128 : V = 512	.1600	.1600	.1555	.18604	.1671	.07381
V = 128 : V = 1024	.1605	.1582	.1564	.18445	.1532	.10293
V = 128 : V = 2048	.1567	.1713	.1556	.18664	.1577	,09351
V = 256 : V = 512	.1576*	.2011*	.1456*	.30980*	.1709*	.04459*
V = 256 : V = 1024	.1601*	.1845*	.1544*	.25780*	,1529	.11086
V = 256 : V = 2048	.1566*	.2080*	.1555*	.25150*	.1577	.09306
V = 512 : V = 1024	.1607*	.1472*	.1565*	.17600*	.1480*	.22122*
V = 512 : V = 2048	.1566*	.2188*	.1555	.18980*	,1577	.14634
V = 1024 : V = 2048	.1562*	.3937*	.1555*	.21800*	.1577*	.00093
Average[a]	.1598	.1799	.1637	.16022	.15945	.09179
	(.159)	(.174)				
Average unmarked values	.1605	(.1616)	.1629	.14356	.15891	.09343
		.163				

[a] The averages given in the parentheses include some of the data left out of these tables because of lack of space.

Summary

1. The velocity of the reversible addition of ethyl alcohol to *p*-bromobenzonitrile at 25° has been measured in solutions of sodium, potassium and lithium ethylates in concentrations varying from $N/32$ to $N/2048$ to learn whether both the ethylate ion and the cations and the non-ionized ethylate molecules are catalytically active.

2. By substituting all the different values of α and K_N in the equation $K_N = K_i\,\alpha + K_m\,(1 - \alpha)$, we obtain a series of simultaneous equations whose solution gives us the corresponding individual and best average values for K_i and K_m for each ethylate in Table VIII.

3. It is found that the constants expressing the activity of the ethylate ion in unit concentration are the same for all three ethylates within the inherent experimental errors of about 2%. These values for K_i are about 0.161, 0.163 and 0.159 for sodium, potassium and lithium ethylates, respectively. The corresponding values for K_m are 0.163, 0.144 and 0.093.

This value of K_i is the sum of the activities of the ethylate ion in the two opposing reactions and K_m is the corresponding sum of the activities of the non-ionized metallic ethylate; both constants are independent of the equilibrium constant.

4. The substitution of these values of K_i and K_m for each ethylate in the above Equation (3) gives calculated values for K_N, which agree on the average with the experimental data within about 2% for all concentrations from $N/32$ to $N/2048$ (see Tables V, VI and VII).

5. By the use of this theory of catalysis and these values for K_i and K_m for the different ethylates, we can explain in a satisfactory manner the fact that the values of K_N are practically independent of a and dilution of sodium ethylate from $N/32$ to $N/2048$; change only slightly for potassium ethylate; increase 34% for lithium ethylate; and become substantially identical for all three of these alcoholate bases at $N/2048$ when only ethylate ions are present (see Tables V, VI and VII).

6. The above facts and studies with added halogen salts of these metals in dilute and concentrated solutions of ethylates show that in these dilute solutions any possible activity of the metal cations may be disregarded. In the more concentrated solutions a salt effect becomes apparent.

7. The broad equations have been developed for applying this theory of ion mole activity to reversible monomolecular reactions and determining the relation of the equilibrium and total velocity constants to the ionization of the catalyst and its separate ionic and molecular activities for the two opposing reactions. The same idea can be applied to all other reactions in pure or pseudo catalysis.

8. These conclusions agree with the application of this ion mole theory of catalysis to sixty-two quantitative studies of (a) reactions worked out by our associates and (b) our re-interpretations of the work of other investigators.

BROOKLYN, N. Y., AND WASHINGTON, D. C.

[COMMUNICATION NO. 366 FROM THE KODAK RESEARCH LABORATORIES]

THE FOGGING BY ACIDS AND OXIDIZING AGENTS AND THE INTENSIFICATION OF THE PHOTOGRAPHIC LATENT IMAGE[1,2]

BY E. P. WIGHTMAN

RECEIVED JULY 27, 1928 PUBLISHED NOVEMBER 6, 1928

It was discovered in 1901 by Luppo-Cramer that various strongly diluted acids produce latent fog on certain types of high speed plates,[3] especially if the solution contains potassium bromide. That sulfurous acid causes the same effect was noticed by him in 1908.[4] In addition to this it was found by him that acidified ammonium persulfate causes latent fog as well as acting as a desensitizing agent.[5] The explanation which Lüppo-Cramer gave for these phenomena was that the acids and oxidizing agents tend to destroy the ripening germs, or the latent image specks, on the grains, producing a more dispersed condition of the silver in them. This tends at first, he says, to make the speck more active in producing developability.[6]

Recently, the writer offered a different explanation for the action of certain oxidizing agents and acids in producing latent fog.[7]

Liippo-Cramer has since questioned this viewpoint[8] and reiterates his own hypothesis. He has also given some evidence which he considers supports his own view and is in opposition to that of the writer. The present paper offers a further discussion of the writer's hypothesis and some additional experimental evidence in its support. It also presents an explanation of the opposing facts cited by Liippo-Cramer.

The hypothesis of the writer was, and still is, that since most plates and films contain an excess of soluble bromide (KBr), the oxidizing agents give with this some free bromine, a trace of which remains in the gelatin after the excess oxidizing agent is destroyed and washed away. It then gradually returns to that portion of the silver sulfide sensitivity speck which had not been affected by the oxidizing agent, and reacts in a manner described in a previous paper on the intensification of latent image by hydrogen peroxide.[9]

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[1] In memory of Ira Remsen.

[2] Presented at the Convention of the American Chemical Society, September, 1928.

[3] Liippo-Cramer, *Phot. Korr.*, 38, 159 (1901).

[4] Liippo-Cramer, *ibid.*, 45, 552 (1908).

[5] Lüppo-Cramer, *ibid.*, 39, 563 (1902).

[6] For the previous literature covering this subject and for a more complete discussion of the hypothesis see Lüppo-Cramer (a) "Grundlagen der phot. Negativverf," Eder's Handb Vol. II, Pt. 1, Halle, 1927, p. 340; (b) *Camera* (*Luzern*), 3, 14 (1924).

[7] E. P. Wightman, *Brit. J. Phot.*, 74, 447 (1927); see W. Clark, *ibid.*, 74, 121 (1927).

[8] (a) Liippo-Cramer, *Z. wiss. Phot.*, 25, 121 (1928); (b) *ibid.*, 25, 129 (1928); (c) *Phot. Korr.*, 64, 49 (1928).

[9] E. P. Wightman and R. F. Quirk, *J. Franklin Inst.*, 204, 731 (1927).

That very dilute bromine solution causes the formation of latent fog was discovered by Lüppo-Cramer,[10] and was more recently verified by the writer, who found that it also causes, in a concentration of 1:200,000, marked intensification of latent image. In addition to this, it was observed, as S. E. Sheppard and others had already stated,[11] that bromine is strongly retained by gelatin, even when the latter was set and washed with sodium bicarbonate solution or with a solution of oxalic acid containing a small amount of manganous sulfate, the bromine which remained after this washing having the power to react with colloidal silver to give colloidal silver bromide.

That potassium iodide solution without acid present, and more so when it is present, soon turns yellow with the formation of free iodine is a well-known fact. Light is no doubt a catalytic agent in this reaction for even in a dimly lighted room the decomposition seems to take place slowly.

Light also has an effect on the acid solutions of the' alkali bromides. One per cent. potassium bromide solution containing sulfuric acid to $P_H = 3$, which when freshly made shows no trace of bromine, gives a definite free bromine reaction after standing for a few hours.[12]

Such a solution causes fog on the photographic plate, as Liippo-Cramer has previously discovered;[6b] although if present during exposure it also causes a lowering of sensitivity. Neutral bromide under corresponding conditions causes lowering of sensitivity without the fog formation. When the plate is bathed before or after exposure with either acid or neutral bromide, there is no sensitivity decrease or latent light image alteration but merely a fog effect from the acid bromide.

As an argument against the hypothesis of the writer that latent fog is produced through bromine formation, Liippo-Cramer cites the fact that a sulfurous acid solution or sulfur dioxide gas causes fog and that, obviously, bromine would not be formed in the presence of such a solution.[4,8c] When potassium bromide also is added the fog is increased, he found.

Another very interesting fact which he observed was that while ordinary plates of various kinds when bathed for two minutes in a solution containing 20 g. of potassium bromide and 1 cc. of concentrated sulfurous acid per liter showed marked fog on development in metol–hydroquinone; several different brands of ortho-chromatic plates showed even less fog than the control plate which was given no treatment before development.[8a]

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[10] Lüppo-Cramer, "Phot. Probleme," Halle, 1907, p. **132.**

[11] See S. E. Sheppard, "Gelatin in Photography," Monograph No. 3, Vol. 1, 1923, **pp. 153–156.**

[12] E. P. Wightman and S. E. Sheppard, "Effect of Certain Salts on the Photographic Sensitivity," paper presented at the Detroit Meeting, American Chemical Society, September, 1927, in press.

The same phenomenon was observed with special plates to which various color-sensitizing dye solutions were added for two minutes prior to the $KBr-H_2SO_3$ solution treatment. Even 0.1% hydrogen peroxide for two minutes did not cause fog on the dye-impregnated plates.

Recently, in another connection, the writer found that ordinary air containing up to 0.08% by volume of sulfur dioxide did not cause the formation of latent fog or appreciable change of sensitivity of either an Eastman Speedway plate or of a W. and W. panchromatic plate in fifteen hours of treatment; whereas an even less quantity of sulfur dioxide in air saturated with moisture in only a few hours caused bad fog on similar plates. Moderately dry air containing 0.16% sulfur dioxide caused a slight increase in sensitivity of a pan plate but no increase in fog.

It seems very likely that the action of sulfurous acid in producing fog is first an absorption into the plate and then an increase of solubility of the silver bromide grains on the surface. A certain amount of silver bromide goes into solution; the amount may be very minute, only a few molecules or ions. Then this in the presence of some of the larger sensitivity specks acting as nuclei oxidizes the sulfurous acid to sulfuric acid and a trace of silver deposits on the specks, increasing the size of the largest ones to the developable condition, thus[13]

$$2Ag^+ + 2Br^- + 2H^+ + SO_3^{--} + H_2O = 2Ag + 4H^+ + 2Br^- + SO_4^{--}; \quad \Delta F = -40{,}216 \text{ cal.}$$

The addition of potassium bromide increases this effect by increasing the solubility of the silver halide.[14] When the sensitizing dye is present it forms a protective layer, preventing the silver halide from going into solution and in some cases absorbing the sulfur dioxide.

As was said above, the author's hypothesis was based partly on a previously proposed mechanism of latent image intensification by hydrogen peroxide.[9] In a paper presented before the recent International Congress of Photography, some additional evidence for this mechanism has been set forth.[15]

It was found, for instance, that a latent image produced by x-rays on either fast or slow plates cannot be intensified by hydrogen peroxide. A. P. H. Trivelli had suggested that this should be the case since "an x-ray quantum of energy is of the order of 100 to 1000 times greater than

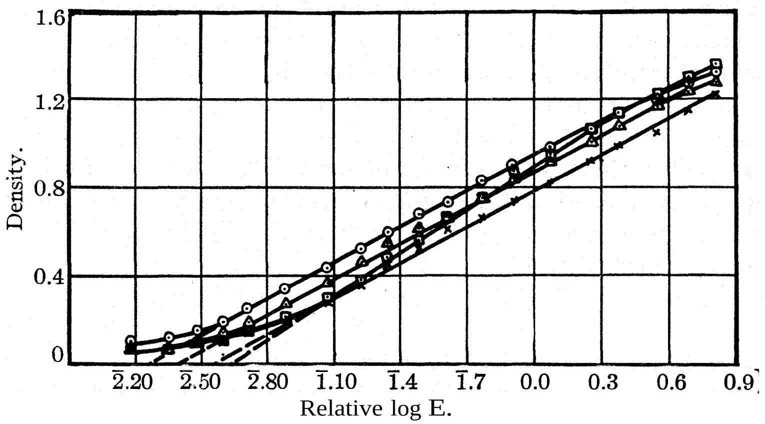
[13] The reason a sulfite containing developer does not do this is probably because of the interstabilizing effect of the developer reducing agent on the sulfite and vice *versa.*

[14] The solubility would be depressed only where very low concentrations of soluble bromide were used, that is, less than that already present in most emulsions. It is true that activity of silver decreases as solubility increases, but complex ions containing silver are formed which also may be reduced to metallic silver.

[15] E. P. Wightman and R. F. Quirk, "Intensification of the Photographic Latent Image," to be published in the Proceedings of the Seventh International Congress of Photography.

that of visible actinic light, so that even the smallest latent image speck produced by it is probably greater in size than that necessary to induce developability, and hence if there are no intermediate sized specks (as we had supposed to be present in the case of the ordinary light) there should be no intensification of an x-ray latent image."

Second, since the hypothesis supposed the formation of bromine by the acid–peroxide from the soluble bromide in the plate, the presence of a bromine acceptor along with the hydrogen peroxide should prevent or lessen latent image intensification. Acetone semicarbazone which Svedberg, Schunk and Andersson had used previously as such an acceptor to prevent solarization on the photographic plate[16] was tried. It was found, as anticipated, that since acetone semicarbazone increases developability of latent image to some extent in the middle and higher exposure regions, it does not prevent entirely intensification of latent image by hydrogen peroxide, but does lessen it instead of adding to it, as would be expected if there were no bromine absorbing action. The result is shown in Fig. 1.



□, Control, acetone semicarbazone treated; △, H_2O_2 and acetone semicarbazone treated; X, control, H_2O treated; ⊙, H_2O_2 treated.

Fig. 1.—Effect of acetone semicarbazone on latent image intensification by H_2O_2.

Third, it has been found that an organic peroxide, benzoyl peroxide, also intensifies latent image, although to a less extent than hydrogen peroxide. One reason for the less vigorous action is, no doubt, the low solubility of the former in water.

We have now found some further evidence for our viewpoint. An Eastman Speedway plate was exposed behind an Eder-Hecht wedge and then one-half of it lengthwise was treated with a solution containing 1 part

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[16] T. Svedberg, O. H. Schunk and H. Andersson, *Phot. J.*, 64, 272–274 (1924).

of chromic acid and 0.4 part of sulfuric acid in 500,000 of water. The treated half was bathed for one minute in 0.1% bicarbonate solution and the two halves were developed together. There was a distinct intensification of latent image, about two steps or 4° E. H., and a faint increase in fog on the treated plate as compared with the control. This experiment will be repeated varying the concentration of oxidizing agent and time of treatment, also using some other oxidizing agents.

In one of Lüppo-Cramer's recent papers,[8b] he shows an interesting result obtained by treating a Kranz-Ultra-rapid plate which had been exposed behind a neutral gray wedge tablet with hydrogen peroxide for

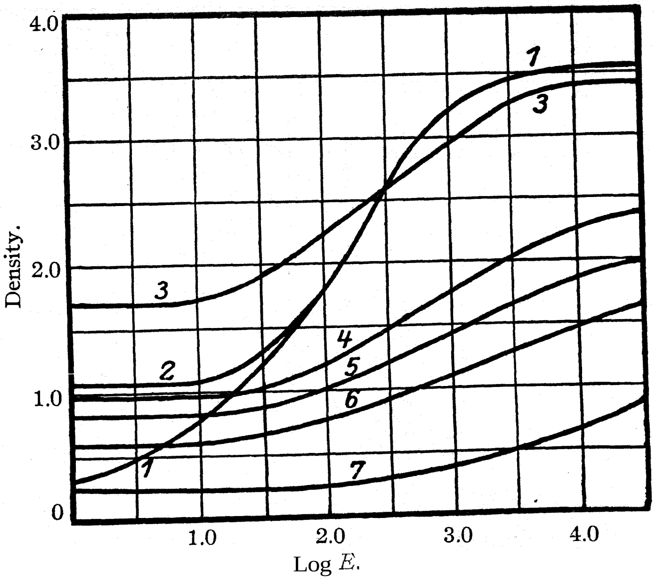

Fig. 2.—What Lüppo-Cramer calls intensification of latent image (Curves 2 and 3) and reversal of latent image (Curves 4 to 7) by hydrogen peroxide.

varying lengths of time as follows: 1—control, no treatment; 2—15 minutes in 1% H_2O_2 solution after exposure; 3—3 to 7—fifteen, thirty, sixty, ninety and two hundred and ten minutes in 5% H_2O_2 solution. The result is shown in Fig. 2. In discussing it he says: "Already in Curve 2, but outspokenly in 3, we find besides the intensive fog formation, at the beginning of the rise of the curves, what I had already described in principle in 1915,[17] and what Wightman and Quirk recently designated as intensification of latent image."

It would seem from this that there is a misunderstanding of what the latter investigators call intensification of latent image, since it was stated

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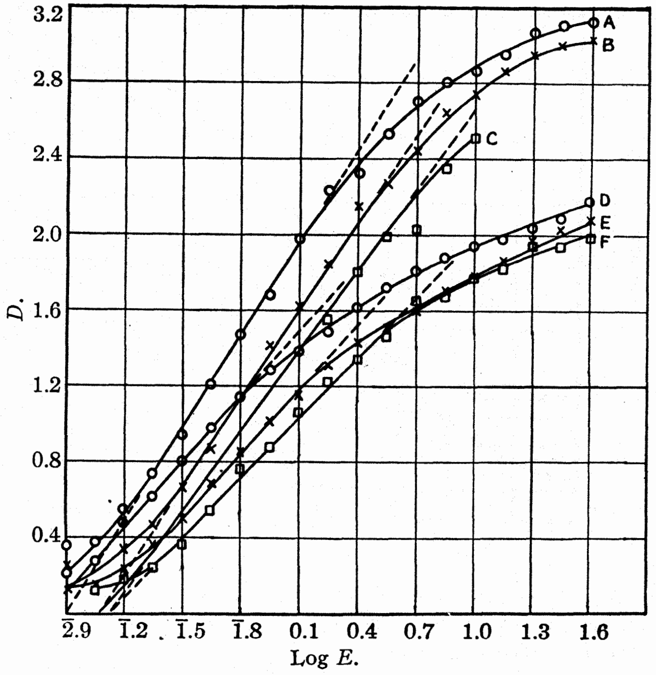
[17] Lüppo-Cramer, *Phot.* Korr., 52, 135 *(1915).*

in their paper that the effect is produced by such a concentration of hydrogen peroxide as causes a practically negligible amount of fog. This happens to be, in the case of an Eastman Speedway plate, with which the Kranz-Ultra-rapid should more or less correspond, a concentration of about 0.008%, and the time of treatment is one minute. The intensification extends through most of the exposures. A comparison of Fig. 2 with Fig. 3, taken from Wightman and Quirk's paper, will show the fundamental difference. The entire effect in Curves 2 and 3, Fig. 2 (below where 3 crosses 1 and 2) appears to the writer to be a fog effect and not that of intensification as defined.



□, Blank; ×, H_2O treated; ○, H_2O_2 treated.

10-Minute development	Speed	λ	4-Minute development	Speed	λ
A, H_2O_2	876	1.60	D, H_2O_2	1102	1.12
B, H_2O	593	1.53	E, H_2O	593	1.15
C, Blank	516	1.42	F, Blank	516	1.05

Speed ratio: A/C = 1.70, B/C = 1.15, D/F = 2.15, E/F = 1.15

Fig. 3.—Intensification of latent image, high speed emulsion.

The reversal effect in the remaining curves in Fig. 2 is very interesting. As mentioned in a note in the British Journal of *Photography*[18] it seems likely that Lüppo-Cramer's idea of an increased dispersity of the latent image can be used to explain the reversal effect.

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[18] E. P. Wightman, *Brit. J. Phot.*, **75**, 189 (1928).

Summary

Further arguments are given in support of the viewpoint of Wightman that the cause of latent fog formation from the action of certain oxidizing agents and acids is probably formation of bromine from the soluble bromide in the plate, with which hypothesis Lüppo-Cramer is in disagreement. The hypothesis was originally based on the fact, discovered by Lüppo-Cramer himself, that very dilute bromine solution causes fog and on a previously proposed mechanism of latent image intensification and fog formation by hydrogen peroxide, further evidence for which is now presented.

ROCHESTER, NEW YORK

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

OBSERVATIONS ON THE RARE EARTHS. XXX. STUDIES IN THE ABSORPTION SPECTRA[1]

BY LAURENCE L. QUILL AND PIERCE W. SELWOOD WITH B. S. HOPKINS

RECEIVED JULY 28, 1928 PUBLISHED NOVEMBER 6, 1928

The purpose of this investigation was to make a careful examination of the effects of a common ion on the absorption spectra of solutions of certain rare earth salts. The spectra of the colored rare earths are an invaluable aid for the rapid estimation of these elements, and although there are several references in the literature to the fact that the absorption bands are displaced by the presence of other substances, yet there appears to be little definite information available as to the precise nature of the changes to be observed. These studies were therefore undertaken with the intention of determining the conditions under which the absorption spectra may be relied upon for the analysis of rare earth mixtures.

An extensive bibliography of the literature prior to 1920 is given by Yntema.[2] Since then methods of quantitative spectral analysis for the rare earths have been suggested by Inoue[3] and by Delauney.[4] Irregularities in the absorption spectrum of neodymium have been observed by Prandtl[5] as mentioned in his criticism of the discovery of illinium.

Delauney, on the assumption that Beer's Law is observed by rare earth salt solutions, has suggested a method of quantitative analysis based on the variation in the width of certain of the absorption bands with change in concentration. He made analyses of solutions of praseodymium and neodymium nitrates and his results were accurate to 5%, which is better

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[1] In memory of Ira Remsen.

[2] Yntema, THIS JOURNAL, 45,907 (1923).

[3] Inoue, Bull. *Chem. Soc., Japan,* 1,9 (1926).

[4] Delauney, *Comfit. rend.,* 185, *354* (1927).

[5] Prandtl, *Z. angew. Chem.,* 39,897 (1926)

than can be done without a very careful equivalent weight determination. He also states that any changes in the neodymium nitrate bands on the addition of nitric acid are within the limits of experimental error.

Experimental

Procedure.—The absorption spectra were photographed on a Hilger quartz prism spectrograph with a dispersion of approximately 20 cm. Trichromatic "Spectrum Process" plates were used and the source of illumination was a tungsten ribbon incandescent lamp which gave a steady light and a continuous spectrum. The iron arc was used as standard of reference. The absorption spectra were exposed for five minutes in all cases. A Baly absorption cell with quartz windows was used throughout the investigation. The neodymium was atomic weight purity material which had been prepared in this Laboratory. The praseodymium contained about 1% of lanthanum. The samarium (except that purposely mixed with neodymium) was a few fractions removed from atomic weight material. The erbium was relatively impure, being several fractions removed from atomic weight material and containing thulium and yttrium. The various solutions were made up by weighing the freshly ignited oxides and dissolving them in nitric or hydrochloric acid as the case might be and evaporating just to dryness several times. The dry salts were then dissolved in water or in acid of the desired strength and made up to the required concentration in a volumetric flask. With the less basic samarium and erbium it was impossible to remove the last trace of acid without hydrolysis taking place. The trace left was insufficient to affect the absorption bands appreciably.

Neodymium Nitrate.—In the first part of the work 0.1 N neodymium nitrate solutions were prepared in various concentrations of nitric acid. The effect with the lower acid concentrations is very slight. Nevertheless, there is an unmistakable shift of 3 or 4 Å. toward the red in the 5700–5800 Å. region and the three bands visible tend to merge into one another. No change is observed in the 5200 Å. region, while the sharp band at 4272 Å. becomes very faint and is shifted about 1 Å. toward the red. As the acid concentration increases, the shifts become more and more pronounced until in 15.8 N acid the appearance of the spectrum is greatly altered. Spectrum No. 2 shows 0.1 *N* neutral $Nd(NO_3)_3$ through 5 cm. of solution and No. 1 shows 0.1 N $Nd(NO_3)_3$ in 15.8 N nitric acid through the same depth of solution. The three bands at 5710–5726 Å., 5731–5763 Å. and 5775–5780 Å. have merged together to 5758–5800 Å., while the region 5701–5758 Å. is only slightly absorbed.[6]

With increasing concentrations of neodymium the effect of adding nitric acid is similar, with, however, the addition of several new bands. Spectra 5, 6, 7, 8 and 9 show 0.5 *N* $Nd(NO_3)_3$ in acid concentrations of 15.8, 10, 5, 2.5 N and neutral, respectively, through 5 cm. of solution. A new band is to be seen in No. 5 at 5970 Å. In still more concentrated neodymium the addition of acid brings out a line between 5360 and 5370 Å. This is very plain in No. 3, while No. 4 shows the appearance of the neutral salt at the same concentration. These bands at 5970 Å. and 5360–5370 Å. are entirely distinct from any hitherto mentioned in the literature and might be mistaken by an inexperienced worker for bands characteristic of praseodymium and holmium, respectively. In addition to these changes the following were observed: the band at 6875–6908 Å. is spread out and shifted toward the red, while the band at 6774–6806 Å. is broadened and shifted toward the violet. The 5800 Å. region is broadened and shifted

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[6] The figures given for the positions of the bands refer to the outer edges, rather than to the centers, and owing to the diffuse nature of the absorption edges the measurements are only approximate.

nearly 50 Å. toward the red. The bands in the region 5100–5200 Å. are in general broadened and shifted more to the violet than to the red. The band at 4744–4762 Å. is shifted to the violet to 4726–4763 Å. and becomes very faint; the band at 4683–4693 Å. is shifted to 4698–4709 Å. and the 4272 Å. band is broadened and shifted toward the red

The next examination was made on the influence of magnesium nitrate on the absorption bands of neodymium nitrate. This suggested itself not only because magnesium nitrate is very soluble but also because it is commonly associated with the cerium group rare earths in the form of the double magnesium nitrates used in fractional crystallization. The solutions, all of which were neutral, were made up as before with the addition of the calculated amount of magnesium carbonate, which was dissolved in as little nitric acid as possible. The 10 N $Mg(NO_3)_2$ solution was, of course, considerably supersaturated and after introduction of the hot solution to the absorption cell it was carefully cooled to room temperature and the photograph was taken without delay. The absorption bands of the neodymium were shifted by the magnesium nitrate in the same manner as by nitric acid. In a 0.25 *N* $Nd(NO_3)_3$ solution containing 0.25 N $Mg(NO_3)_2$, which corresponds to the composition of the neodymium double magnesium nitrate, the changes are slight but readily apparent. The most noticeable effect is the broadening of the bands in the 5800 Å. region.

While the changes produced by magnesium nitrate are similar to those produced by nitric acid, they are slightly more pronounced for a given normality. Spectrum No. 10 is of 0.5 *N* $Nd(NO_3)_3$ in 10 *N* HNO_3 while No. 11 is of 0.5 *N* $Nd(NO_3)_3$ in 10 *N* $Mg(NO_3)_2$. Both pictures were taken on the same plate and through the same depth of solution. The magnesium nitrate produces a slightly greater broadening of the 5800 Å. band, while the bands at 5089–5113 Å. and at 5190–5254 Å. are smaller, particularly the former. The differences become more apparent with solutions more dilute with respect to neodymium.

It was next desired to examine the influence of the nitrate of a tervalent metal and especially that of other rare earths on the absorption bands of neodymium nitrate. The extraordinary difficulty attendant upon the preparation of the pure rare earths made it undesirable to mix such pure salts as were at hand. However, by mixing lanthanum, of which a considerable amount was available, with neodymium, no very great damage was done because although these elements lie close together in the solubility series it is possible to introduce cerous salts between them in a fractionation series and so quantitatively separate the lanthanum from the neodymium. The cerium may then be removed by oxidation, lea ing pure lanthanum on the one hand and pure neodymium on the other. It was also desirable to examine the effect of a colored rare earth and especially that of samarium because it occurs close to neodymium in the natural sequence of the elements and because of the bearing it has upon the control of concentration of illinium in neodymium and samarium rich fractions. On no account was it desired to mix pure neodymium with pure samarium, but fortunately a large quantity of material was available which was free from neodymium and was composed chiefly of samarium and gadolinium with traces of europium, terbium and holmium. The chief interest lay in the 5800 Å. region and this material was free from absorption bands in that vicinity. Both lanthanum and samarium solutions were made up 0.5 *N* in $Nd(NO_3)_3$ and 5 *N* in $La(NO_3)_3$ and $Sm(NO_3)_3$, respectively. In order to show which bands are characteristic of samarium itself, a photograph (No. 12) was taken of its spectrum before the addition of the neodymium. Spectrum No. 13 shows the neodymium and samarium, while No. 14 shows the neodymium and lanthanum. As lanthanum has no bands in the visible region it was not necessary to photograph its spectrum alone. Spectrum No. 15 shows 0.5 N $Nd(NO_3)_3$ in the pure state. The differences between the changes caused by lanthanum nitrate and by samarium nitrate are slight and unimportant but they both produce changes similar to those brought about by the addition of magnesium nitrate. Compared with the pure neodymium it is found that the bands in the extreme red have disappeared, the 5800 Å. region is extended about 50 Å. toward the red, the 5200 and 5100 Å. bands are narrower, the 4690 Å. band has disappeared, while the 4272 Å. band is shifted slightly toward the red.

Several investigators have assumed that Beer's Law is observed by the rare earth salt solutions. In order to show conclusively that this is not the case, a comparison was made on the same plate of two neutral neodymium nitrate solutions, one 0.025 N the absorption spectrum of which was taken through a depth of 500 mm. of solution, and the other 10 N which was taken through a depth of 1.25 mm. The two solutions should be of equivalent thickness, that is, the incident illumination strikes an equal number of neodymium atoms or ions as the case may be in the two solutions. The changes in the absorption bands are very pronounced. Spectrum No. 16 shows the concentrated solution and No. 17 the dilute solution. In the former the 5800 Å. region has been extended about 30 Å. toward the red. The 5209–5231 Å. band is narrower and shifted toward the red. The 5198–5208 Å. band has disappeared, while the faint bands at 5082–5092 Å. and 5108–5131 Å. are more diffuse and much fainter. The 4744-4757 Å. and 46834692 Å. bands have disappeared. The 4272 Å. band is much fainter and shifted toward the red. In addition to these changes it is possible in the case of the concentrated solution to see a faint band at 5970 Å. (compare p. 2930) provided a spectroscope of low dispersion is used. This band does not appear to have been reported hitherto for neutral neodymium nitrate.

During the course of the work several absorption bands were photographed in the ultraviolet. These bands have received little attention from investigators in this field and are probably identical with the bands recently reported by Gardiner.[7] Inoue reports no bands for neodymium chloride in the ultraviolet.

Praseodymium Nitrate.—Since nitric acid had such a marked effect on the absorption spectrum of neodymium nitrate, it was decided to investigate its effect on other rare earth nitrates. The changes observed in the case of praseodymium were not as pronounced, in general, as in the case of neodymium. Spectrum No. 18 records the absorption of a 5 cm. layer of 1.0 N $Pr(NO_3)_3$ in the presence of 15.8 N HNO_3, while No. 19 is a neutral solution of the same concentration and depth. The band at 5985–5840 Å. suffers a marked decrease in intensity and is narrowed approximately 48 Å. to 5969–5872 Å. The band at 4839–4799 Å. is shifted slightly toward the red, the more refrangible edge being more so than the other. The band at 4725–4629 Å. is narrowed 35 Å., and the band at 44974380 Å. is narrowed 30 Å. The absorption edges were in all cases more diffuse. In the case of 0.1 N $Pr(NO_3)_3$, the shifts and variations in intensity were similar to those in the more concentrated solutions.

Samarium Nitrate,—The effect of free nitric acid upon the absorption spectra of samarium nitrate was also studied. Samarium does not exhibit as strong absorption in the visible region as do neodymium and praseodymium, except in highly concentrated solutions. It shows very strong absorption, however, in the violet and ultraviolet, especially from 3000 Å. to 4400 Å. The spectra of samarium reproduced here do not show below 4100 Å. but marked changes were observed as low as 3000 Å. upon the addition of nitric acid. Spectrum No. 20 is the absorption of 1.0 N $Sm(NO_3)_3$ in 15.8 N HNO_3, while No. 21 is that of the neutral solution through the same depth, 5 cm. The acid decreases the intensity of absorption in the 4823-4736 Å. region, as is also the case with the 4661–4613 Å. band. The two bands in the blue ordinarily listed as 4177 Å. and 4154 Å. are blended together in the acid solution, the resulting absorption area being about 20 Å. less in width than the total width of the two original bands.

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[7] Gardiner, J. *Chem. Soc.*, 1926, 1518.

The 4154 **if.** band may be said to have shifted toward the red in forming the new band, The **4071** Å. and **4013** Å. bands are also blended into one by the acid. The decrease in width is marked by a shift toward the blue of the less refrangible edge. In general the absorption is less in the acid than in the neutral solution. Observations on other depths of solutions agree with the above, with other bands of less persistence appearing in the neutral solutions and also being changed by the acid.

Erbium Nitrate.—Erbium exhibits, with neodymium, the largest number of absorption bands of any of the rare earth elements. It seemed advisable, therefore, to study the effect of excess nitric acid on erbium nitrate, since the acid caused such decided shifts in the case of neodymium. Although the erbium material was impure, and the presence of foreign salts does affect the absorption spectrum of an element, the presence of nitric acid caused a marked change. As seen in spectrum No. **22,** there is a slight decrease in intensity of the band occurring at 6536–6486 **A.** with a shift toward the blue of about **5** Å. in the **15.8** N acid as compared with the slightly acid solution shown in No. **23.** The bands in the 5350–5400 Å. region are broader and more diffuse in the acid solution and are shifted toward the blue. The same is true of the 5170–**5240** Å. region, the absorption area being increased about **40** Å. and shaded off on both sides. The 4860–4878 Å. band is increased in width to 4830–4920 Å. with the heaviest absorption being shown from 4830–4855 Å. This is a decided shift toward the blue of the maximum of absorption and a broadening of the band at the same time. The 4495–**4500** Å. is shifted toward the violet about **10** Å. Whenever two bands are in close proximity in the neutral solution, they are blended together by the acid.

Neodymium Chloride.—In order to determine whether or not the changes in the absorption bands were peculiar to the nitrates, the effect of concentrated hydrochloric acid was studied on neodymium chloride. The changes in this case were different from what they were for neodymium nitrate, showing that the effect of different acids upon the absorption of a rare earth element is not the same. The concentration of the solution with respect to neodymium was that of a saturated solution of neodymium chloride in **12** N hydrochloric acid. As is the case with most chlorides, the solubility of the rare earth chlorides is repressed to a very considerable extent by the presence of free hydrochloric acid. The concentration of the neodymium chloride was approximately **0.4** N. Spectrum No. **24** represents the absorption of a neutral solution of **0.4** N $NdCl_3$ **5** cm. thick, and No. **25** is that of the same concentration of $NdCl_3$ in **12** *N* HCl. In the extreme red the acid brings out a new band at 6821–6848 Å. The change in the 5800 Å. region is very pronounced. The band shades off toward the red with an increase in width of between 90 and 100 Å. The **5200–5220** **if.** band is shaded off toward the red by the acid. The **5123** Å. band is narrowed about 5 Å. The **5091** Å. band is very much fainter and seems to be shifted to the blue slightly. The **4754** Å. band is fainter in the acid solution and is broadened toward the red. The **4691** Å. band is repressed and shifted toward the red. In the neutral solution there is ***only*** one distinct band at **4271** Å., while in the acid solution there are three faint, fuzzy bands at **4330** Å., **4297** Å. and **4271** Å.

Discussion of Results

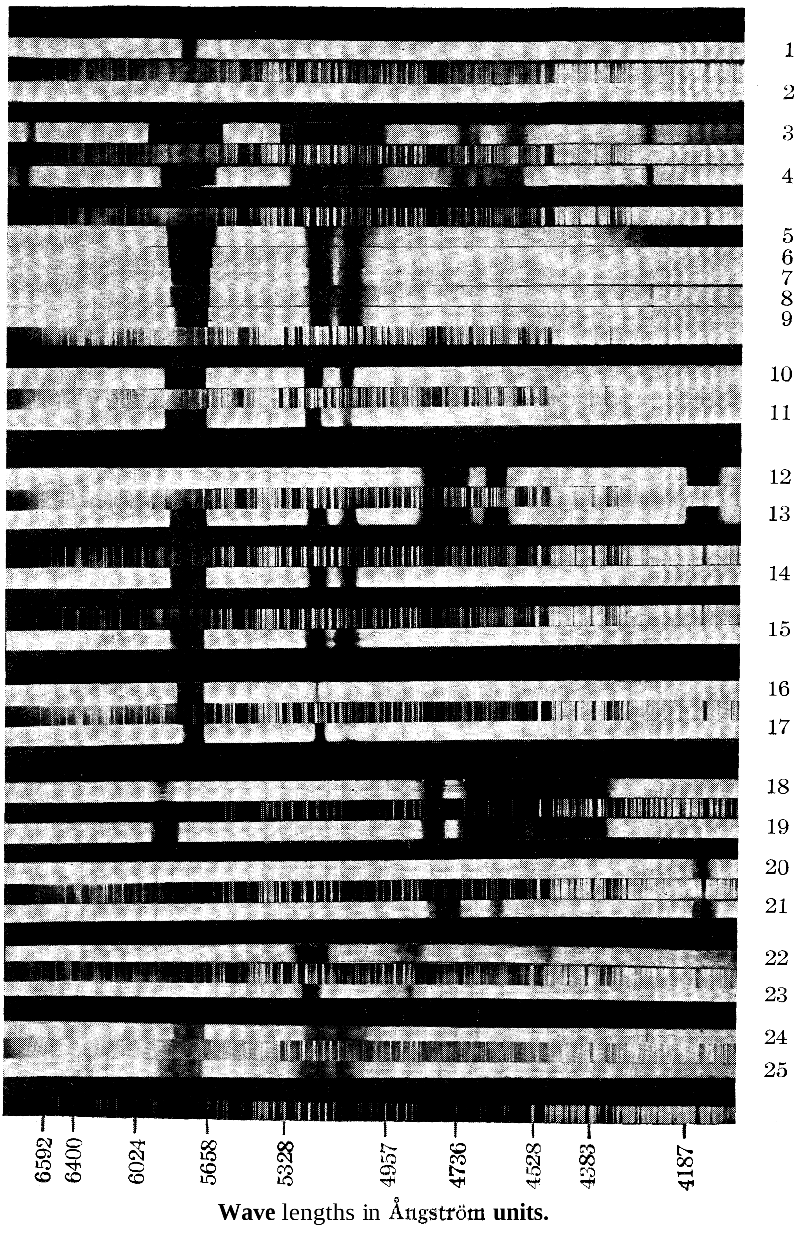
In view of the present unsatisfactory state of our knowledge of atomic structure, it seems unwise to attempt any interpretation of **the** results presented here in terms of one of the current theories. It is known that even in the case of strong electrolytes the oppositely charged ions in a solution may approach close enough to one another to cause distortion of the outer electron shells. It is probable that this distortion may be

DESCRIPTION OF PLATE

All solutions taken through a 5cm.
layer unless otherwise designated.

1. 0.1 N $Nd(NO_3)_3$ in 15.8 N HNO_3
2. 0.1 N $Nd(NO_3)_3$ in neutral solution.
3. 1.0 N $Nd(NO_3)_3$ in 15.8 N HNO_3.
4. 1.0 N $Nd(NO_3)_3$ in neutral solution.
5. 0.5 N $Nd(NO_3)_3$ in 15.8 N HNO_3.
6. 0.5 N $Nd(NO_3)_3$ in 10 N HNO_3.
7. 0.5 N $Nd(NO_3)_3$ in 5 N HNO_3.
8. 0.5 N $Nd(NO_3)_3$ in 2.5 N HNO_3.
9. 0.5 N $Nd(NO_3)_3$ in neutral solution.
10. 0.5 N $Nd(NO_3)_3$ in 10 N HNO_3.
11. 0.5 N $Nd(NO_3)_3$ in 10 N $Mg(NO_3)_2$.
12. 5.0 N $Sm(NO_3)_3$ for reference.
13. 0.5 N $Nd(NO_3)_3$ in 5 N $Sm(NO_3)_3$.
14. 0.5 N $Nd(NO_3)_3$ in 5 N $La(NO_3)_3$.
15. 0.5 N $Nd(NO_3)_3$ in neutral solution.
16. 10 N $Nd(NO_3)_3$ through 1.25mm. layer.
17. 0.025 N $Nd(NO_3)_3$ through 500mm. layer.
18. 1.0 N $Pr(NO_3)_3$ in 15.8 N HNO_3.
19. 1.0 N $Pr(NO_3)_3$ in neutral solution.
20. 1.0 N $Sm(NO_3)_3$ in 15.8 N HNO_3.
21. 1.0 N $Sm(NO_3)_3$ in slightly acid solution.
22. 1.5 N $Er(NO_3)_3$ in 15.8 N HNO_3.
23. 1.5 N $Er(NO_3)_3$ in slightly acid solution.
24. 0.4 N $NdCl_3$ in neutral solution.
25. 0.4 N $NdCl_3$ in 12 N HCl.

VARIATIONS IN THE ABSORPTION SPECTRA.



communicated in part, as small energy changes, to the electrons composing the inner sub-group which is thought to be the seat of the spectrum bands in the visible region.[8] Recent observations by Ephraim and Bloch[9] on the ammonia complexes of praseodymium chloride have been successfully explained by them on the basis of their theory of the deformation of the inner electron shell.

The idea is by no means original that the changes in the absorption bands are intimately connected with repression of ionization. This relation is certainly suggested by the similarity between the shifts produced by the addition of a common ion and those produced by increased concentration alone. In view of the fact, however, that the shifts reported here are neither uniform throughout the spectrum of a given salt nor of a similar nature in different salts, it seems that the theory of repression of ionization is inadequate to account for all the facts. Another difficulty is found in connection with the effect of magnesium nitrate. Magnesium nitrate is not commonly supposed to yield a high concentration of nitrate ion, yet there is unmistakably a greater change in the bands of neodymium nitrate upon the addition of 10 N magnesium nitrate than upon the addition of 10 *N* nitric acid. It was suspected that the metal ion might have something to do with the phenomenon and further investigation on this point is under way. No doubt we have more than one influence to deal with here and the formation of solvates, as suggested by Jones,[10] probably plays a part.

The large deviations observed from Beer's Law suggest that investigations wherein it has been assumed to hold are in error. It has been impossible to confirm Delauney's report on the effect of nitric acid on the absorption bands of neodymium nitrate. In the course of his work he used a spectroscope of only 2 cm. dispersion while the work here was done upon an instrument of 20 cm. dispersion. As the maximum shift observed was of the order of 2 mm., the greatest change which Delauney could have seen would have been about 0.2 mm. Inoue states that the characteristic bands of samarium at 4071 Å. and 4013 Å. remain unchanged upon mixing samarium chloride with the chloride of lanthanum, praseodymium or neodymium. We have found that in the case of the nitrate these bands are blended together and shifted toward the violet on the addition of nitric acid.

The effect of hydrochloric acid on neodymium chloride is interesting because while the changes in the absorption bands are in some degree

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[8] Hevesy, "Die seltenen Erden vom Standpunkte des Atombaues," Julius Springer, Berlin, 1927, p. 40.

[9] Ephraim and Bloch, ***Ber.***, 59B, 2692 (1926), and 61B, 72 (1928).

[10] Jones, "Absorption Spectra of Solutions," Carnegie Institute of Washington Publications, No. 130, No. 160.

similar to those produced by nitric acid yet they are by no means identical differing both in intensities and in the positions of the new bands.

The portion of the work to which the greatest practical interest is attached is that in connection with the influence of one rare earth salt upon the absorption bands of another. It has been shown that in the presence of a colored or colorless rare earth the absorption bands of an element present in small proportions cannot be relied upon for its quantitative analysis and should be used for its identification with the utmost caution. In the cases observed the changes took the form of a distinct shift toward the red, particularly in the 5800 Å. region and of a marked diminution of intensity of the bands in the blue and violet. None of the changes observed was of such a nature as not to be distinct from the bands at **5816** Å. and **5123** Å. reported for illinium by Harris and Hopkins[11] and criticized by Prandtl. In dealing with relatively pure rare earth salts, it should be sufficient to remove all excess of the common ion and particularly to remove all excess acid before attempting spectroscopic analysis; but the quantitative estimation of a small amount of one rare earth in the presence of a large amount of another cannot be relied upon unless use is made of other means than the visible absorption spectra.

Summary

1. The absorption spectra of solutions of praseodymium, neodymium, samarium and erbium nitrates, which were the only ones investigated, are influenced by the addition of nitric acid. Salts of other rare earths showing absorption are undoubtedly affected.
2. No generalization can be made as to the effect of excess nitric acid on the nitrates of the different rare earths.
3. Hydrochloric acid does not produce the same effect as nitric acid on the corresponding neodymium salts.
4. Addition of magnesium nitrate to neodymium nitrate solutions produces a similar but slightly greater change than an equal normality of nitric acid.
5. Colored or colorless rare earth nitrates affect the bands of neodymium nitrate similarly to magnesium nitrate.
6. The deviations from Beer's Law of neodymium nitrate solutions resemble to some extent the effect of the addition of nitric acid.
7. Observations of Jones and others have been confirmed, while it has been impossible to confirm the work of Delauney.
8. Absorption spectra of solutions of rare earth salts should be used for qualitative analysis with the utmost caution and are not suitable for their quantitative estimation in the presence of one another.

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[11] **Harris and Hopkins, This Journal, 48,1585 (1926).**

9. In no case do the observed changes coincide with those reported by Harris and Hopkins during the concentration of illinium.

Urbana, Illinois

[Contribution from the Chemical Laboratory of The Johns Hopkins University]

THREE LABORATORY DEVICES: A VACUUM STIRRER, A PRESSURE ALTERNATOR AND A GAGE FOR MEASURING LOW PRESSURES OF PERMANENT GASES IN CONDENSABLE VAPORS[1]

By Roger K. Taylor

Received July 30, 1928 Published November 6, 1928

An apparatus devised by the author for the stirring of liquids *in vacuo* has been of service in several researches at this University, and may be useful elsewhere. The purpose for which it has been used is the freeing of liquids from dissolved gases; periodic removal of the vapor above the liquid is ineffective, unless the liquid is stirred.

One form of the device is shown in Fig. 1. The liquid, resting above mercury, is contained in bulb A; above it is C, a tower of beads. By a method to be described, the level of the mercury is alternated between l_1 and l_2. The cycle of operation is this: when the mercury falls to l_2, it drains from the small bulb B, which fills with the liquid from **A.** Then, as the mercury rises again to l_1, it refills B, and the liquid contained is forced into C, where it spreads over and trickles through the beads and returns to A. In this way the establishment of equilibrium of dissolved gas between the liquid and vapor phases, which ordinarily is a very slow process, is rapidly effected. This results both from the large surface offered by the beads and the fact that the liquid is constantly being withdrawn from the bottom and returned to the top of A. Periodic removal of the vapor in A and C soon leaves the liquid practically free of dissolved gases.

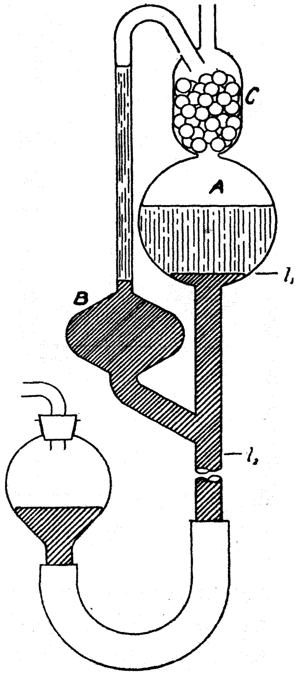

Fig. 1

In one case, where air was to be removed from an alcoholic soap solution, it was feared that the beads would occasion troublesome foaming. The difficulty was avoided by replacing C with a helix of tubing wide enough to permit the solution to flow along its bottom instead of filling it completely.

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[1] In memory of Ira Remsen.

A pressure alternator, designed to operate the stirrer just described, is shown in Fig. 2. By its use atmospheric pressure, and a pressure less than atmospheric by any desired amount, may be alternately applied, the operation being automatic.

A water pump or other vacuum pump is attached to C; the apparatus in which the pressure is to change is connected to B, and A is open to the air. As the pump operates, the pressure in C and B decreases, and the mercury in A rises until it reaches the position a. Thus the pressure in B, originally atmospheric, falls by an amount represented by the vertical distance from a to the mercury level in A. Further pressure decrease causes the mercury to siphon rapidly into B, shutting off communication between B and the pump and leaving B open, through A, to the atmosphere. The distance h_2 is made greater than h_1, so that further decrease in pressure in C must take place before the mercury rises to b; that is, time is allowed for the pressure in the apparatus connected to B to rise fully to atmospheric. When the mercury finally carries over from B into C, it returns quickly through the bottom of C to A, stopping the admission of air, and the cycle starts afresh.

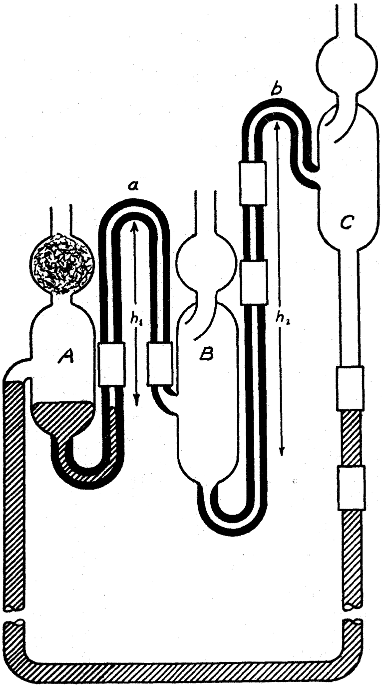

Fig. 2.

The amount by which the pressure changes is, of course, determined by the distance h_1. The time required for the pressure to decrease by this amount depends on the volume of the apparatus attached to B, and on the rate at which the pump is operating. The time that B remains open to the atmosphere depends on the rate of operation of the pump and on the difference between h_1 and h_2. All of these factors may be readily adjusted.

An apparatus of this sort may be used for various purposes. As an actuating mechanism for the stirrer previously described, B is simply attached to the leveling bulb, which is so placed that atmospheric pressure within it holds the mercury at l_1, and h_1 is made equal to the difference between l_1 and l_2.

This pressure alternator was designed without a search of the literature for similar devices; the fundamental principle, however, is not new. Maass[2]

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[2] Maass, THIS JOURNAL, **41,** 53 (1919).

describes something of the sort and mentions a number of possible applications; and recently Weaver and Shepherd[3] depict a modification as the actuating mechanism for an automatic high-vacuum pump. The present device, however, contains one feature absent from Maass' apparatus, namely, the arrangement to cut off communication with the pump while the pressure in B is rising to atmospheric; and as compared with the corresponding part of Weaver and Shepherd's ingenious apparatus, this is of somewhat simpler construction.

A McLeod gage, slightly modified, may be employed to detect the presence and determine the partial pressure of small amounts of permanent gases in a condensable vapor, for instance, traces of air in water vapor.

The arrangement is shown in Fig. **3.** If the volume of the bulb and capillary is A, and the volume of the capillary above the mark is a, then when a permanent gas is present alone at low pressure and the mercury is brought to the mark on the central capillary, the pressure is given by the reading on the scale of the open capillary multiplied by a/A. It may also be determined by reading the position of the mercury on the scale of the closed capillary: if r is the latter reading, b the volume of the right-hand capillary above the mercury when the reading is taken, and B that of the entire side tube, then $\mathbf{P} = ar/[A - (Ba/b)]$. As B is small in relation to A, the ratio a/b does not need to be known accurately; since the capillaries are all supposedly of the same bore, a comparison of the corresponding lengths on the scale is close enough. When r is small, the simpler expression $\mathbf{P} = ar/(A - B)$ is approximately true.

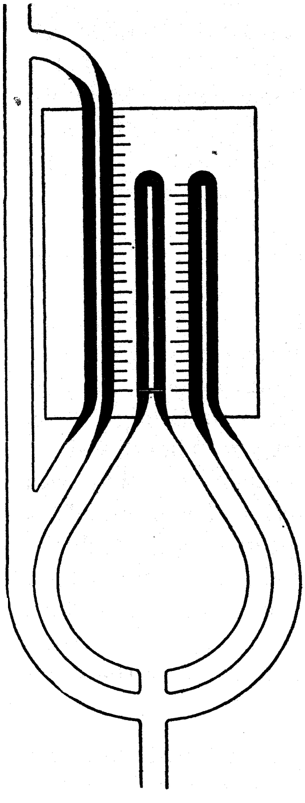

Fig. 3.

If now in addition to the permanent gas there is present a condensable vapor, in such amount that condensation takes place in the closed capillaries when the mercury is brought to the mark, *it contributes the same pressure,* namely, the vapor pressure of the liquid in question at the temperature of the gage, in *both capillaries;* accordingly, the partial pressure of the permanent gas is determined by

Weaver and Shepherd, THIS JOURNAL, 50,1829 **(1928).**

taking the same readings on the right-hand capillary and making the same calculations as when the condensable vapor is absent.

BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE JOHNS HOPKINS UNIVERSITY]

THE INFRA-RED ABSORPTION SPECTRA OF ORGANIC CARBONATES[1]

BY FREDERICK K. BELL[2]

RECEIVED AUGUST 1, 1928 PUBLISHED NOVEMBER 6, 1928

Introduction

There are few instances in which an acid, the metallic salts of which are available in large crystals, also yields a series of well-defined organic salts or esters. These conditions are fulfilled, at least partially, by carbonic acid. A number of inorganic carbonates are found in nature in crystals of sufficient size to permit cutting, polishing, etc., for optical examination. Similarly a considerable number of esters of carbonic acid have been prepared and are described in the literature.

In a rather recent paper Schaefer and his co-workers[3] have measured the infra-red absorption spectra between **1.0** and 17.0μ of six inorganic carbonates: $MgCO_3$, $CaCO_3$, $CaMg(CO_3)_2$, $FeCO_3$, $BaCO_3$ and $PbCO_3$. In view of this work it seemed to the present author that a similar examination of a series of organic carbonates would yield results of particular significance and interest. The absorption spectra of such a series of compounds might be expected to offer also further information concerning the $C{=}O$ bond, which is surely among the most' common linkages of organic compounds. The organic carbonates also represent one of the numerous series of compounds of organic chemistry which are especially suited for spectroscopic study of a systematic nature, one part of the molecule remaining unchanged as different hydrocarbon residues are introduced.

It is with these ideas in mind that the infra-red absorption spectra of seven organic carbonates have been examined between 1.0 and 12.0μ. The results of these examinations are presented and discussed in this paper.

Experimental

A detailed description of the experimental method employed in the present work has been given elsewhere.[4] The preparation of the absorption cells, however, has been altered. All cells were prepared from polished plates of rock salt.

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[1] In memory of Ira Remsen.

[2] Grafflin Scholar.

[3] Schaefer, Bormuth and Matossi, *Z. Physik,* 39,648 (1926).

[4] F. K. Bell, THIS JOURNAL, 47, 2194 (1925).

The cleaved plates were first ground on emery cloth until all irregularities of the cleaved surface had disappeared. The grinding was then continued on a coarsely sanded glass plate (treated with crocus and water) until all of the deep emery scratches were removed. As the next step, the plates were polished on a cotton cloth which was stretched over a suitable plane surface and then treated with crocus and moistened with water. This procedure was repeated using jewelers' rouge instead of the crocus. The final polishing was accomplished in a similar manner using jewellers' rouge and 95% alcohol.

The construction of the absorption cell was carried out as previously described, but it was soon evident that the cement used could not contain much water. Thus, Le Page's glue, which was found to be quite satisfactory for cementing cells of cleaved plates, was entirely useless for present purposes. Similarly, a litharge–glycerol paste was found to contain sufficient water to ruin the polished surfaces. The cement finally used was DuPont Household Cement. The solubility of this material in certain non-aqueous solvents offers an important advantage in that cells may be readily taken apart for cleaning and repolishing without damage to the plates.

Three different cells were used in the study. No cell was used a second time until it had been taken apart, cleaned, repolished and cemented together again. A number of check experiments were made which failed to reveal any measurable variations due to differences in the cells. It therefore appears that this cell error which existed in the author's previous work has been eliminated, at least in relation to the other sources of error in the experimental method. The use of polished cells was prompted by a desire to reduce losses in the intensity of the transmitted radiation and to obtain some basis for a closer comparison of the intensity of absorption bands in different compounds. It is believed that the results obtained have entirely justified this point of view.

The carbonates selected for examination are the following: dimethyl, diethyl, dipropyl, dibutyl, di-*iso*butyl, di-*iso*-amyl and diphenyl. All of these substances were obtained from the Eastman Kodak Company and were used as received without any attempt at further purification. Diphenyl carbonate was examined in the molten state at 50°. All of the other carbonates selected, being liquids, were examined in the usual manner at room temperature. The thickness, *T*, of the absorption cell was 0.025 mm. in each case.

The absorption spectra obtained are shown graphically in Figs. 1 to 7 by means of the customary wave length–percentage transmission curves.

Discussion

The dimethyl ester is the only carbonate of the present study the infrared absorption of which has been previously described in the literature. A comparison of Coblentz'[5] curve for this substance with that shown in Fig. 1 demonstrates clearly the influence of the polished cell. Coblentz, using a cell made from cleaved plates of rock salt, employed a cell thickness of 0.01 mm. and his curve indicates a higher degree of general opacity than the present curve in which the cell thickness is 0.025 mm. In comparing the two curves it should also be noted that there is a difference in the resolving power of the optical systems employed in each case.

All of the compounds examined display a marked uniformity in general transparency as shown in Figs. 1 to 7 and it is to be recalled that one

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[5] W. W. Coblentz, *Carnegie Inst. Publ.*, No. 35, 1905, p. 65.

aryl compound (diphenyl carbonate) is included. The regions between 1.0 and 3.0μ and between 3.6 and 5.0μ are particularly striking in this

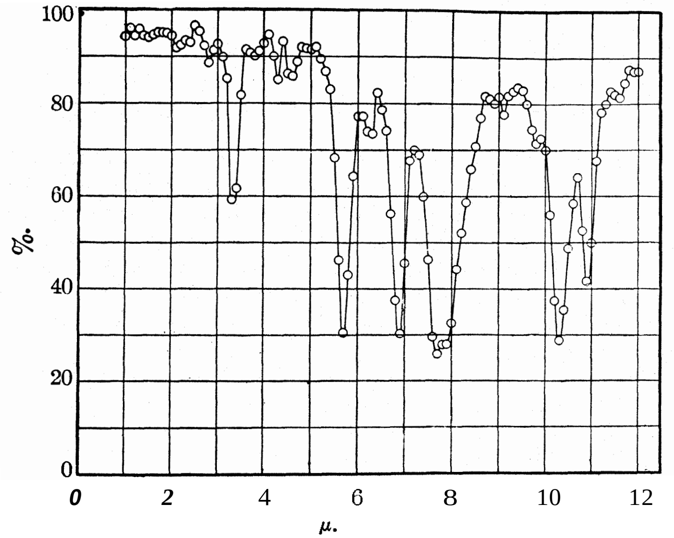

Fig. 1.—Dimethyl carbonate, T = 0.025 mm.

respect. A considerable increase in the thickness of the absorbing layer is undoubtedly necessary for a closer examination of these two transparent regions.

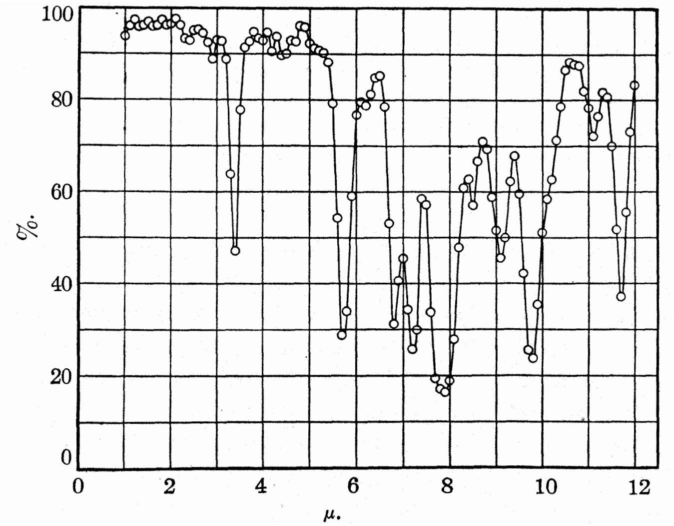

Fig. 2.—Diethyl carbonate, *T* = 0.025 mm.

In the region between 8.0 and 12.0μ marked differences occur in the absorption to such a degree that no difficulty would be encountered in differentiating between the various carbonates examined. However, between 3.0 and 8.0μ pronounced similarities appear. The C—H band at 3.4μ and bands at 5.7μ and 6.9μ are sharply defined in each curve. A broad region of absorption occurs in each spectrum at 7.8μ and the curve for di-isobutyl carbonate (Fig. 5) indicates the presence of two bands in this region. A weak absorption appears in the region of 6.2μ

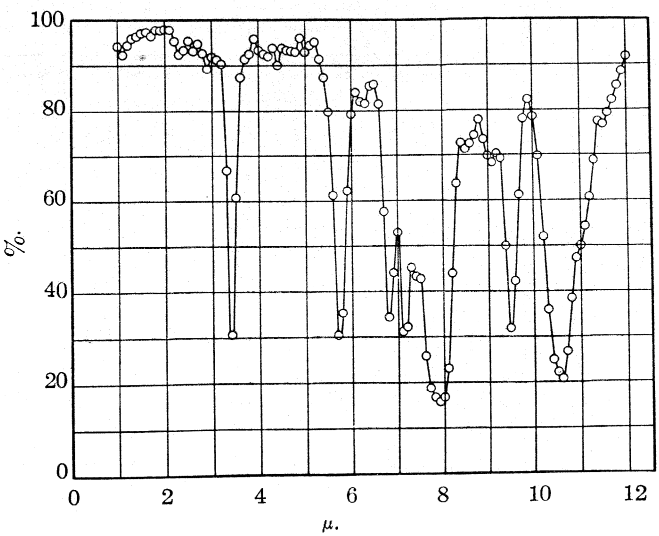

Fig. 3.—Dipropyl carbonate, $T = 0.025$ mm.

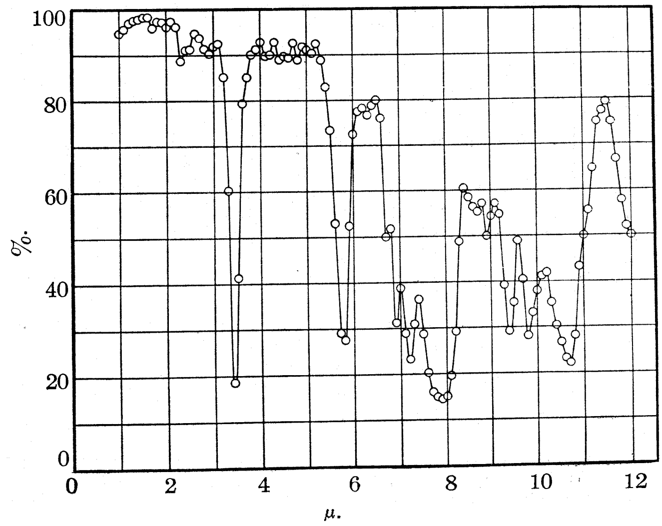

Fig. 4.—Di-n-butyl carbonate, $T = 0.025$ mm.

for each of the alkyl carbonates and in interpreting the more marked absorption in diphenyl carbonate (Fig. 7) at that wave length it is to be remembered that benzene derivatives have a characteristic absorption at 6.25μ.

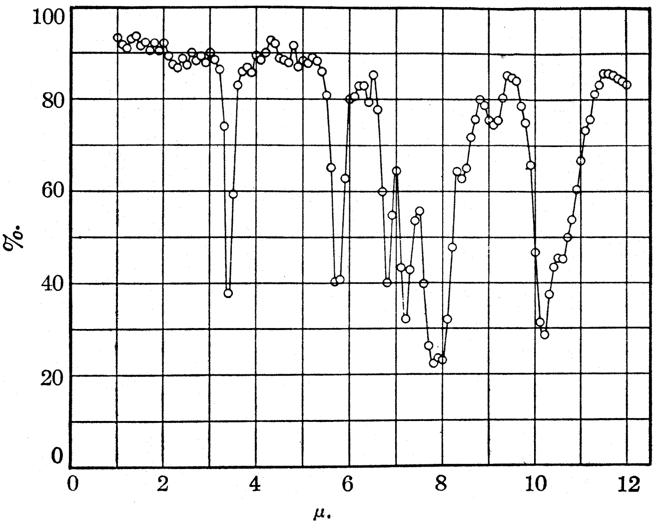

Fig. 5.—Di-isobutylcarbonate, T = 0.025 mm.

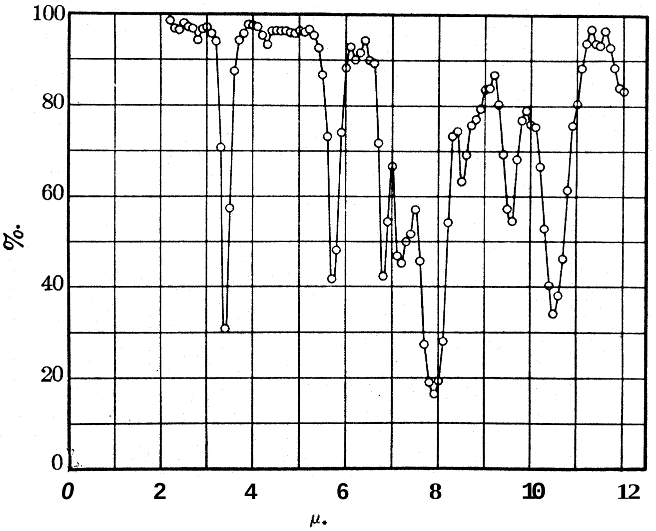

Fig. 6.—Di-iso-amyl carbonate, T = 0.025 mm.

Another region of interest is located at 7.2μ. In dimethyl carbonate (Fig. 1) no characteristic absorption occurs at that point, the transmission passing through a maximum; while in each of the other curves a well-defined minimum appears. This band, the location of which approximates that of the fourth member (at 7.0μ) of Ellis'[6] band series for the C—C linkage, may be regarded as characteristic of the C—C bond.

One of the components of the broad region at 7.8μ may be regarded as the 7.67μ band of methane, which Cooley[7] has examined with high dispersion. Dennison[g] regards this band as the result of one of the fundamental frequencies of the methane molecule. Similarly, the 6.8μ absorption band of the present curves corresponds to a frequency commonly attributed to one of the fundamental vibrations of the C—H pair. However, as will be noted below, another factor probably plays an important role in the absorption in this region.

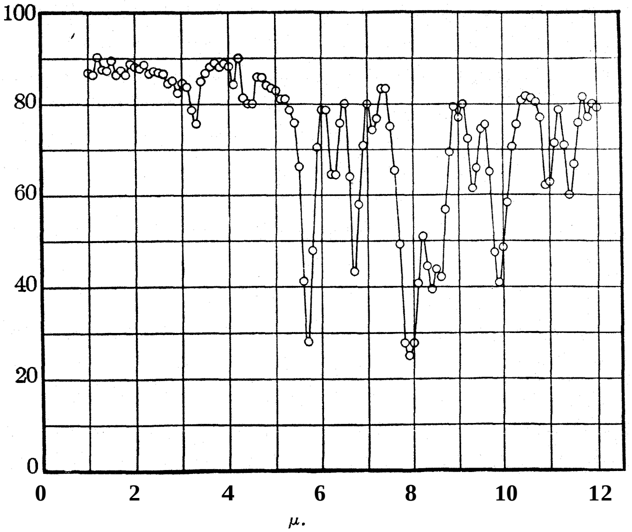

Fig. 7.—Diphenyl carbonate, T=0.025 mm., temp.=50°.

A well-defined absorption at 5.75μ which occurs with marked regularity in the spectrum of each of the compounds examined may- be regarded as characteristic of the C=O linkage. A survey of the absorption spectra of the large number of compounds containing the C=O group which have been recorded in the literature lends support to this opinion. Even in the rather complicated molecules of some of the tropine alkaloids, which the author[g] has examined, this band was sharply resolved (at 5.8μ).

In comparing the absorption spectra of the organic carbonates with those of the inorganic carbonates as measured by Schaefer and his collabo-

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[6] J. W. Ellis, *Phys. Kev.*, 27, 309 (1926).

[7] J. P. Cooley, *Astrophys. J.*, 62, 73 (1925).

[8] D. M. Dennison, *ibid.*, 62, 84 (1926).

[9] F. K. Bell, *J. Pharm. Exptl. Therap.*, 29, 533 (1926).

rators[3] it must be noted that the inorganic carbonates were examined as plates of 0.1 mm. thickness in comparison with the 0.025 mm. thickness used in the present study. Furthermore, the difference in density between these two types of carbonates must be considered.

In interpreting their experimental findings, Schaefer and his co-workers were guided by several factors: (I) the carbonates are characterized by five fundamental frequencies corresponding to (approximately) 7μ, 14μ, 30μ, 60μ and 90μ; (2) the CO_3 ion is characterized by four "inner" vibrations, according to Bresters[10] and Kornfeld,[11] at (approximately) 7μ, 11μ, 14μ and 8μ, which is the calculated wave length for an inactive frequency; (3) a combination of an inactive and an active frequency may result in an active frequency.

Between 2μ and 9μ the absorption of the inorganic carbonates is similar for each carbonate and this region, in which the influence of the metallic ion is apparently negligible, is regarded as the region of activity of the "inner" vibrations of the carbonate ion. A broad region of total absorption occurs at 7μ in each case and the authors have determined the location of the minimum by calculation from the first harmonic at approximately 3.5μ and checking this value against the reflection spectrum in the region of 7μ. Having determined the location of this 7μ band (frequency ν_1), the location of the inactive frequency (ν_0) was calculated from the absorption at 3.9μ, regarding this band as the resultant of the combination $\nu_1 + \nu_0$. The wave length corresponding to this combination lies between 9 and 10μ. The 14μ (frequency ν_2) and 11p (frequency ν_3) bands were definitely resolved. The authors thus determined the location of the four fundamental frequencies (ν_0, ν_1, ν_2, ν_3) for each carbonate. Other bands occurring between 2μ and 9μ are then satisfactorily accounted for as resulting from combinations of two or more of these four fundamental frequencies.

Difficulties are encountered at once in attempting to apply a similar method of analysis to the present curves. The relatively inactive metallic ions of the inorganic carbonates have been replaced by hydrocarbon radicals which are known to display characteristic absorption between 2μ and 9μ. Furthermore, the intensities of these hydrocarbon bands are relatively much greater than those of the carbonate ion. Thus the intensity of the 3.5μ (first octave of the 7μ band) band of the carbonate ion as shown in the absorption of the inorganic carbonates is not sufficiently great to affect the location of the 3.4μ of the C—H pair in the present curves. Likewise, the presence of the 3.9μ band of approximately the same intensity as that of the 3.5μ band cannot be detected in the spectra of the organic carbonates.

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[10] C. I. Bresters, *Z. Physik*, 24, 324 (1924).

[11] H. Kornfeld, *ibid.*, 26, 205 (1924).

Another factor to be noted is that a number of the characteristic carbonate bands are located near or superpose characteristic C—H bands, for example, 3.5μ, 7μ and 14μ; so that both the location and intensity of the absorption bands of the organic carbonates are to be interpreted with caution.

The 5.75μ band of the present curves approximates, in location, a similar band which occurs in the inorganic carbonates, thus affording additional evidence that this band is characteristic of the C=O linkage. Schaefer and his collaborators regard this band as resulting from the combination $\nu_1 + \nu_0 - \nu_2$ (see above). As has been noted already, the broad region at 7.8μ of the organic carbonates has one component corresponding to the 7.67μ C—H band. Another component of this region may be located at 7.9μ. This band cannot be regarded as characteristic of the C=O linkage since an absorption of comparable intensity does not occur at that wave length in the spectra of the inorganic carbonates. It is suggested that this band is a combination band resulting from a combination of frequencies characteristic of the C—H and C=O linkages.

A consideration of the intensities of several of the more prominent absorption bands reveals some interesting relations. In Table I the transmissions (to the nearest per cent.) of the 3.4μ, 5.75μ, 6.8μ, 7.2μ and 7.85μ bands are given for each carbonate. It is at once seen that in the case of the normal alkyl hydrocarbon radicals the intensity of the 3.4μ band shows an increase with increase in molecular weight. Similar observations have been made by Henri and Bonino. Henri[12] examined a number of normal alcohols of the methane series. Although he failed to resolve the OH band at 3μ and the 3.4μ band, he found that the molecular coefficient of maximum absorption of the resultant band (at approximately 3.3μ) showed an increase with increase in molecular weight. By regarding this coefficient as an additive function and assigning values to the OH group and the CH_3 (or CH_2) group, he was able to obtain calculated values in good agreement with the observed data.

TABLE I

TRANSMISSION OF BANDS

			Transmission at		
	3.4s	5.75μ	**6.89**	*7.2s*	7.85μ
Methyl	0.60	0.30	0.30	absent	0.25
Ethyl	.47	.29	.31	**0.26**	.16
Propyl	.30	.30	.35	**.31**	.16
Butyl	.18	.28	.31	.24	.15
*Iso*butyl	.38	.40	.40	.32	.22
Iso-amyl	.30	.42	.42	.45	.16
Phenyl	.75	.28	.43	.74	.25

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[12] V. Henri, "Études de Photochimie," Gauthier-Villars et Cie, Paris, 1919, p. 42.

Bonino[13] examined the absorption of several ketones containing only normal hydrocarbon residues of the methane series. He likewise found that the molecular coefficient of absorption of the 3.4μ band increased with increase in molecular weight. However, Bonino interpreted the intensity of the 3.4μ band as a function of the number of hydrogen atoms in the hydrocarbon radical and on this basis derived the empirical relation

$$\epsilon_2 = \epsilon_1 + C \log \frac{n_2}{n_1}$$

where ϵ_1 and ϵ_2 are the molecular coefficients of absorption and n_1 and n_2 are, respectively, the number of hydrogen atoms in the two homologs. By substituting the observed values of ϵ and the corresponding values of n, C was found to be a constant.

It is not necessary to express the absorption maxima of the present curves at 3.4μ in terms of the corresponding coefficients, in order to recognize at once that Bonino's empirical relation fails to hold; for it requires that the absorption maxima at 3.4μ should be the same for the butyl and *iso*butyl carbonates, since these two compounds contain the same number of hydrogen atoms. These two carbonates have approximately the same density and therefore the observed maxima are directly comparable and should be equal if Bonino's equation applies. The value for the dibutyl carbonate is approximately 0.19; that for the di-isobutyl carbonate is 0.38. The difference in these two values is, of course, far beyond the limit of experimental error. It is seen that the value of 0.38 falls between the values for ethyl and propyl carbonates. The value for di-iso-amyl carbonate is greater than that of the di-isobutyl carbonate and is approximately the same as the value for dipropyl carbonate.

A closer analysis of the intensity of the 3.4μ band would surely have to take into consideration the influence of the 3.5μ C=O band (as found in the inorganic carbonates). This influence should become more significant with decrease in molecular weight of the ester radical. The relative weakness of the 3.4μ band in dimethyl carbonate is striking, especially when it is considered that two methyl groups are present. Even more striking in this respect, is the aryl C—H band in diphenyl carbonate where the relative depth of the band is only ten percentage units.

The present curves, however, seem to show conclusively that the intensity of the 3.4μ band cannot be regarded merely as a function of the number of hydrogen atoms in the hydrocarbon radical, nor can it be regarded as a simple additive function depending upon the number of CH, CH_2 and CH_3 groups.

The intensities of the 6.8μ band, as shown in Col. **3** of Table I, are strikingly constant for the four normal esters. As has been noted above, this band, like the 3.4μ band, is regarded as resulting from one of the

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[13] G. B. Bonino, *Gazz. chim. ital.*, **55, 335 (1925).**

fundamental vibrations of the C—H pair. It is therefore surprising that the intensity of this band fails to parallel the increase of that of the 3.4μ band with increase in molecular weight. This apparent discrepancy might be explained by assuming the presence of a carbonate band at 6.9μ (at 7.0μ in the inorganic carbonates) the intensity of which is considerably greater than that of the 6.81, band. Thus in dimethyl carbonate the 6.81, band would be expected to have a minimum intensity, which is probably less than that of the 3.41, band. The location of the observed band (at 6.9μ) would therefore be that of the relatively more intense C=O band and the observed intensity would be the summation of the intensities of the 6.81, and 6.9μ bands. The absorption of dibutyl carbonate (Fig. 4) may be interpreted to support this point of view. In this case the 6.9μ band has been definitely resolved and the 6.81, band appears to have been shifted to the shorter wave length region as indicated by the poorly defined minimum near 6.7μ.

The intensities of the 6.81, band in di-isobutyl and di-iso-amyl carbonates are approximately equal, but their value is considerably less than those of the normal esters.

The 7.2μ and 7.8μ bands do not display any consistent variations in intensity in passing from one carbonate to another, as shown in Table I. In addition to being poorly defined, the region of 7.8μ is too opaque to reveal clearly any differences in intensity. Thinner layers of the absorbing substances must be employed in order to obtain a satisfactory analysis of this region.

A consideration of the intensity of the 5.751, band as shown in Col. 2 of Table I offers a serious objection to the opinion, expressed above, that the 5.751, band is due to the C=O pair. The intensity values for the four normal esters are practically equal. Since the densities of these substances are of the same order of magnitude, it is obvious that the molecular absorption coefficient at 5.75μ will show an increase with increase in molecular weight. However, if the 5.751, band is due to the carbonate group, the molecular absorption coefficient should remain constant for each carbonate. The same reasoning may be applied to the case of the two *iso*-esters where, however, the intensity of the 5.75μ band, although the same for each of the two compounds, has a considerably smaller value than that of the normal esters.

It must also be noted that there is at least an approximate equality in the intensity values of the 5.751, band and of the 6.8μ band in each of the compounds (with the exception of diphenylcarbonate), a condition which can hardly be regarded as coincidental.

The most obvious explanation of these observations is the assumption that another absorption band (perhaps due to the CH pair) occurs near the location of the C=O band, so that the intensity of the observed band at 5.75μ is that due to the superposition of two bands. However, little evidence can be found in support of this assumption.

The present study includes the examination of only two iso-esters and therefore offers little conclusive information concerning the absorption of that type of compound. From the above discussion, however, it is difficult to avoid the generalization that the normal esters and the *iso*-esters of carbonic acid form two distinct types of compounds in which the factors determining the intensities of the absorption bands characteristic of the C—H and C=O linkages are the same qualitatively but differ quantitatively for each type.

The absorption spectra of the organic carbonates offer a further indication, perhaps more clearly than previous work, of the definite possibilities of utilizing the intensity of characteristic absorption bands for purposes of identification. For example, it is readily seen that there would be no difficulty in differentiating between the four normal esters of carbonic acid by means of the intensity of the absorption at 3.4μ.

Summary

1. The absorption spectra of dimethyl, diethyl, dipropyl, dibutyl, di-*iso*butyl, di-iso-amyl and diphenyl carbonates have been examined between 1.0 and 12.0μ, using absorption cells made from polished rock salt plates.

2. These absorption spectra show a marked similarity in the number and location of absorption bands between 3.0 and 8.0μ; while no consistent variations or similarities can be detected in the region between 8.0 and 12.0μ.

3. The absorption spectra have been discussed in their relation to the results obtained by Schaefer and his co-workers in the examination of some inorganic carbonates.

4. An increase in the intensity of the 3.4μ band with increase in the molecular weight of the ester radical has been observed. However, the intensity values of the 3.4μ band in di-isobutyl and di-iso-amyl carbonates are not satisfactorily accounted for by the relations derived either by Henri or Bonino.

5. The intensity relations of the 5.75μ band in the various organic carbonates offer an important objection to the idea that the 5.75μ band depends solely on the presence of the carbonate group.

6. An analysis of the variations in intensity of characteristic absorption bands in the various organic carbonates indicates that the normal and the iso-esters may be regarded as two distinct types of carbonates.

BALTIMORE, MARYLAND

[Contribution from the Physical Chemistry Laboratory of the State University of Iowa]

THE VAPOR PRESSURES OF AQUEOUS SOLUTIONS OF POTASSIUM IODIDE AND SODIUM BROMIDE AT 25°[1]

By J. N. Pearce, M. D. Taylor and R. M. Bartlett

Received August 2, 1928 Published November 6, 1928

In the study of the colligative properties of solutions use has been made of methods involving the lowering of the freezing point, the lowering of the vapor pressure and the elevation of the boiling point of the solvent by the solute, and the application of electromotive-force methods. Because of the ease and the accuracy of the measurements, most of the work hitherto has been confined to the freezing point and electrometric methods. Of all of the properties of solutions, however, none are more accessible to thermodynamic treatment than the vapor pressure. While the vapor pressure method is free from all of the disadvantages, and in addition possesses many advantages over the others named, chiefly in that it can be used at any temperature, the results obtained have not been all that could be desired.

Four general methods have been employed for measuring the vapor pressures of solvents and solutions: (1) static, (2) indirect, **(3)** differential and (4) dynamic. The principles involved and the difficulties met with in their application have been discussed in a previous paper.[2] Of these the most convenient and rapid is the dynamic, or air-saturation method; moreover, it is based on a simple application of Dalton's Law of partial pressures. The essential features of the method as commonly used are: **(1)** a measured volume of air is saturated with vapor by passing it over the surface of, or bubbling it through the liquid contained in the saturator; (2) the weight of the solvent evaporated is determined by the loss in weight of the saturator, or by the gain in weight of the absorber which removes the solvent vapor from the effluent air; **(3)** the total pressure exerted by the gaseous mixture in contact with the liquid is obtained from barometer and manometer readings. From the data thus obtained the vapor pressure of the solvent may be calculated.

A survey of the vapor pressure data obtained by the dynamic method shows not only a wide variation in the values reported by different investigators for a single liquid, but also very frequently a considerable variation in the data given by a single investigator. The chief reasons for these deviations are few, but they have been difficult to overcome. The Earl of Berkeley and Hartley[3] have concluded that the failure of the original Walker-Ostwald method is due to variations in the hydrostatic pressure in the several vessels. They also suggest that liquid spray is carried mechanically

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[1] In memory of Ira Remsen.

[2] Pearce and Snow, J. Phys. Chem., 31, 231 (1927).

[3] Earl of Berkeley and Hartley, *Proc. Roy. Soc.*, 77, 156 (1906).

from the solution to the pure solvent. Attempts to eliminate both of these sources of error have been made by a number of men.[2] Another difficulty is our inability to measure accurately, and at the same time conveniently, the large volume of air required for a single determination. The error thus introduced will be greater or less, depending upon the magnitude of the vapor pressure of the liquid studied. Owing to the surface film effect any form of apparatus which requires the passing of air over the surface of the solvent or solution must present a large liquid surface. Moreover, the surface should be in constant motion. Forms of apparatus involving the bubbling of air through the liquid are obviously more compact, but they introduce error for the reason that while a bubble may be saturated with vapor in the depth of the liquid, it will expand on rising and may leave the surface without becoming entirely saturated, Again, the mathematical formulas which have been used heretofore are often highly complicated; slight errors of observation are highly magnified in calculating the vapor pressures.

Pearce and Snow[2] have devised a rapid method which apparently eliminates all of the previous sources of error. The method introduces the following new features. Instead of measuring the volume of air which passes through the solution, hydrogen and oxygen are generated electrolytically and the volume of the mixed gases, as well as the number of moles of each, is calculated from the weight of silver deposited in a coulometer. The actual calculation of the vapor pressure requires the knowledge of three values only: the corrected barometric pressure, P, and the weight of vapor, W_W, taken up by the P_2O_5-absorber while W_S grams of silver are being deposited in the coulometer. The number of moles of water vapor, n_1, and the total number of moles of hydrogen and oxygen generated, n_2, are calculated from W_W and W_S, respectively. From these data the vapor pressure of the solvent can be calculated by means of the simple relation $p = [n_1/(n_1 + n_2)]P$.

Experimental Results

The experimental procedure is described in detail in the previous paper." It need only he said that the utmost care was taken to insure purity in all materials used. The pure "Analyzed" salts were repeatedly crystallized from conductivity water distilled from a large still containing a strong alkaline solufion of potassium permanganate. The solutions were accurately made up on the weight molal basis. The entire vapor pressure apparatus, except for the generators, preheaters and absorbers, was immersed in a large Freas water thermostat maintained at 25 ± 0.01° throughout the two-hour run.

The essential data are given in Tables I and II. Each vapor pressure value is the mean of at least three independently determined values which do not differ over all by more than a few 0.001 mm. The symbols used at the top of each column are self-explanatory.

TABLE I

VAPOR PRESSURE DATA FOR AQUEOUS SOLUTIONS OF SODIUM BROMIDE AT 25° (R.M.B.)

M	p, mm.	p_0-p, mm.	$(p_0-p)/p_0$	P, atm.	a_1	a_1/N_1	$\gamma_2\pm$	$-\Delta F_1$, cal.	$-\Delta F_2$, cal.	$-\Delta F_2^{0.1}$, cal.
0 0	23 752	...	....	. ..	1 000	1 000	1 000	....	....	..
. I	23.675	0.077	0 003241	4.42	0.997	0 999	0.782	1.92	—3020	0000
.2	23 608	.144	.006062	8 27	.994	997	,752	3 77	—2246	773
.4	23 448	.304	,012799	17.53	,987	.994	.731	7 68	—1457	1562
.6	23 292	.460	019360	26 57	980	992	.724	11.71	− 987	2032
.8	23.136	.616	,025935	35 70	.972	986	.711	15 65	− 657	2362
1 0	22.973	.779	.032798	45 37	,968	,985	(.697)	19.49	− 428	2592
1 5	22.556	1.196	.050353	70.15	.948	.973	721	31.35	4 94	3114
2 0	22 128	1 624	.068373	96.03	.929	962	.754	43.68	+ 488	3508
2 5	21 670	2.082	.087656	124.37	.919	.960	.794	56.55	724	3744
3 0	21 181	2 571	10824	155 21	.886	,934	.863	71.96	1125	4145
3 5	20 655	3 097	.13039	189.17	861	.915	943	88.89	1416	4436
4 0	20.094	3.658	.15401	226.25	.836	.896	1020	105.87	1662	4682
4.5	19 501	4.251	.17902	266 59	.804	.889	1.170	129.24	1967	4987
5 0	18 876	4 876	.20524	309 60	.772	.841	1 329	153.04	2244	5264
5 5	18 242	5 510	23202	356.11	.739	.812	1 528	179.07	2524	5544
6 0	17 603	6 149	,25888	403 83	.706	.782	1.740	206.35	2735	5755
6 5	16 934	6 818	.28705	455.54	.667	.745	2.086	240.65	3091	6111
7.0	16 234	7.518	.31652	511.77	.629	.708	2 443	274.25	3366	6386
7.5	15.570	8.182	,34448	567.28	.591	.671	2.911	311.28	3655	6675
8.0	14 888	8.864	.37319	626.70	.551	.630	3.500	352.96	3950	6970
8.5	14.231	9 521	.40081	686.28	.512	.590	4.224	396.52	4245	7265
9 0	13.582	10.170	.42817	747.97	.473	.550	5.111	442.77	4539	7559
9 131^a	13.409	10.343	,43546	764.85	.462	.538	5.432	457 21	4626	7646

^{a} Saturated.

TABLE II

VAPOR PRESSURE DATA FOR AQUEOUS SOLUTIONS OF POTASSIUM IODIDE AT 25° (M.D.T.)

M	p, mm.	p_1-p, mm.	$(p_0-p)/p_0$	P, atm.	a_1	a_1/N_1	$\gamma_2\pm$	$-\Delta F_1$, cal.	$-\Delta F_2$, cal.	$-\Delta F_2^{0.1}$, cal.
0.0	23.752	...	....	....	1.000	1.000	1.000	....	....	..
.1	23686	0.066	0.002778	385	0.997	0.999	0.917?	1.65	—2819	0000
.2	23 620	.132	,005557	7 58	994	.998	.813?	3 31	—2153	266
4	23.486	.266	.011199	15 31	.988	996	740	6.71	—2443	1376
.6	23 348	.404	.017009	23.32	.983	.996	.687	10 10	--1051	1768
.8	23.211	.541	,02385	31.31	.977	.991	.662	13 82	− 753	2065
1.0	23.072	.680	.02863	39.46	.971	.988	(.649)	17.47	− 512	2306
1 5	22.702	1.050	,04421	61.31	.955	.980	.633	27 42	− 61	2758
2.0	22.316	1.436	.06046	84.42	.938	.972	.623	38.15	+ 261	3080
2.5	21 922	1 830	.07704	108.74	.920	.961	.639	49.48	556	3375
3.0	21.516	2.236	,09414	134.02	.901	.950	656	61.60	803	3622
3 5	21.100	2.652	.11165	160.40	.882	.937	.678	74 50	1024	3854
4 0	20.681	3.071	.12929	187.46	.862	924	.707	88 02	1232	4051
4.5	20.253	3 499	.14731	215.66	.841	.909	.732	102.41	1413	4232
5.0	19.822	3 930	.16546	244.61	.820	.894	.765	117.53	1591	4409
5 5	19 392	4.360	.18356	274 10	.798	.878	.800	133.28	1756	4576
6.0	18.966	4.786	.20150	303 93	,777	.861	,839	149.59	1816	4635
6.5	18.529	5.223	.21990	335.19	.754	,843	.868	167.10	2051	4870
7.0	18.082	5.670	.23872	367.90	.731	.823	.937	185 89	2230	5049
7.5	17.635	6 117	25754	401.39	.707	.802	.993	205.62	2381	5199
8 0	17.190	6 562	.27627	435.52	.683	.781	1.049	226.29	2528	5347
8.5	16.750	7.002	.29480	470.11	.658	.759	1.120	247.82	2672	5491
8.938^a	16.370	7.382	.31079	500.67	.637	.739	1.180	267.32	2793	6512

^{a} Saturated.

In the present paper we intend only to show briefly the results obtained in the study of two salt solutions by the new dynamic method recently devised in this Laboratory. The general discussion of the theories involved will be left for a later paper.

The change in the vapor pressure, p, and in the fractional lowering $(p_0 - p)/p_0$ with increasing concentration, are shown graphically in Fig. 1. These curves show at once the influence of hydration upon the vapor pressure of solutions. The p-curve for sodium bromide is at all concentrations below that for potassium iodide; its curvature toward the concentration axis becomes more and more pronounced as the concentration increases. On the other hand, the curve for the fractional lowering, $(p_0 - p)/p_0$, produced by the sodium bromide lies at all concentrations above that given for potassium iodide. Solutions formed by such salts are far from ideal solutions; the positions and the slopes of the $(p_0 - p)/p_0$ curves show, perhaps more than anything else, the rate of change in the apparent mole fraction of the water actually present as solvent. Lewis defines an ideal solution as one which obeys Raoult's law at all concentrations and pressures, that is, $(p_0 - p)/p_0 = n/(N + n)$. A plot of the mole fraction

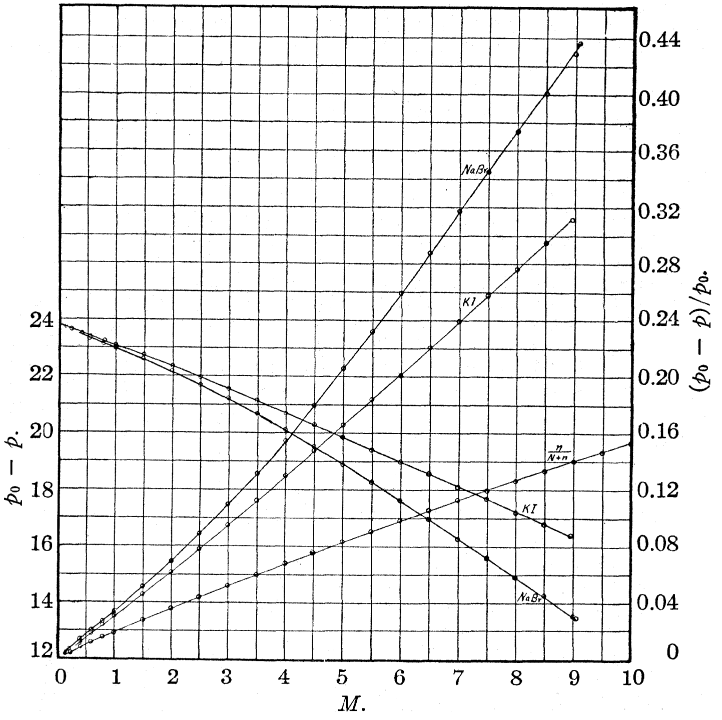

Fig. 1.

of the solute against the corresponding molalities should give us graphically the change in the fractional lowering with increase in concentration for an ideal solution. Such a plot is included in Fig. 1. As should be expected the curve shows a slight bend toward the concentration axis as the concentration increases,

The vapor pressures of solutions give us immediately a means of calculating osmotic pressures. The theories and the relations involved in the consideration of osmotic pressure have been most admirably discussed in a recent paper by Bancroft and Davis.[4] Of the many relations which have been suggested for calculating osmotic pressure from vapor pressure data, we shall mention only two for the present. The first is the one presented by Fraser,[5]

$$p_1 = \frac{RT}{V_0} \ln \frac{p_0}{p} \tag{1}$$

In this V_0 is the volume of one mole of the solvent, which, as we have used it, is the volume occupied by 18.016 g. of water at 25°. Fraser states that this is an exact expression even at large concentrations, provided the perfect gas laws apply to the vapor and the effect of pressure on the molal volume V_0 is negligible.

By thermodynamic means Lewis has derived a relation which holds more rigidly over a very wide range of concentration, namely

$$P - \frac{\beta}{2} P_2 = \frac{RT}{V_0} \ln \frac{p_0}{p} \tag{2}$$

Here β is the coefficient of compressibility of the water and V_0 is the molecular volume as before. For small values of P the effect due to the compressibility term vanishes and (2) becomes equivalent to (I). We have calculated the osmotic pressures by both equations. Within limits of error the osmotic pressures by the two formulas agree to within 0.01 atm. up to 0.8 M, but from this point on they begin to diverge. At saturation the value of P (1) for sodium bromide is 13.3 atm. greater than for P by (2); P by (1) for potassium iodide is 5.27 atm. greater than that calculated by (2). For the sake of brevity me are inserting only those osmotic pressures calculated by (2). The value of β for water at 25° was interpolated from compressibility data[6] at 20° and 30°.

The vapor pressure apparatus used makes possible the rapid determination of thermodynamic data. The activity of the solvent α_1 in a solution may be calculated from the fractional lowering of the vapor pressure by means of the series relation.[7]

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[4] Bancroft and Davis, J. Phys. *Chem.*, **32,** 1 (1928).

[5] Taylor, "Treatise on Physical Chemistry," D. Van Nostrand Company, Inc., New York, 1924, p. 275.

[6] "International Critical Tables," Vol. III, p. 40.

[7] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, 1923, p. 274.

$$\ln \alpha_1 = -\frac{p_0 - p}{p_0} - \left(\frac{p_0 - p}{p_0}\right)_2 - \left(\frac{p_0 - p}{p_0}\right)_3 - \ldots.$$

In very dilute solutions only the first term is of importance; in making our calculations of α_1 other terms were added until the influence of an added term became negligibly small. The values of α_1 and α_2/N_1 are given in Cols. 6 and 7, Tables I and II. For pure water $\alpha_1/N_1 = 1$ and the departure of α_1/N_1 from unity is the measure of the variation from a perfect solution.

Further, to calculate the activities of the solute α_2 and from these the activity coefficients, γ^*, we made use of the thermodynamic relation

$$\int d \ln \alpha_2 = -\int \frac{N_1}{N_2} d \ln \alpha_1$$

To this end we plotted the values of N_1/N_2 against log α_2 and from the area under the curve, measured by means of a planimeter, determined the difference between the values of log α_2 at given different concentrations and the value of log α_2 for a molality whose activity coefficient had been determined previously by other means. From these we have obtained quantities which are proportional to α_2. Upon taking the square roots of these and dividing by M we found another series of quantities, $k\gamma$, which are proportional to γ. To evaluate γ it was necessary to find the value of k. We did this by assuming the values of γ obtained by Harned and Douglas[8] for the two 1 M solutions. Dividing the value of k thus found for each salt into each of the products, $k\gamma$, we obtained the values of the activity coefficients given in Col. 8. These activity coefficients have been plotted against the corresponding values of M, Fig. 2. The agreement between the values of γ for sodium bromide and those calculated by Harned and Douglas for the same concentration range is exceptionally good; that between the values of γ for solutions of potassium iodide at the three

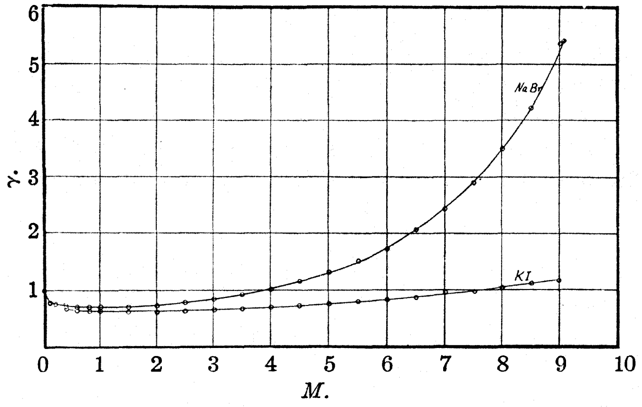

Fig. 2.

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[8] Harned and Douglas, This Journal, 48, 3095 (1926).

lowest concentrations is not good. This is not surprising when we consider the roundabout way in which y is calculated. Even very slight errors in the vapor pressure readings are highly magnified when working with vapor pressures at concentrations less than 1 M.

From the activities of the solvent and the solute it is possible to calculate also three other important thermodynamic quantities. Thus the relation $-\Delta F_1 = \overline{F}_1 - F_1^0 = RT \ln \alpha_1$ gives the increase in free energy accompanying the transfer of one mole of water from the pure solvent to a solution of the given molality. Likewise, $-\Delta\overline{F}_2 = \overline{F}_2 - F_2^0 = RT \ln \alpha_2$ gives the corresponding change in free energy for the solute. The values of $-\Delta F_1$ and $-\Delta F_2$ thus calculated are given in Cols. 9 and 10. In making these calculations we have taken R = 1.9885 cal. and T = 298.12". In the last column of each table under $-\Delta F_2^0$ is tabulated the increase in free energy accompanying the dilution from any concentration M to one exactly 0.1 M.

In this paper we have made all of our calculations on the basis of "weight molal" concentrations, that is, moles per 1000 g. of water. While we have attributed the deviations from the laws of ideal solutions to hydration, we have not been oblivious to the newer development of the solution theory brought out by Debye and Hiickel. More recently Hiickel[g] has extended the interionic attraction theory to concentrated solutions and he states that the interionic attraction theory provides a better explanation for these deviations than does hydration. He also states that the variation of the activity coefficient with the concentration can be expressed by the relation

$$\log f = -\frac{0.354\sqrt{2c}}{1 + A\sqrt{2c}} + B \cdot 2c$$

where A and B are constants and c represents the concentration in moles per liter.

The experimental method presented makes it possible to determine vapor pressures for all concentrations from 0.1 M up to saturation. The data obtainable should give us a good opportunity to test the validity and range of application of the Hiickel equation to saturated solutions. Unfortunately, no accurate density data are available for converting our concentrations to the molar concentration basis used by Hiickel. We are now determining the densities of these solutions and will report our test of the Hiickel equation in a forthcoming paper.

Summary

1. The vapor pressure of solutions of sodium bromide and potassium iodide have been determined at 25° for concentrations lying between 0.1 M and the saturated solutions.

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

2. From the data obtained we have calculated the osmotic pressures, the activities of the solute and solvent, the activity coefficients and various changes in free energy accompanying change in concentration.

3. For all concentrations the magnitude of these solution values is greater for solutions of sodium bromide than for solutions of potassium iodide.

Iowa City, Iowa

[Contribution from the Chemistry Laboratory of The Johns Hopkins University]

A NEW METHOD FOR MEASURING OSMOTIC PRESSURE[1,2]

By R. V. Townend

Received August 2, 1928 Published November 6, 1928

Introduction

In the past the study of osmotic pressure has been hampered by the experimental difficulties involved in making exact measurements. At least partly for this reason, the possibilities of osmotic pressure as a means for investigating the nature of solutions of electrolytes have been largely overlooked. The subject is treated briefly in many textbooks of chemistry, although its fundamental importance in other lines, such as plant and animal nutrition, has long been recognized by botanists and others. As a means for determining the activity of dissolved substances it ranks with such methods as vapor pressure lowering, freezing point lowering, and boiling point raising. With the exception of vapor pressure measurements, it is the only method of directly measuring activity at any and all temperatures. The osmotic method also has certain advantages over that which depends on the estimation of difficultly soluble substances in the presence of other salts. In the latter case it is necessary to make certain assumptions, such as the "ionic strength principle," whereas this is unnecessary in the case of the osmotic method. Moreover, the fact that a thousandth molal potassium chloride solution has a freezing point lowering of about 0.00368°, whereas the same solution has an osmotic pressure of about 36 mm., indicates clearly that as a means for investigating dilute solutions it would be of unsurpassed value provided certain experimental difficulties could be overcome.

The Measurement of Osmotic Pressure

The ordinary method for measuring osmotic pressure and the only one which has so far given satisfactory results consists in the use of a porous

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[1] In memory of Ira Remsen.

[2] The substance of this paper was presented by the author to the Board of University Studies of The Johns Hopkins University as part of the requirement for the degree of Doctor of Philosophy.

clay cell, which acts as a support for a copper ferrocyanide membrane. The solution is placed on one side of the cell, a suitable manometer attached and the equilibrium pressure determined when pure solvent is placed in contact with the other side of the membrane. The method has been refined so as to give reliable results with solutes of high molecular weight but up to the present it has not been applicable to solutions of electrolytes, on account of the difficulty in obtaining suitable membranes which would be impermeable to the ions.

The present method makes use of two general properties of liquids which are not ordinarily considered: first, that changing the pressure on a liquid surface changes its vapor pressure, and, secondly, that liquids possess an internal pressure or cohesion force so that (in the absence of excess dissolved gases) it is possible to place a tension on the two ends of a column of liquid.[3]

Outline of the Method

In the method to be described here, the solution to be measured—for example a salt solution—is placed in contact with its vapor. Some of the pure solvent is also placed in contact with the vapor. Since the vapor pressure of the solution is less than the vapor pressure of the pure solvent at the same temperature, in the case mentioned, water vapor will distil from the pure solvent into the solution. It is seen that the vapor phase may be regarded as a perfect semi-permeable membrane permitting the passage of the molecules of solvent only.

In order to permit the measurement of the osmotic pressure the liquid water is located within the capillaries of a thin porous plate. The capillaries are of sufficient size to permit the liquid water to pass readily to the surface of the plate, but so small that the maximum capillary rise is somewhat greater than the maximum osmotic pressure to be measured. Below the plate is a quantity of liquid water and below this a column of mercury. The weight of the water and mercury places a tension on the water at the surface of the plate. At equilibrium this force (corrected for any difference in heights between the water and solution) equals the osmotic pressure of the solution. The equilibrium point is determined by measuring the rates of distillation from the plate to the solution under different tensions. These rates are plotted against the corresponding tensions. The osmotic pressure, which corresponds to the tension at zero distillation, is obtained from the curve by extrapolating to zero.

There are several experimental details mentioned below which, in the course of working out this method, were found to be necessary for success. From the large amount of work carried out in this Laboratory on vapor pressure, it was known that in order to obtain a satisfactory distillation

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[3] See also Washburn, *J. Am. Ceram. Soc.*, **1**, 29 (1918).

from (or into) the surface of a liquid, the system must be practically air-free.

In order to insure absolute uniformity (both of temperature and composition) throughout the solution at all times, gentle stirring was necessary. Violent agitation at the surface was to be avoided, as it might give high results due to the fact that potassium chloride is negatively adsorbed at the surface of water solutions.

The porous disk involved considerable experimentation in order to secure the required porosity, as pointed out above. In addition, the disk must be mechanically supported to withstand the stress applied and all surfaces must be thoroughly wetted by the liquid.

Temperature control is of primary importance. At 25° the vapor pressure of water changes approximately 1.4 mm. per degree, while a 0.001 *M* solution lowers the vapor pressure by approximately 0.00074 mm. Thus it is seen that a drop in temperature of about 0.00053" has the same effect on the vapor pressure as a 0.001 molal solution.

Since in the process of removing the air from the system, the concentration of the solution was changed by an unknown amount, the solutions were analyzed after the measurements were completed. These analyses were made by means of the Zeiss interferometer, after the instrument had been calibrated against solutions of the same salt of known concentration. In the case of the most dilute solution, the total amount of solid used was less than five milligrams and it was necessary to concentrate a portion of the solution by evaporation before a satisfactory reading could be obtained on the interferometer.

By this method the measurements of osmotic pressure are made on air-free solutions. Since the solubility of air in water under ordinary conditions is nearly 0.001 M, this may well affect the measurements which are made on dilute solutions, in which the solute is present to only a fraction of this amount. In the majority of instances this factor has been entirely neglected.

Details of the Apparatus

The thermostat used in this work was a cylindrical copper tank, sixteen inches high and of the same diameter. It was covered on the sides and bottom with a layer of asbestos. Vigorous circulation was effected by means of a three and one-half inch propeller with suitable baffles. No temperature difference could be detected with a Beckmann thermometer in various parts of the bath. The usual heating lamp in series with a lamp bank of nominally 300 volts, and coil carrying tap water for cooling were used. It was found necessary to shield the contents of the thermostat from strong light during the course of *a* run, due to local superheating. Consequently the windows and top were covered during these periods.

The thermoregulator was of the toluene–mercury type constructed as follows. Twelve feet of thin, one-quarter inch diameter copper tubing was coiled into a helix about twelve inches in diameter. One end was squeezed tightly together and soldered along the seam. To the other end a four-inch length of brass tubing of slightly larger diameter was fitted carefully and soldered. The other end of the brass tubing was attached to the glass part of the regulator by means of a "soldered joint." This was made as follows: the brass tube was reamed out sufficiently to allow the glass to slide inside for a distance of about an inch. The inside of the brass tube was "tinned" and a slight excess of solder melted into the inside. The glass was roughened slightly by rubbing with fine emery paper, carefully cleaned and dried. After having coated the surface of the roughened part with a layer of platinum (produced by evaporating a solution of platinum chloride on this surface and decomposing the chloride by heating to dull redness), the two pieces were heated to about the same temperature and pushed together.

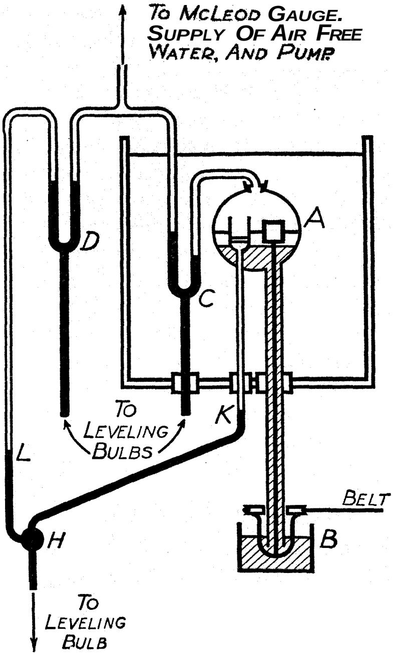

Fig. 1.

Under the best conditions the regulator described held the temperature of the bath sufficiently constant so that no movement of the mercury of the Beckmann thermometer was detected. The room temperature was held not more than two or three degrees from the temperature of the bath and in particular sudden fluctuations of temperature were avoided. It was found advantageous to make the measurements at night and in most instances this was done. In the experiments the bath varied slightly in temperature but not over two or three thousandths of a degree. As a matter of fact, due to the lag in registering, it is questionable whether the Beckmann readings are much more reliable than this. As will be shown later, this figure does not represent the difference in temperature between the solvent and solution, which is the important point. The temperature of the bath was determined by comparison with a thermometer standardized by the Bureau of Standards to 0.02°.

The porous disk was composed of equal parts by weight of the special clay used in this Laboratory for making osmotic pressure cells and Pyrex glass powder. The glass was first ground wet in an agate mortar, dried and sieved through a two hundred mesh sieve. The clay and glass were then thoroughly mixed together with the addition of the smallest amount of distilled water, moulded into a disk on a porous plate, dried at 100°, and then fired for about three-quarters of an hour at 850 to 900°. This is well above the melting point of Pyrex and it gave a disk of fair mechanical strength and good porosity. The sides and edges were ground smooth and the disk fused into a Pyrex glass funnel. The disks used were one inch in diameter and slightly less than an eighth of an inch in thickness. In preliminary tests, the capillaries in the disks held a pull of thirty-five inches of mercury and showed no indications of having reached their limit even at this figure.

In order to maintain the solution and the solvent in the porous disk at the same temperature, the glass funnel with its porous disk was placed within a large glass bulb of about 700 cc. capacity in the thermostat. Inside the bulb and surrounding the funnel was placed the solution which was floated on mercury. This arrangement gave the system a certain lag which—at least in part-counteracted the slight periodic changes in bath temperature incident to thermoregulator control and furnished good thermal contact between the solvent and solution.

The general arrangement of the apparatus is indicated in Fig. 1. A represents the bulb in the thermostat which holds the solution and the small glass funnel with its porous disk. Just to the right of the funnel is shown the stirrer, consisting of a small platinum paddle driven as indicated through a mercury seal at B.

From beneath the porous plate, a two millimeter capillary extended to a small bulb at H. This capillary contained the column of water which was placed under tension by the mercury in contact with it at K. In the absence of air no trouble whatever was experienced in getting the water to adhere to the plate, or the mercury to the water. Bulb H was connected by means of a length of rubber tubing to an ordinary leveling bulb which was open to the atmosphere. This permitted adjustment of the tension by moving the leveling bulb up or down by means of a screw.

Also from H a capillary tube extended vertically upward, giving a direct measurement of the zero reading of the mercury meniscus at I,. The upper part of this tube was completely evacuated and closed off by the mercury Y at D. By using the same size of tubing at K and I,, no correction for capillary depression was necessary.

A bulb of 300 cc. capacity was sealed into the system to provide a volume into which the vapor of the solution could be expanded. Another bulb containing air-free water was also sealed into the apparatus. This served as a source of water vapor to sweep the air from the system or to fill the space beneath the porous disk with water vapor. In the absence of air, it was a simple matter to distil water from one part of the system to another by a slight difference in temperature. Neither of these two bulbs is shown on the diagram.

The readings of the heights at K and at I, and of the surface of the solution in A were made by means of a cathetometer and a standard meter scale mounted vertically at a convenient distance.

Method of Procedure

Between 200 and 250 cc. of freshly redistilled water was collected in a Pyrex Erlenmeyer flask fitted with a cork stopper covered with tin foil. After cooling, the flask and water were weighed and an amount of pure salt was added to give approximately the desired concentration. This solution was run into a round Pyrex bulb of about 300 cc. capacity provided with a glass stopcock on one side. To the opposite side of the bulb, an ordinary mercury leveling bulb was attached by means of a rubber tube and about four inches of glass tubing. The height of mercury was adjusted so that the mercury came just to the glass bulb and the rubber tubing was closed with a screw clamp. The solution was then readily introduced by partially evacuating the bulb and connecting a glass funnel to the outer end of the glass stopcock by means of a short piece of clean rubber tubing. On opening the stopcock the solution was quickly drawn in.

The bulb was tilted at a slight angle and the solution brought to the boiling point by placing a small flame underneath. The solution was allowed to simmer for some minutes with the stopcock left open. The elimination of air from the solution is a direct function of the time and it was found advantageous to extend this simmering period for an hour or even longer. The solution was then heated to vigorous boiling for a moment or two in order to expell completely the air from the vapor space above the liquid, and while still boiling the mercury was allowed to run in rapidly from beneath, forcing the solution up past the stopcock, which was at once closed. After allowing the whole to cool, a short piece of rubber tubing was attached and sufficient mercury added from a small pipet to displace the solution above the stopcock and completely fill the rubber tubing. One end of a capillary glass tube about nine inches long was then forced into the rubber connection so that the mercury went part way up the capillary. The other end of the glass tube had previously been drawn out and the tip bent up at an angle.

In order to introduce the solution into the apparatus the system was evacuated completely and filled with water vapor to prevent the sudden evaporation of the first solution added. The tip of the capillary tubing was placed beneath the mercury, which sealed the stirrer column (at B in the figure), the screw clamp removed and the stopcock opened sufficiently to let a little of the solution by. This pushed a column of mercury down the capillary tube, which forced the air ahead of it. The tip was then hooked beneath the end of the glass tube carrying the stirrer shaft and the solution flowed in slowly and up the tube. Under these conditions it was possible to introduce the solution nearly air free and without spattering.

To remove the slight amount of remaining air, the solution was stirred and the vapor above the liquid drawn off at periodic intervals. The system beyond the trap C in the thermostat was evacuated by means of the pump. The mercury seal located between trap C and the pump was closed and C opened momentarily. This was repeated about every ten or fifteen minutes at first and less frequently as the amounts of air decreased. About a day was generally required to reduce the air to 0.0001 mm. pressure, as read on the McLeod gage, after standing for a fifteen-minute period. This was probably about one-third that actually present above the solution. On standing overnight less than 0.001 mm. developed.

It was found possible to make measurements with a somewhat greater amount of air than this (0.0001 mm.) and in most instances this was done. As far as could be noted the rates of distiilation observed were nearly independent of the amounts of air present at these very small concentrations.

As soon as the solution was practically air free, a small amount of water was evaporated over into the bulb at H, either from the solution or the supply in the bulb provided. It was found possible to distil this water directly through the disk and this had the advantage of partly sweeping any air ahead of it, so that the air could more easily be removed. All but the smallest trace of air had to be eliminated from beneath the porous disk or the water would not adhere. The last trace of air dissolved in the liquid and when once the liquid stuck no further trouble was encountered. In fact, the column of water beneath the disk could be left adhering to the disk from one experiment to the next even though the space above the disk was exposed to the atmosphere. In order to make the liquid break away from the under side of the disk it was necessary to force the water completely through the disk. Then the mercury column could be broken in the larger part of the column.

After the water had stuck to the lower side of the disk, if necessary, the mercury meniscus could be drawn up by opening the solution (and upper side of the disk) directly to the pump for a moment or two at a time. About one millimeter evaporation could be obtained at each opening. It was found best to adjust the mercury so it could be read beneath the bottom of the thermostat, since in this way greater accuracy could be obtained than by looking through several inches of water and, also, the necessity of directing a strong beam of light through the thermostat was avoided.

As soon as the mercury height at K had been adjusted, the space above I, was completely evacuated and closed off. Measurements could then be started when sufficient time had elapsed for the system to come to temperature. At least an hour, and frequently longer, was required for conditions to become constant after any removal of vapor or slight change in temperature.

By means of the leveling bulb connected to H, the desired tension (as indicated by the height of the mercury at L) was placed on the water. The reading at L was at once taken and the hair line of the cathetometer focused on the meniscus at K. The upward movement of the mercury was followed by means of the cathetometer screw and the readings were immediately plotted against the time. This had the advantage of indicating how soon constant conditions were obtained. A precaution was taken to approach the reading from the same direction in order to eliminate any possible play in the cathetometer. As soon as the desired number of readings had been taken, the zero point was generally redetermined and a new set of readings started. It was of interest to note the increased recession of the water into the capillaries of the porous disk as the amount of tension was increased.

As soon as the series of measurements on any one solution had been completed, air was admitted to the system and a sample of solution removed for analysis in the interferometer.

Determination of the Osmotic Pressure

The tension exerted was made up of three parts: first, a portion of the mercury column; second, the water from the meniscus of the mercury to the porous disk, and third, the net height of vapor between the surface of the porous disk and the surface of the solution. This last component will be equal to a column of water of the same height, for if we consider a column of water under tension separated from a column of vapor by a suitable membrane (for example, a porous plate) and that equilibrium exists at one point, it is seen that equilibrium must exist throughout the whole column. The fact must also be taken into account that the vapor pressure of the solution is present in the bulb and lacking above the zero reading at L.

The tension can then be calculated by adding together the vapor pressure of the solution at the temperature in question, the mercury equivalent of a column of air-free water from K to the surface of the solution, and the reading at K. The zero reading at L is subtracted from this total. Throughout, the measurements are corrected to the density of mercury at 0°.

Whenever the tension was closer to the equilibrium point than four or five millimeters, it was not possible to obtain good rates of distillation. The same held true if the total pull on the plate was reduced below about five millimeters. It was also not found possible to make measurements of back distillation, that is, from the solution to the plate.

In order to determine the osmotic pressure of the solution, the various rates of distillation were plotted as ordinates against the tensions as abscissas. The points fell on a straight line which could readily be extrapolated to zero.

During the distillation the high heat of evaporation acted to cool the surface of the disk and to warm the solution. Probably the small thermal head causing heat to return to the disk by conduction was largely responsible for the slow rates of evaporation found. However, the rate of heat flow will depend on the temperature difference between various parts of the system and this, in turn, on the evaporation and condensation of the liquid. Consequently, in the last analysis, the rate will be indirectly dependent alone on the differences in vapor pressure as controlled by the concentration of the solution and the amount of tension on the plate. Zero distillation must represent temperature as well as pressure equilibrium.

In conclusion, the author wishes to express his appreciation to Dr. J. C. W. Frazer and to Dr. W. A. Patrick, who suggested this investigation and under whose supervision it was performed.

Summary

A new method for measuring osmotic pressure has been described which can be applied to dilute solutions of any non-volatile solute in a volatile solvent.

This method makes use of the vapor phase as a diaphragm which separates the pure solvent from the solution and is permeable to the solvent only. The pure solvent is located at the surface of a porous plate in such a way that a tension can be applied to the liquid. This changes the

normal curvature of the surface so that the vapor pressure of the liquid is reduced. The rates of distillation from solvent to solution under different tensions were measured and these plotted to give the tension corresponding to equilibrium or the osmotic pressure.

This method extends the possibility of direct osmotic pressure measurement to aqueous solutions of electrolytes and possibly colloids, and to solutions in organic liquids. It is particularly applicable to extremely dilute solutions where a knowledge of the properties is desirable from a theoretical standpoint. Moreover, it has the advantage that measurements are made under air-free conditions.

BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OR THE JOHNS HOPKINS UNIVERSITY]

A STUDY OF VAPOR PRESSURES IN SMALL CAPILLARIES. PART I. WATER VAPOR. (A). SOFT GLASS CAPILLARIES[1,2]

BY J. L. SHERESHEFSKY

RECEIVED AUGUST 2, 1928 PUBLISHED NOVEMBER 6, 1928

Introduction

When a liquid bounded by a curved surface is in a state of tension, the pressures on each side of the surface layer are not equal. The pressure on the concave side of the surface is greater than that on the convex. When such a system is in a state of equilibrium we know from the laws of mechanics that the algebraical sum of the work done by these forces when the body undergoes a small displacement is zero. This pressure difference as deduced on the basis of the well-known theory of Laplace, in the case of a sphere of radius r, is given by the equation

$$p = \frac{2\sigma}{r} \qquad (1)$$

where a is the surface tension.[3]

Suppose we have a capillary dipped into a liquid contained in a large vessel. At the plane surface, since the radius of curvature is infinite, the pressure difference, p, is zero. On the other hand, at the concave side of the meniscus

$$p = \frac{2\sigma}{r} \qquad (2)$$

r being assumed to be equal to the radius of the capillary. Since the vapor pressure of the liquid in the capillary is lower than the vapor pressure of

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[1] In memory of Ira Remsen.

[2] The substance of this paper was presented by the author to the Board of University Studies of the Johns Hopkins University as part of the requirement for the degree of Doctor of Philosophy.

[3] "Scientific Papers," Vol. II, p. 564, by Clerk Maxwell.

the liquid over the plane surface, we may look upon the surface layer in the capillary as upon a semi-permeable membrane on which it is necessary to impose a pressure, p, in order to produce the above lowering of the vapor pressure.

The relationship between the pressure, p, and the vapor pressure, P, is expressed by the equation of Willard Gibbs

$$-\frac{dP}{dp} = \frac{v}{V} \tag{3}$$

which states that the change of vapor pressure, P, with respect to the pressure, p, is equal to the ratio of the molar volumes of the substance in the liquid state, v, and the gaseous state, V.

Assuming that at low pressures the gas laws hold, we obtain by substitution in Equation **3** and subsequent integration

$$\ln P = -\frac{v}{RT}p + C \tag{4}$$

When p is zero, that is, in the case of a plane surface, the vapor pressure is P_0, and

$$C = \ln P_0 \tag{5}$$

Substituting in the above, we get

$$\ln P = -\frac{v}{RT}p + \ln P_0 \tag{6}$$

or

$$\ln \frac{P}{P_0} = -\frac{V}{RT}p \tag{7}$$

Combining with Equation 1, we obtain the expression

$$\ln \frac{P}{P_0} = -\frac{V}{RT}\cdot\frac{2\sigma}{r} = -\frac{2\sigma v}{RTr} \tag{8}$$

which is the well-known equation first deduced by Lord Kelvin,[4] where P_0 and P are the vapor pressures over the plane and concave surfaces, respectively, at temperature T, R is the universal gas constant, a is the surface tension and v and r are as indicated above.

Laplace in his monumental work on capillarity assumes that the forces that give rise to capillary phenomena are "insensible for sensible distances, and sensible for insensible distances," that is, as far as surface tension is concerned, its value would be the same for small drops, or liquids in small capillaries, as for liquids in bulk. Thus surface tension would begin to undergo a change only when the radius of the drop or the capillary would approach the range of influence of molecular forces, which he assumed to be the same for all substances. This led many experimenters to measure the radius of molecular forces.

Plateau[5] observed the thickness of soap bubbles and concluded that the

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[4] Sir W. Thomson, *Phil. Mag.*, [4] **42, 448 (1871).**

[5] Plateau, "Statique experimentale et theorique des liquides."

range is not larger than 0.056μ. Drude's[6] observations assign a value of 0.009μ, while Reinold and Rucker[7] give about 0.006μ.

Quincke,[8] using a different method, measured the range to be about 0.05 and 0.08μ.

Here it is noteworthy to mention that Plateau also observed that the viscosity of the surface layer in thin films is different from that of the interior of the liquid, and that this viscosity change varies in sign with different liquids, a fact that would justify us in doubting whether the above values correspond to the magnitude of the range of molecular forces in the interior of the liquid.

In light of the above discussion of the fundamental assumptions of Laplace and the experimental facts concerning thin films, it would appear that the surface tension term in Equation 8 is constant and does not depend on the radius of the capillary, but this conclusion is not in conformity with many experimental facts and certain theoretical considerations that will follow.

Patrick and Eberman[9] in correlating the extensive work of the former and his collaborators on adsorption by silica gel from both liquid and vapor phases, express the internal volume of a gram of gel by the equation

$$V = Kr^{1/n} \tag{9}$$

since adsorption by silica gel is caused by the capillaries in the adsorbent. By combining this equation with Equation 8, they eliminate r and get a relationship between volume adsorbed, V and the equilibrium pressure, P. Calculating r from Equation 8 they plot V against the radius for many substances. They state "it is obvious that if we plot radius as found by Equation 8 against (V) as measured, we should obtain a parabolic curve which should be the same for all substances adsorbed by the same sample of gel whether from the gas or from solution—regardless of temperature. For, if adsorption consists in capillary condensation, the same volume of internal gel space must hold the same volume of liquid regardless of circumstances."

The curves that they obtain for water, sulfur dioxide at different temperatures and butane are parabolic but do not coincide. After a consideration of such factors as density and molecular weight that figure in Lord Kelvin's equation and also the possibility of polymerization, they come to the conclusion that "the surface tension of a liquid is a function of curvature; that a liquid existing in small drops has a much lower surface tension than ordinarily, and that the liquid has a much greater surface tension if its surface is highly concave. . . ."

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[6] Drude, *Wied. Ann.*, 43,158 (1891).

[7] Reinold and Rucker, *Phil. Trans.*, 177, Part II,627 (1886).

[8] Quincke, *Pogg. Ann.*, 139, 1 (1870); 160,371 (1877).

[9] Patrick and Eberman, *J. Phys. Chem.*, 29,220 (1925).

Patrick, Preston and Owens[10] studied the adsorption of carbon dioxide at several temperatures by silica gel, expressing the adsorption equilibrium by the equation

$$V = K\left(\frac{P\sigma}{P_0}\right)^{1/n} \tag{10}$$

where V is the volume adsorbed, P_0 the saturation pressure and P the equilibrium pressure, and K and n are constants dependent upon the sample of gel used. Plotting log V against log $(P\sigma/P_0)^{1/n}$, they get a straight line, where $(1/n)$ is the slope of the curve and K the intercept on the log $(P\sigma/P_0)^{1/n}$ axis. They find that only when the surface tension term σ varies are they able to have the curves at the various temperatures coincide, that is, to get the same value for K. They also deduce that the change of a with the radius is greater at higher temperatures, that is, $d\sigma/dr$ is also a function of temperature. Further evidence as to the increase of surface tension with the decrease of the radius of the capillary is given by the reported changes in physical properties of liquids such as freezing point, critical temperature and density.

F. W. Parker[11] observed a depression of the freezing point of water, benzene and nitrobenzene when contained in capillary systems. Plotting liquid content against freezing-point depression, he obtained curves showing a gradual increase in depression with decrease in liquid content—in other words, with decrease of capillary radius—in case of the latter two liquids, and a rather steep curve indicating an enormous increase in depression with decrease of liquid content in case of water.

Bouyoucos and McCool[12] ascribe this phenomenon mainly to the dissolved impurities. While this cannot be true of benzene and nitrobenzene, it is surely the case with water; for, if we consider the phase diagram of the system, water and ice, we notice that the equilibrium curve is inclined toward the pressure axis, that is, the temperature increases with decrease in pressure and, inasmuch as the water in a capillary system is under a negative pressure, we should expect a rise in the freezing point.

A. S. Coolidge,[13] similarly, finds that the adsorption isotherm for benzene is continuous when the free liquid is below the freezing point, that is, the adsorbed material is in a liquid state even below the freezing point of the free liquid.

Patrick, Preston and Owens[10] observed no break in the adsorption of carbon dioxide and nitrous oxide between the temperatures 30° and 40°, thus indicating a rise in the critical temperature of the adsorbed substance. The significance of the above phenomena is very well pointed

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[10] Patrick, Preston and Owens, J. Phys. Chem., 29,421 (1925).

[11] Parker, THIS JOURNAL, 43,1011 (1921).

[12] Bouyoucos and McCool, *Mich. Agr. Expt. Sta.* Tech. Bull., 1915, 24; **1917,** 31

[13] Coolidge, THIS JOURNAL, 46, 596 (1924).

out by Patrick and Eberman,[9] "if condensation of a gas does take place in a capillary above the critical temperature and, in other cases, at pressures always below the saturation pressure; and, if adsorption does take place from liquids above the critical solution temperature—it follows that the critical temperature for a fluid in a capillary is higher. If the critical temperature is higher, the surface tension must be correspondingly higher, inasmuch as the temperature–surface tension curve cuts the temperature axis at or near the critical temperature."

Leslie[14] was the first to show that the rise of a liquid in a capillary was due to the greater pressure in the stratum of liquid adhering to the wall. The direct result of the excess pressure normal to the side of the tube would be to spread the liquid over the surface of the solid. When we plunge a capillary into a liquid, the above pressure would cause the liquid to spread and cover all the surface of the tube were it not for the liquid adhering to the ascending film and balancing the pressure and in this way stopping further wetting of the solid. We may look upon this tendency to spread as a result of a negative pressure or a tension in the film, which is balanced in case of a capillary open at both ends. Were we to prevent by some method some liquid from adhering to the ascending film, the pressure would remain unbalanced, unless the tension in the adhering film increases. This is precisely the condition existing in a capillary closed at one end and partly filled with liquid. It is obvious that the tension would increase with decreasing radius. This theory was expressed by W. A. Patrick[15] as follows, "a film-of molecular thickness may have the same surface tension as the liquid in bulk, but when this film is stretched, it is certain that such an operation will cause, according to the principle of Le Chatelier, an increase in the surface tension of the liquid film." Independently and from different considerations Freundlich[16] arrives at the same conclusions.

Experimental

Let vessel A containing a capillary be in communication with vessel B containing some aqueous solution, and let us assume that the water vapor has wetted the walls of the capillary. If the vapor pressure of the solution is greater than the vapor pressure of pure water in the capillary, the vapor will condense and fill up the capillary. Now, if we concentrate by some method the solution in B until its vapor pressure is lower than the vapor pressure of pure water in the capillary, the process will be reversed and evaporation of the water in the capillary will take place. The condition under which no evaporation from or condensation into the capillary will take place will indicate a state of equilibrium at which the vapor

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[14] Leslie, *Phil.* Mag., 14, 193 (1802).

[15] Patrick, *Kolloid-Z.*, *36*, 276 (1925).

[16] Freundlich, "Kapillarchemie," Akademische Verlagsges., Leipzig, 1922, p. 63.

pressure of the pure water in the capillary is equal to the vapor pressure of the solution.

To attain a state of equilibrium by trying solutions of various strengths would be rather tedious and time consuming. Furthermore, it would involve a complication in the temperature control, since the attainment of an equilibrium state would extend over a period of hours beyond the constancy of any temperature regulating device.

This difficulty may be overcome by measuring the rate of condensation or evaporation. If we start with a dilute solution whose vapor pressure is known and which is higher than the vapor pressure of pure water in the capillary, vapor will condense into the capillary with a rate proportional to the vapor pressure difference, $\Delta p = p_1 - p_2$, where p_1 is the vapor pressure of the solution and p_2 that of water in the capillary. For a given capillary p_2 is constant. By concentrating the solution we decrease p_1 and simultaneously Δp, and also the rate of condensation. If we continue to concentrate the solution we may reach values for p_1 which will be lower than p_2, Δp being negative. In such cases we measure the rate of evaporation from the capillaries. Now, if we plot these values of Δp against the rate we get a curve that approaches assymptotically the rate axis from two directions. By extrapolation we may evaluate the point of equilibrium when $\Delta p = 0$ and $p_1 = p_2$. Since p_2, the vapor pressure of pure water in a given capillary, is constant, we plot p_1 against rate and the extrapolated value will be p_1 when $\Delta p = 0$, that is, it will give us the value for p_2.

In a system completely freed from air the rates of condensation or evaporation are measurable quantities, as it was shown in the course of this experiment. The vapor pressure was not measured directly. It was calculated from the measured concentration as determined by conductivity. For this reason we have used potassium chloride solutions whose vapor pressures for a wide range of concentrations have been very accurately measured in this Laboratory by Frazer, Lovelace and Sease.[17] For calculations of the vapor pressures of very dilute solutions we have also used the freezing point data collected by Noyes and Falk.[18]

Apparatus

The apparatus as shown in the accompanying Fig. 1 is merely an elaborated form of the simple scheme we have discussed in the previous section.

It is made of soft glass. The two bulbs A and B serve as reservoirs of pure water; their capacity is 500 cc. each. To one of the bulbs is attached a side arm, C, through which the liquid is introduced. The tube connecting the water reservoir with the rest of the apparatus is surrounded by a water jacket, D, to keep the liquid from spreading over the apparatus when it is distilled from one bulb into the other.

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[17] Frazer, Lovelace and Sease, THIS JOURNAL, 43, 102 (1921).

[18] Noyes and Falk, *ibid.*, 32, 1020 (1910).

The rest of the apparatus consists of three branches. One branch connects (through the mercury trap F) the water reservoir with the conductivity cell E, designed for the purpose of measuring the change in conductivity of the pure water from time to time during the course of the experiment. The second branch connects the water reservoir, through the mercury traps, G, H and K, with the conductivity cell L, containing the potassium chloride solution. This cell is in communication with the mercury reservoir N, and the mechanical stirrer, O, designed to stir the solution. The third branch connects through the mercury traps, G, H and R, the water reservoir with the vessel, S, containing the capillaries. The capillaries may be brought in contact with the solution by closing trap H and opening the traps, K and R. The trap T connects or disconnects the whole apparatus, or each branch individually, with or from the mercury diffusion pump, J, and the auxiliary Cenco high vacuum pump (not shown on the diagram).

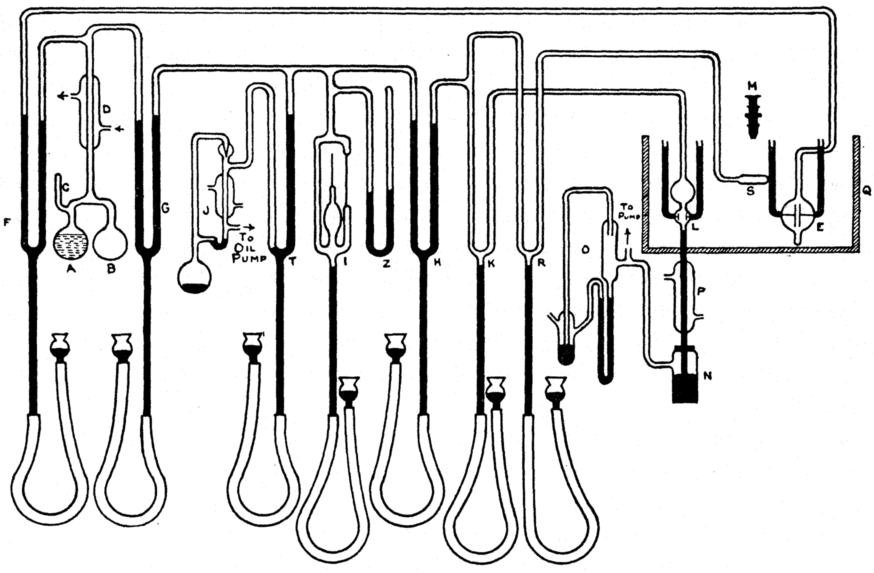

Fig. 1.

I and Z are a McLeod gage and a closed manometer, respectively. The vessels, L, S, and E are immersed in an accurately regulated thermostat, Q. The filling or the emptying of the capillaries is observed through the microscope, M, whose objective is an inch and a half below the surface of the water in the thermostat. The field is illuminated by a 150-watt lamp whose rays are made to pass through a vessel filled with water to absorb the heat rays, and then brought to a focus at a point on the capillary under observation by a system of lenses.

Capillaries

If we calculate from Equation 8, deduced by Lord Kelvin, the percentage lowering of the vapor pressure of water due to capillarity, we notice that the lowering is inappreciable until we approach the magnitude of 1×10^{-4} cm. for the radius of the capillary. As seen from Table I the percentage lowering increases very rapidly with decrease of radius.

TABLE I

CHANGE IN PERCENTAGE LOWERING

r, cm.	1×10^{-4}	0.8×10^{-4}	0.6×10^{-4}	0.4×10^{-4}	0.2×10^{-4}	0.1×10^{-4}
$100\Delta p/p_0$	0.01	0.14	0.18	0.27	0.53	1.06

Although a more pronounced effect in the lowering of the vapor pressure was expected, we were certain to have to work in about the same region of magnitudes. Furthermore, the capillaries had to be uniform in bore for a considerable length.

The method devised for producing such capillaries proved to be very successful. It consists of a string supported by two pulleys attached to the ceiling; on one end of the string a weight is hung and the other end is fastened to the top of a short length of capillary tubing of about 0.5mm. diameter. This tubing is clamped to the table top.

When a small area of the tube is heated up to a bright red heat the weight is allowed to fall, thus drawing out the heated portion of the tube to 4 meters—the distance between the table top and the ceiling.

The burner used in heating the tube consisted of a terra cotta cylinder with six evenly distributed perforations normal to the walls. Glass tubes with fine jets at one end are placed in these perforations in such a manner that the jets point toward the center of the cylinder. The ends that protrude outside the cylinder are connected by means of T-tubes, producing the effect of a wheel. A mixture of gas and air introduced into these jets produces a very intense and fine circular flame. The smallest capillary we have been able to draw by this method had a radius of 0.25μ.

Microscopic Measurements

The bore of the capillaries was measured microscopically. For capillaries ranging between 1 and 4μ in radius a combination of lenses giving a magnitude of about 900 is sufficient. Such a magnification was obtained by using a fluorite objective of focal length *2.6* mm. and initial magnification of 70 in combination with a filar screw micrometer eyepiece of a magnification of 12.5, giving a total magnification of 875 times.

The filar screw micrometer has been calibrated against an objective micrometer divided into 0.01 mm. Knowing the number of divisions on the eyepiece micrometer that correspond to one division on the objective micrometer, we may replace the latter by a capillary and determine its size.

The hollow of a capillary tube when observed under a microscope appears black at the sides of the wall and shades off into a gray toward the center of the capillary when the hollow is filled with a gas or a vapor. In case the capillary is filled with a liquid, the hollow appears bright and bounded by very thin black lines at the interface of the liquid and the glass.

Thermostat

The thermostat as shown in Fig. 1 contained the two cells and the capillary vessel. The former were in the main body of the thermostat; the latter was placed in a chamber projecting out at the side and in full communication with the rest of the thermostat. The projecting side chamber had a window through which the capillaries were illuminated.

The water in the thermostat was agitated by two stirrers symmetrically placed. The heating device was made up of two 150-watt Westinghouse heating lamps, and water running through a copper coil was used for cooling the thermostat.

The thermo-regulator was of the toluene–mercury type. It consisted of twenty feet of half-inch copper tubing coiled into a helix nine inches in diameter, filled with toluene and sealed to a glass head. The temperature of the thermostat was kept at 18° as read from Bureau of Standards thermometer No. **31091.**

The constancy of the temperature was read from two Beckmann thermometers graduated in **0.001°.** One was placed near the solution cell and the other near the capillary vessel, The thermometers indicated a temperature lower by **0.003°** at the solution cell. This was probably due to the fact that the solution cell was nearer to the cooling coil than the capillary vessel. For any one portion of the thermostat the temperature remained constant to 0.002° for over ten hours.

Observations

It was noted quite early in the course of the experiment that the condition of freeing the system of air was essential. Air present in the system clogged the capillaries and interfered with the formation of a uniform unbroken column of liquid. A capillary column formed under such conditions was invariably made up of a chain of intermittent air and water layers. As the system was made more air-free, this effect was minimized but even a slight trace of air remaining in the system was sufficient to cause the formation of broken columns of water.

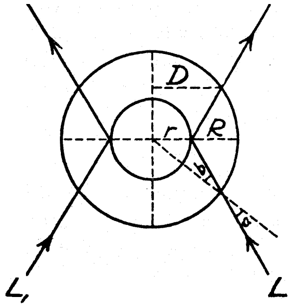

Fig. 2.

Although the above phenomenon prevented the measuring of the rate of condensation or evaporation, it did not interfere with the process of condensation per se.

Experiment I.—The capillary chamber was filled with water vapor by bringing it into communication with the water reservoir for a moment. The chamber was closed and allowed to stand for several hours until the capillaries were filled. The chamber was opened to the potassium chloride solution by closing trap H and opening traps K and R. The five capillaries were observed for several hours; no evaporation from any one occurred.

The chamber and the concentration cell were discommunicated, and the conductivity of the solution determined after the solution in the cell was thoroughly stirred. To verify the observation the process was reversed. The capillary chamber was evacuated and brought into communication with the solution cell by adjusting the traps as above. The capillaries seemed to fill up slowly. They were left in this condition for several hours until they filled up completely. Then they were discommunicated and the conductivity of the solution measured again.

TABLE II

MEASUREMENTS

X = 30.2; $(\Lambda_0-\Lambda)$ = 17.5; Concn. = 0.11; $(P_0-P_1)_X$ = 0.055

Capillary	I	II	III	IV	V
r (μ)	**1.076**	**2.284**	**2.443**	**3.019**	**4.052**
$(P_0-P_1)_K$	**0.015**	**0.007**	**0.007**	**0.0056**	**0.004**

Table II gives the observed measurements of the radii, r, of the capillaries; X, the resistance of the solution, $(P_0 - P_1)$ the vapor pressure lowering corresponding to the measured resistance, X, and $(P_0 - P_1)_K$ the vapor pressure lowering as calculated from the equation of Lord Kelvin.

Experiment 11.—The solution in the cell was concentrated by bringing the latter into communication with the reservoir which was subjected to an ice-bath. When the resistance indicated a concentration of about 0.13-0.14 N, the concentrating process was stopped.

The capillaries were allowed to fill up in a manner similar to Experiment I. When they were brought in contact with the solution, no signs of evaporation were observed. When the reverse process was carried out the capillaries filled up. Table III records the measurements of this experiment.

Experiment 111.—The solution was still further concentrated, and the experiment carried out as before. The data of this experiment are given in Table IV.

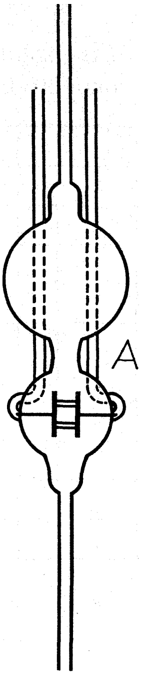

Fig. 3A.

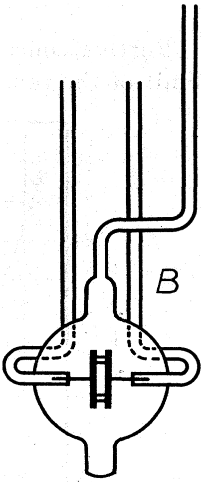

Fig. 3B.

Experiment IV.—When the solution was concentrated still further and the full capillaries were opened to the solution, Capillary V began to vaporize. The others did not show any change. When the procedure was reversed, Capillaries, I, II, III and IV filled up, but Capillary V remained empty. This observation was reproduced twice. Table V gives the data of this observation.

Table III

Measurements

X = 26.9; $(\Lambda_0 - \Lambda) = 18.45$; Concn. = 0.12; $(P_0 - P_1)_X = 0.060$

Capillary	I	II	III	IV	V
r (μ)	1.076	2.284	2.443	3.019	4.052
$(P_0 - P_1)_K$	0.015	0.007	0.007	0.0056	0.004

Table IV

Observations

$X = 23.4$; $(\Lambda_0 - \Lambda) = 19.35$; Concn. = 0.148; $(P_0 - P_1)_X = 0.074$

Capillary	I	II	III	IV	V
r (μ)	1.076	2.284	2.443	3.019	4.052
$(P_0 - P_1)_K$	0.015	0.007	0.007	0.0056	0.004

TABLE V

OBSERVATIONS

$X = 18.1$; $(\Lambda_0-\Lambda) = 20.95$; Concn. $= 0.183$; $(P_0-P_1)_X = 0.092$

Capillary	I	II	III	IV	V
r (μ)	1.076	2.284	2.443	3.019	4.052
$(P_0-P_1)_K$	0.015	0.007	0.007	0.0056	0.004

Further concentrating of the solution was not advisable since the higher limit of the range of the conductivity cell had been exceeded already.

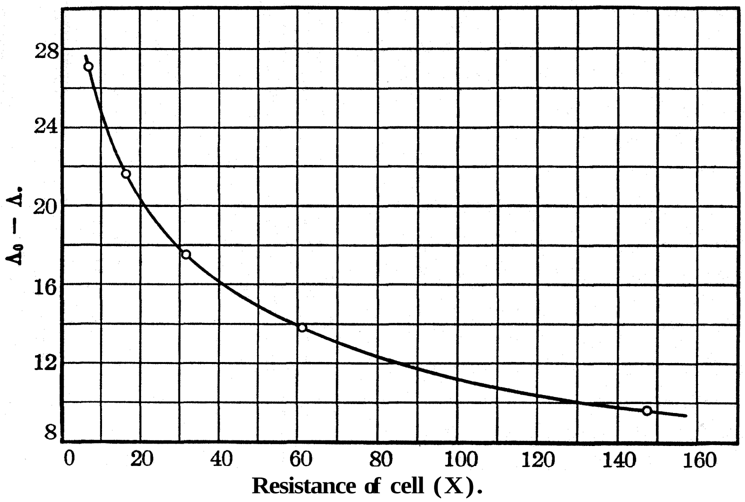

Fig. 4.

The values in Tables II, III, IV and V were obtained in the following manner. Knowing X and Λ_0 which is 129.5, the value for Λ was read from Fig. 4. Substituting these values, and also the relative viscosity read from Fig. 5, in the equation of Bates, the concentration was obtained. $(P_0 - P_1)_X$ was read from Fig. 6. The value for $(P_0 - P_1)_K$ was calculated from Lord Kelvin's equation.[19]

Since $V = M/D$, where M = mol. wt. and D = density

$$\log \frac{P_1}{P_0} = -\frac{0.4343 \times 2\sigma M}{RT\,d\,r} = \frac{-0.4343 \times 2 \times 73 \times 18.016}{8.32 \times 10^7 \times 291 \times 0.99862 \times 1.076 \times 10^{-4}} = 0.00044$$

$$\log P_1 = \log (P_0) - 0.00044 = \log (15.477) - 0.00044 = 1.18925$$

$$P_0 - P = 0.015 \text{ mm. of mercury.}$$

Although we have not as yet been able to determine quantitatively the vapor pressure lowerings corresponding to each capillary, we have definitely established that the lowering is enormously greater than can be accounted for by Lord Kelvin's equation.

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[19] Calculation: $\ln \frac{P_1}{P_0} = -\frac{2\sigma V}{RTr}$, or $\log \frac{P_1}{P_0} = -\frac{(0.4343)(2\sigma V)}{RTr}$.

Experiment IV also indicates an approximate value for the lowering of the vapor pressure in a capillary of about 4×10^{-4} cm. in radius.

According to the classical equation, the vapor pressure lowering for a capillary of 4.052μ in radius is 0.004 mm. of mercury. The value we have obtained is approximately 0.092 mm. of mercury, *23* times as great.

Now, if we consider for a moment Equation 8 we see that its right-hand member contains two terms, a and V, surface tension and molal volume, respectively, properties of liquids that would be different in a capillary from liquid in bulk. Which term must be changed in order to account for the enormous increase in the term $\ln (P_1/P_0)$? While it is possible that the molal volume V would be increased due to the decrease in density, it is highly improbable that the decrease in density would assume such magnitudes. The increase in the left-hand term must therefore be due mainly to the increase in the surface tension term, a.

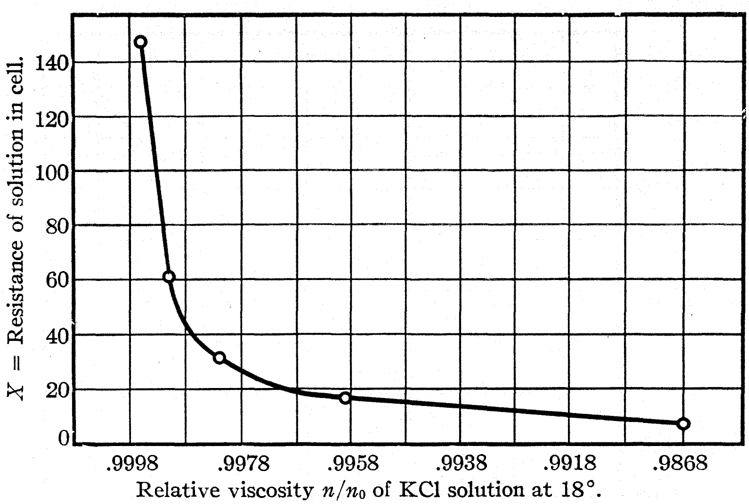

Fig. 5.

(B). Quartz Capillaries

If the depression of the vapor pressure in a given capillary is due to capillarity alone, then the rate of evaporation into a solution of a given concentration should stay constant irrespective of time. It was found, however, that in case of capillaries made of soft glass the rate of evaporation into a solution of a given concentration became smaller and smaller with time, the measurements being taken at one hour intervals. This indicated that the pressure became less and less. Since the solution was kept at the same concentration, the vapor pressure of the water in the capillary must have become lower. The latter could be due only to the solubility of the glass. In order to eliminate the effect of solubility mentioned above, it was decided to make similar studies in which the glass capillaries should be replaced by capillaries made of pure quartz.

Method

The apparatus was essentially the same as described in the foregoing work with the exception of the observing instrument, which consisted of a microprojector with a scale in the eyepiece instead of a microscope.

The procedure was to open a full capillary to the vapor of a concentrated solution of potassium chloride and observe the time required for a definite length of the water column in the capillary, as read on the scale in the eyepiece, to evaporate.

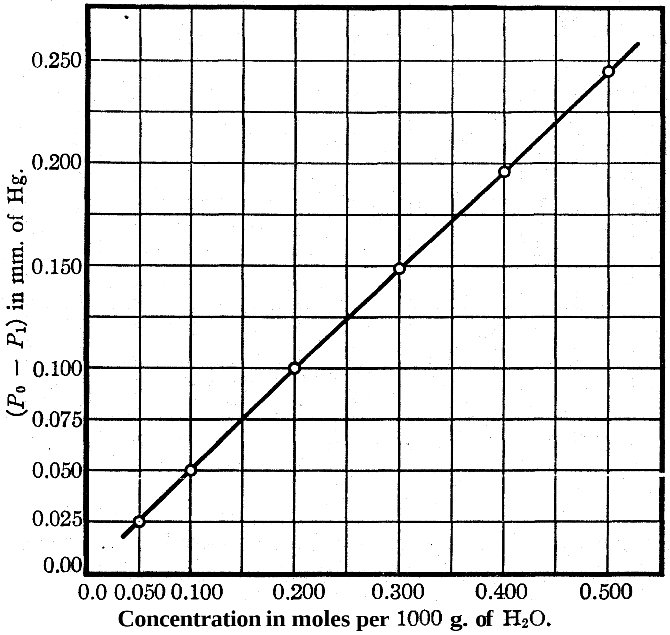

Fig. 6.

For a given capillary the rate of evaporation is proportional to Δp, the pressure difference between that of water in the capillary and the potassium chloride solution. Having obtained various rates corresponding to different concentrations of the solution, a curve was plotted of rate against Ap. The intercept on the Ap-axis will be the depression of the vapor pressure in the capillary.

Quartz Capillaries

These capillaries were drawn by the same method as described previously for the production of soft glass capillaries. Their size had been measured by means of a microscope supplied with a filar screw micrometer, and the true size calculated by using the approximate formula $r = D/n$, where D is the apparent radius and n the refractive index of the quartz.

Table VII gives the rates of evaporation from a capillary 5.51μ in radius, the corresponding concentrations of the potassium chloride solution and the lowering of the vapor pressure $P_0 - P_1$ where P_0 is the vapor pressure of water and P_1 is that of the solution.

TABLE VI

DATA WITH QUARTZ CAPILLARY

$r = 5.51\mu$ $t = 18°$

Expt.	Rate, mean value	Soln., N	$\Delta p = P_0 - P_1$, mm. Hg	Date of expt.
1	562	0.4105	0.205	Jan. 10 3 P.M.
2	284	.2154	.109	Jan. 6 4 P.M.
3	276	.2154	.109	Jan. 7 2 P.M.
4	235	.1815	.092	Jan. 8 11 A.M.
5	181	.1440	.074	Jan. 7 8 P.M.
6	179	.1345	.068	Jan. 11 3 P.M.
7	155	.1090	.056	Jan. 12 11 A.M.
8	127	.0930	.048	Jan. 11 8 P.M.
9	97	.0785	.041	Jan. 12 2 P.M.
10	93	.0690	.036	Jan. 13 11 A.M.

In the above table we observe that although there is a lapse of time of twenty-two hours between Measurements 2 and 3, there is a very slight change in the rate, showing that the solubility of the quartz is insignificant. When we plot the rate against Δp, a straight line is obtained which cuts the Δp-axis at 0.05 mm. of mercury. This means that at zero rate, when no evaporation takes place, that is, when the vapor pressure of the solution is equal to the vapor pressure of the water in the capillary, the depression is equal to 0.005 mm. of mercury.

The value calculated by means of Lord Kelvin's equation

$$\ln \frac{P_1}{P_0} = -\frac{2\sigma M}{RT\,dr}$$

is equal to 0.004 mm. of mercury.

TABLE VII

OBSERVATIONS

$r = 2.07\mu;\ t = 18°$

Expt.	1	2	3	4	5	6	7
Rate, mean value	471	340	288	270	213	144	78
Soln., N	0.4285	0.3508	0.3585	0.2982	0.2780	0.2304	0.1890
$\Delta p = P_0 - P_1$, mm. Hg	0.216	0.175	0.179	0.154	0.140	0.116	0.096

The curve derived from the data given in Table VII cuts the Δp-axis at 0.068 mm. of mercury, thus indicating that the depression of the vapor pressure in a capillary 2.07μ in radius is 0.068 mm. of Hg.

The straight line does not run parallel to the one for the larger capillary considered above but recedes from the rate axis with time, showing a slight solubility effect increasing with age of the capillary, that is, with the time the capillary is in contact with water. The value calculated by means of Lord Kelvin's equation for this capillary is 0.08 mm. of mercury.

In conclusion, the author wishes to express his appreciation to Dr. W. A. Patrick, who suggested this research and under whose supervision it was performed. He is also indebted to Dr. J. C. W. Frazer for his interest and advice rendered during this investigation.

Summary

1. A method is described for measuring vapor pressures of liquids in small capillaries.

2. By means of this method it has been established that the vapor pressure lowering of water in small capillaries is much greater than can be accounted for by Lord Kelvin's equation.

3. It is shown that the greater lowering of the vapor pressure is due to the increase in surface tension.

BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

A STUDY OF VAPOR PRESSURES IN SMALL CAPILLARIES. PART II[1]

BY J. L. SHERESHEFSKY

RECEIVED AUGUST 2, 1928 PUBLISHED NOVEMBER 6, 1928

Paper I dealt with the direct measurement of vapor pressures of water in glass and quartz capillaries. It was found that in case of capillaries made of thermometer glass the lowering of the vapor pressure was abnormally great. It was first suspected and afterward shown that a great fraction of this lowering was due to the solubility of the glass. From this point the work proceeded with quartz capillaries. The quartz from which the capillaries were drawn was obtained from the General Electric Company and was of the highest purity. The lowerings of vapor pressure in this case were smaller than before, but still abnormally greater than can be accounted for by the Lord Kelvin equation.

There may or may not be any solubility effect in the case of quartz, but when the ratio of the surface to the volume in the capillaries we were dealing with is considered, any negligible solubility may assume considerable importance. Therefore, a non-polar liquid was employed, such that a solubility effect cannot reasonably be involved.

Apparatus

The method of measuring the depression of the vapor pressure and the underlying theoretical considerations are fully discussed in the first paper. Certain changes and

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[1] In memory of Ira Remsen.

improvements in the original apparatus, necessitated by the use of the organic liquid, are described below. Referring to the diagram of the original apparatus, vessel I, was substituted by a cylindrical vessel of 200-cc. capacity, provided with a magnetic stirrer. There was no need for vessel E and trap F; they were therefore eliminated. The bulbs A and B, serving as a means for removing the dissolved air and as a reservoir for the liquid, were substituted by a vessel shown in the accompanying Fig. 1. This proved less troublesome and much more efficient in freeing the liquid from the last traces of air. It was operated by means of a suction interrupter similar to the one designated by O. When the water pump diminishes the pressure over the mercury in the reservoir, the column of mercury, over which the liquid in the lower bulb rests, falls and allows the liquid to fill up the small side bulb; when the suction is broken by the interrupter, the column of mercury rises to its original height, fills the side bulb with mercury and pushes the liquid into the upper bulb filled with glass beads. The spreading of the liquid in such a manner over a large surface facilitates the removal of the dissolved gases. Many repetitions of this procedure, followed by pumping, removed the last traces of air in the course of several days.

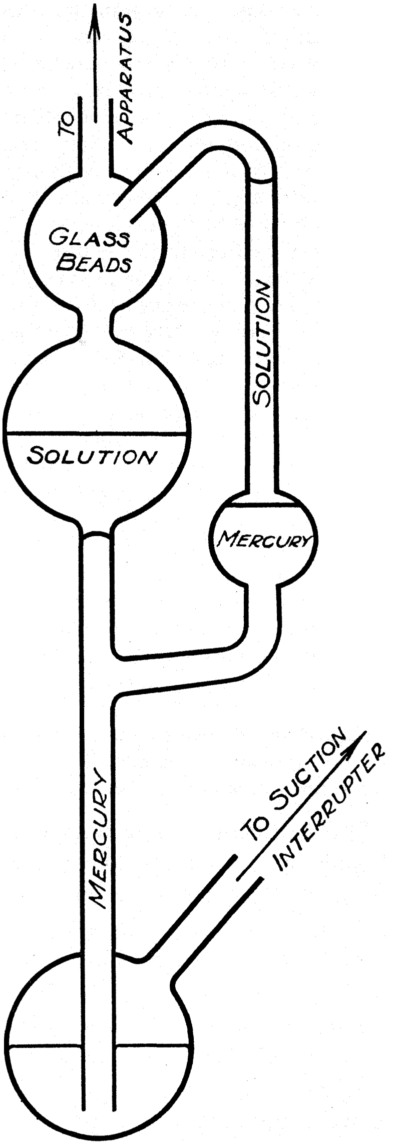

Fig. 1.

This apparatus used for the removal of air is essentially that devised by Dr. R. K. Taylor of this Laboratory in connection with the study of the vapor pressure of alcoholic soap solutions made by Dr. R. D. Drinkard, the results of which are to be published later.

In order to transfer desired amounts of liquid from vessels A and B into vessel L, calibrated bulbs of various sizes were sealed into the apparatus between traps T and H. By opening trap G and cooling one of these calibrated bulbs with an ice-water mixture, a desired volume of toluene was obtained. In closing trap G and opening trap K, the liquid was transferred by evaporation into the solution vessel L.

Microprojector.—The capillary was placed in a vertical position and observations were made upon it by means of a microprojector. This optical system consisting of a microscope in a horizontal position, and a low power objective placed between the object and the microscope so as to produce a real image in the focus of the microscope, was a great improvement upon the original method. The whole system was rigidly mounted on a slow motion stand to allow observations of various points along the length of the capillary. This arrangement has been utilized already in part of the work presented in the first paper, namely, the work on quartz capillaries.

Thermostat.—The temperature control was of utmost importance, and to obtain a fairly constant temperature for a considerable time very sensitive regulating devices were used. The thermo-regulator consisted of a coil of 50 feet of $^3/_8$-inch copper tubing filled with toluene. The electrical circuit was so arranged that sparking at the point of contact between the tungsten needle and the mercury was eliminated.[2]

Since the temperature maintained was below that of the room, a device was introduced that controlled the amount of cooling water passing through the cooling coil. This device shut off the cooling water when the heating unit was on and *vice* versa. It consisted of a long piece of heavy wire suspended vertically and fastened at the upper end to the circuit breaker of a strong relay, the coils of which were connected in series with those of the main relay. The lower end of the wire carried a rubber stopper cut to seat securely in the mouth of the cooling water pipe leading to the thermostat. This pipe was mounted in a wide glass tube provided with two side tubes, one near the bottom and above the mouth of the pipe serving as the water inlet, the other near the top as the overflow. By manipulating this device in conjunction with the heating unit, conditions were such that the latter went on and off every fifteen seconds for more than twelve hours.

Under these conditions two Beckmann thermometers, one graduated in 0.002° and the other in 0.001°, showed fluctuations not greater than 0.0015°. The temperature of the thermostat was maintained at 20°; at this temperature the vapor pressure of toluene is 21.60 mm. of mercury. Therefore, the fluctuation in the temperature corresponds to a change of the vapor pressure not greater than 0.0021 mm. of mercury.

In testing various parts of the thermostat by means of a constantan–iron thermopile connected to a galvanometer of 12,400 megohms resistance, a temperature gradient was detected between the part of the thermostat containing the solution vessel and the side compartment holding the capillary. These gradients are established by the currents caused by the stirrer and it was found that changing the direction of stirring reversed the direction of the temperature gradient. Thus, by stirring downward the compartment containing the capillary was colder than the one containing the solution vessel, and by stirring upward the conditions were reversed. Inasmuch as condensation of toluene vapor on the walls of the chamber containing the capillary was to be prevented, the thermostat was stirred upward.

The Solution.—The question of finding the proper solute was a perplexing one. Since Raoult's law was to be used in calculating the vapor pressure of toluene solutions, our first requirement was that the compound to be used as the solute should have as close a relation to the solvent as possible, that is, it should form a mixture close to the ideal. The second requirement was that it should have a high boiling point, so that its partial pressure in a saturated solution would be negligible. Third, it should be fairly soluble in toluene and, lastly, the compound should be stable in solution. Although the second and third demands are inversely related, we were inclined to compromise in favor of the second. Usually a compound related to benzene or toluene that satisfies the first and second requirements is unstable and sensitive to light. After a long search and many trials p-diphenylbenzene was selected. Its melting point and boiling

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[2] A. T. Larson, This Journal, 44, 2893 (1922).

point are 212 and 383°, respectively, and, judging from the work of Hildebrand, its solution in toluene would deviate from the ideal very slightly.

However, the low solubility of p-diphenylbenzene in toluene imposed limitations upon the possible range of measurements as the vapor pressure of the toluene solution is balanced against the vapor pressure of pure toluene in a capillary.

The toluene used was refluxed over sodium amalgam for twenty-four hours; this was followed by distillation, the middle fraction being retained.

The p-diphenylbenzene was obtained from the Eastman Kodak Company.

Experimental

1. Manipulation of Apparatus (Radius of Capillary = 1.10μ; $n/(N - n) = 0.0038$). When vapor from the toluene reservoir was admitted into the capillary chamber, it condensed in the capillary instantaneously, that is, it shot down very rapidly from the mouth of the capillary in the form of a column. The excess liquid on the walls of the vessel (7 mm. Pyrex tubing) and on the outside of the capillary was removed by careful pumping and manipulation of the several mercury traps in the apparatus. The attainment of this condition was ascertained by lowering the mercury trap leading to the capillary so that only a slight amount of liquid near the mouth of the capillary was evaporated. If after some time the capillary did not fill up again, there was no excess liquid present. The trap leading to the solution vessel was lowered, thus bringing into communication the vapor of the solution with the vapor of the pure liquid over the capillary. The latter filled up immediately, indicating that the vapor pressure of the pure liquid over the capillary was less than that of the solution. The trap leading to the solution was then closed and the mercury in the trap leading to the capillary was slightly lowered. The liquid in the capillary began to evaporate, showing the reversibility of the process. The operation was repeated several times and each time the capillary filled completely.

The capillary is completely evacuated; that is, the liquid in it is made to vaporize and then the vessel containing the capillary is closed by means of the trap. By suitable manipulation of the mercury traps in the line leading to the solution vessel, the rest of the apparatus is filled with vapor from the solution. Upon closing off the solution vessel and lowering the mercury in the traps leading to the capillary, this vapor was greatly rarefied; the capillary did not fill up when brought in contact with the rarefied vapor. However, when the capillary was brought into direct contact with the vapor above the solution, it filled rapidly in the same manner as described above.

Similar observations were made on capillaries having radii of 2.13μ, 3.14μ, 4.84μ and 5.33μ. They were subjected to the same treatment as described above, and in every instance they behaved similarly. In other words, the lowering of the vapor pressure in these capillaries was also greater than in the solution. It is worthy of note that in case of the latter two capillaries the filling was much slower and somewhat different. First, a bright spot appeared slightly below the mouth of the tube. This grew to a column of liquid apparently an inch in length (the magnification was about 1000) which then fell rapidly to the bottom of the capillary. This procedure was repeated until the capillary was not quite full. After it reached this point, the level of the liquid slowly rose until the capillary filled up.

2. Observations (Radius of Capillary = 6.12 μ; $n/(N - n) = 0.0038$).—The capillary was filled in the usual manner, that is, by allowing vapor from the toluene vessel to condense into it. Care was taken to remove all the excess liquid, and then it was brought into communication with the solution by opening trap K. The liquid in the capillary began to evaporate; after a few seconds the rate of evaporation was obtained by determining the time required for a desired length of the liquid, as read on the scale in the ocular, to evaporate. The operation was repeated several times, each time beginning the measurement from the same point on the capillary.

Each division in the table below corresponds approximately to about 0.0005 cm. The volume of liquid evaporated in the measured time is about 2.4×10^{-8} cc.

Divisions	40	40	40
Time	1 min. 20 sec.	1 min. 15 sec.	1 min. 18 sec.

This capillary was also subjected to measurements when the thermostat was stirred downward, the thermopile indicating that the compartment holding the capillary was colder than the one containing the solution. Each time it was found that the capillary was filling up at a very slow rate, requiring about a minute longer for the same volume in case of evaporation.

TABLE I

TABULATION OR RESULTS

Solute, *p*-diphenylbenzene; solvent, toluene; temperature, 20°; vapor pressure, 21.60 mm. of Hg; density, 0.866 at 20°; surface tension, 28.56 dynes/cm.^{2}

Expt.	Radius of capillary, 0.0001 cm.	*Pk* in mm. Hg	*n* moles of solute	*N* moles of solvent	P in mm. Hg	Observations
1	1.10	0.049	0.00159	0.41711	0.082	Condensation
2	2.13	.025	.00159	.41711	.082	Condensation
3	3.14	.015	.00159	.41711	.082	Condensation
4	4.84	.011	.00159	.41711	.082	Condensation
5	5.33	.010	.00159	.41711	.082	Condensation
6	6.12	.009	.00159	.41711	.082	Evaporation

In conclusion, the author wishes to express his profound gratitude to Professors W. A. Patrick and J. C. W. Frazer for their assistance in this work.

Discussion and Summary

These results may be best summarized by a consideration of the behavior of Expt. 5. In this experiment a capillary of 5.33μ radius was exposed to a toluene solution whose vapor pressure was lowered to 0.082 mm. by the addition of a solute. It was found that liquid toluene condensed in this capillary, which would indicate that the vapor pressure of the toluene in the capillary was less than (21.60 – 0.082). The classical theory of capillarity, however, tells us that the vapor pressure lowering of toluene at 20° in a tube of this radius should be only 0.009 mm. of mercury. It is therefore obvious that either our experimental work is in error or the classical theory as applied to vapor pressure in capillaries is not correct.

We believe the latter to be true and are convinced that this work has been done with sufficient care to warrant such a conclusion. At this point it may be well to add that such a view does not necessarily conflict with the thermodynamic treatment of this question. Thermodynamically the problem is simply the action of a negative pressure upon the vapor pressure of a liquid. This question is rigorously handled by the well-known relationship of Gibbs. What we have shown here is that the negative pressure in the case of small capillaries may be greater than has been assumed to be the case.

BALTIMORE, MARYLAND

[CONTRIBUTION PROM THE CHEMICAL ENGINEERING DEPARTMENT, THE OHIO STATE UNIVERSITY]

ZIRCONIUM. II. DETECTION OF POTASSIUM BY ZIRCONIUM SULFATE IN THE PRESENCE OF AMMONIUM IONS[1]

BY RUFUS D. REED AND JAMES R. WITHROW

RECEIVED AUGUST 6, 1928 PUBLISHED NOVEMBER 6, 1928

We have shown that zirconium sulfate can be used to detect potassium and that the test can be applied in the presence of sodium.[2] Ammonium ions must be eliminated prior to testing for potassium with other reagents such as sodium cobaltic nitrite, chloroplatinic acid or perchloric acid. The sensitivity of zirconium sulfate for potassium in the presence of ammonium ions was therefore investigated.

The results indicated that zirconium sulfate solution will detect 0.48 mg. of potassium in 2 cc. of reaction mixture in the presence of large amounts of ammonium sulfate. This was practically the same sensitiveness of this reagent for potassium in the absence of ammonium as in the previous work.

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[1] In memory of Ira Remsen.

[2] Reed and Withrow, THIS JOURNAL, 50, 1515 (1928)

Concerning the action of alkali sulfates on zirconium sulfate, Fresenius[3] stated: "A concentrated solution of potassium sulfate rapidly produces a white precipitate of potassium zirconium sulfate. . . . Sodium sulfate and ammonium sulfate do not produce a precipitate." No reference was found indicating the effect of the presence of ammonium sulfate on the reaction between zirconium sulfate and potassium sulfate.

Experimental

In order to determine the sensitiveness of zirconium sulfate for potassium in the presence of ammonium it was necessary to prepare the following solutions.

Zirconium Sulfate Solution.—Impure zirconium sulfate was dissolved in water and the zirconium precipitated by a slight excess of sodium hydroxide. The hydroxide was washed by decantation and filtered and washed until 10 cc. of the filtrate evaporated to dryness and taken up with 2 cc. of water gave no test with sodium cobaltic nitrite. The moist zirconium hydroxide was dissolved in concentrated sulfuric acid. The somewhat dilute solution was concentrated overnight at 60° and allowed to stand for several days to reach constant composition. This solution was found to contain 0.1131 g. of zirconium sulfate and 0.0363 g. more sulfate per cc. due to excess sulfuric acid.

Potassium Sulfate Solution.—This was prepared from c. p. salt and water. Its strength was determined by evaporating a portion to dryness and igniting.

Ammonium Sulfate Solution.—The c. p. salt was dissolved in water. The solution was analyzed for ammonium by the distillation method.[4]

The solutions tested for potassium were prepared by mixing known amounts of the potassium and ammonium sulfate solutions.

Procedure

The procedure was exactly the same as given under the general procedure in the work previously published.[5] The results appear in the table.

TABLE I

SENSITIVENESS OR ZIRCONIUM SULFATE FOR POTASSIUM IN THE PRESENCE OF AMMONIUM IONS

Total volume 2 cc. $Zr(SO_4)_2$, 0.1131 g. per test

Expt.	K, g. per sample	NH_4, g. per sample	Results (time for appearance of a precipitate)
1	0.0000	0.05985	Clear and no ppt. in 5.5 hours at 0°
2	.0000	.01197	Clear and no ppt. in 5.5 hours at 0°
3	.0000	.00599	Clear and no ppt. in 3.5 hours at 0°. Tube broke
4	.02378	.02990	Ppt. in 10 min. at room temperature
5	.0158	.03990	Cloudy in 1 hour at room temp.; ppt. in 10 min. at 0°
6	.0048	.0539	Ppt. in 1 hour at 0°
7	.0024	.0569	Cloudy in 1 hour; ppt. in 1.5 hours at 0°
8	.00095	.0586	Cloudy in 1.5 hours; ppt. in 2 hours at 0°
9	.00058	.0591	Very slight ppt. in 2 hours; increased in 2.5 hours at 0°
10	.00048	.0593	Very slight ppt. in 2.5 hours; increased in 5.5 hours at 0°

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[3] Fresenius, "Qualitative Chemical Analysis," C. A. Mitchell's translation of 17th edition, John Wiley and Sons, New York, **1921**, p. 182.

[4] Treadwell and Hall, "Analytical Chemistry," Vol. II, John Wiley and Sons, Inc., New York, 6th ed., **1924**, pp. 72–73.

[5] Ref. 1, p. 1516.

Discussion

The deposits in Expts. 9 and 10 containing 0.58 mg. and 0.48 mg. of potassium were very small but could be detected by comparison with a blank.

The results indicated that zirconium sulfate will detect 0.48 mg. or more of potassium in 2 cc. of reaction mixture in the presence of large amounts of ammonium ions. This is a distinct advantage over other tests, in all of which ammonium interferes. Bray[6] found "With 1 mg. of NH_4 a precipitate formed in about 10 minutes (with sodium cobaltic nitrite); with 0.5 mg. on standing several hours." Ammonium salts also give precipitates with tartaric acid, perchloric acid and chloroplatinic acid. With perchloric acid or chloroplatinic acid the amount of potassium must be large or alcohol must be added. Zirconium sulfate will detect potassium when present to the extent mentioned in the presence or absence of ammonium ions and no alcohol is needed.

Summary

The sensitiveness of zirconium sulfate for potassium in the presence of ammonium ions was found to be 0.48 mg. or more of potassium per 2 cc. of reaction mixture. This is practically the same sensitiveness of zirconium sulfate for potassium when no other metal ions were present. This detection in the presence of ammonium is a distinct advantage over the other tests for potassium.

COLUMBUS, OHIO

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

THE THICKNESS OF ADSORBED VAPOR FILMS. II[1,2]

BY G. H. LATHAM

RECEIVED SEPTEMBER 10, 1928 PUBLISHED NOVEMBER 6, 1928

There are now three outstanding theories of adsorption, namely, the unimolecular theory of Langmuir, the multimolecular theory of Polanyi and the capillary theory of Zsigmondy. Experimental data in support of each of these theories have been submitted by different investigators. In this paper we are particularly interested in the work of McHaffie and Lenher[3] and in that of Frazer, Patrick and Smith.[4] Both of these investi-

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[6] Bray, THIS JOURNAL, 31, 633 (1909).

[1] In memory of Ira Remsen.

[2] This paper has been taken from the dissertation submitted by the author to the Board of University Studies of The Johns Hopkins University as part of the requirement for the degree of Doctor of Philosophy.

[3] McHaffie and Lenher, J. *Chem. Soc.*, 127, 1559 (1925); 1785 (1926).

[4] Frazer, Patrick and Smith, J. *Phys. Chem.*, 31, 897 (1927).

gations are concerned with the adsorption of water vapor and of toluene on glass surfaces. This paper is a summary of some work recently done in continuation of that accomplished by these investigators.

McHaffie and Lenher studied the thickness of the water film adsorbed on the surface of a glass bulb which had been washed with strong acids and water. They also investigated the adsorption of water vapor upon platinum surfaces. In each case they found that the adsorbed film was multimolecular in thickness.

It was thought by Frazer, Patrick and Smith that the weak point in the work of McHaffie and Lenher was the assumption that the surface of the glass was plane from a molecular standpoint after treatment with acids and water. (McHaffie and Lenher had assumed that they were working with plane glass surfaces and that their results were obtained with such surfaces.) It appeared that such treatment would probably dissolve some of the alkali of the glass and form some amorphous silica on the surface, thus causing a general roughening of the surface. They believed, furthermore, that glass which has been thoroughly melted in a flame and allowed to cool without coming into contact with anything except dry air would present a plane surface for adsorption measurements.

In order to test the correctness of these considerations and to study the adsorption of vapor films upon such "fire-polished" surfaces, Frazer, Patrick and Smith undertook to repeat the work of McHaffie and Lenher using the same method of procedure and apparatus, toluene vapor and both fire-polished and acid-treated glass surfaces.

The results of their work indicated that the thickness of the adsorbed toluene film was never greater than unimolecular on fire-polished glass, while on acid-treated glass it was always multimolecular in thickness. These results confirmed the belief that fire-polished surfaces of glass were plane, while acid-treated ones were not.

There was, however, an objection to the general application of these ideas to adsorption on glass; that is, they did not necessarily hold good for other substances than toluene, especially in the case of polar substances. In other words, the results were true, possibly, of non-polar compounds only.

In order to ascertain whether this objection was valid or not and, if not, to eliminate it and complete the work of Frazer, Patrick and Smith by making the facts applicable to both polar and non-polar substances, the present investigation was undertaken.

The experimental procedure and the apparatus were essentially the same as those used by Frazer, Patrick and Smith, Acetonitrile and nitromethane were the two polar substances selected as well suited for the work; toluene was used also as a check on the work of Frazer, Patrick and Smith and, later, water vapor was used in the work with platinum and silver amalgam surfaces. The use of several other polar substances was abandoned because they were not suitable for the purpose.

The method consisted essentially in measuring the pressure exerted within a small glass bulb by a known amount of vapor at constant volume, through a temperature range such that at the upper limit all of the substance would be in the gaseous condition while at the lower limit some would be present in the form of liquid. By plotting graphically the data thus secured, two curves would be obtained—one the curve for change of pressure with temperature of the substance in the form of vapor, and the other the vapor pressure curve of the liquid. Obviously these two curves on the graph would intersect at the dew point. From the type of curve obtained by plotting these P-T data, it was simple to ascertain whether adsorption had taken place at any time during the measurements and, if so, to what extent.

Measurements were made with a given vapor in bulbs of both fire-polished and acid-treated glass. These bulbs were made of soft glass, blown after thorough cleaning and melting in a flame. All glass-blowing was done through a phosphorus pentoxide bulb to prevent access of moisture. The bulb was cooled while attached to the phosphorus pentoxide bulb and sealed into the apparatus, using a phosphorus pentoxide bulb. It was evacuated with a mercury pump in series with an oil pump, all pressures being read on a McLeod gage. The vapor to be studied, previously freed from air, was admitted to the bulb while the temperature was at the upper limit of the range used. The bulb was closed by a mercury U-tube which served also as a manometer, and keeping the volume constant while gradually reducing the temperature, the corresponding pressures of the vapor were read. Each point obtained was approached both from above and below so that all data would represent equilibrium pressures and temperatures. All readings were checked at least twice and within 0.05 mm. As the saturation point was approached, the readings were made every 0.5 to 0.25 of a degree in order to locate the point accurately. The approximate position of this point on the curve could be foretold from the temperature of the liquid used to fill the bulb with vapor.

The temperature of the vapor in the bulb was controlled by a constant-temperature bath accurate to 0.02°. Pressure readings were made with a cathetometer which was accurate to 0.05 millimeter.

Having made the pressure–temperature measurements with a fire-polished bulb, it was removed from the apparatus and its area and volume were determined as accurately as possible. The area measured was that which had been exposed to the vapor. These data were used later in calculating the amount of vapor in the bulb during the measurements and the thickness of the film adsorbed, if any.

The bulb was then filled with chromic acid and kept at 40–50° for twenty-four hours. It was washed with distilled water, filled with concentrated nitric acid and kept at about the same temperature for twenty-four hours longer. The bulb was next thoroughly washed out with distilled water, evacuated at 180° for five hours and again sealed into the apparatus with the same precautions as before. Another sample of vapor was admitted to the bulb as before and the pressure–temperature measurements were repeated. The data secured from these measurements were plotted graphically and the type of curve obtained was determined.

Before going further into the experimental work and results, it will probably be desirable to describe briefly the method of determining the amount of adsorption taking place on these glass surfaces.

If a definite mass of vapor be kept at constant volume while the temperature is gradually lowered, its pressure at any time will be given by the equation

$$P = P_0(1 + \alpha t) \tag{1}$$

provided, of course, the vapor obeys the perfect gas laws. In the equation P is the observed pressure, P_0 is the pressure of the vapor at 0° (provided none of it condenses above or at this temperature), t is the temperature at the corresponding pressure P, and α is a constant, $^1/_{273}$. From the equation it is clear that under such conditions a series of pressure-temperature data secured from measurements on this vapor will give a straight line so long as no vapor condenses or is removed from the vapor phase in any other way. The slope of the curve will be $P_0\alpha$ and P_0 will be its intercept on the pressure axis. At the dew point, however, part of the vapor will condense and thereafter, as the temperature is lowered, the measurements will give the vapor pressure curve of the liquid. Consequently, at this dew point there will be a sharp break in the curve and the two parts of the curve will intersect at this point as two essentially straight lines. Such a curve is illustrated in Fig. 1, AOB. The curve is purely a theoretical one.

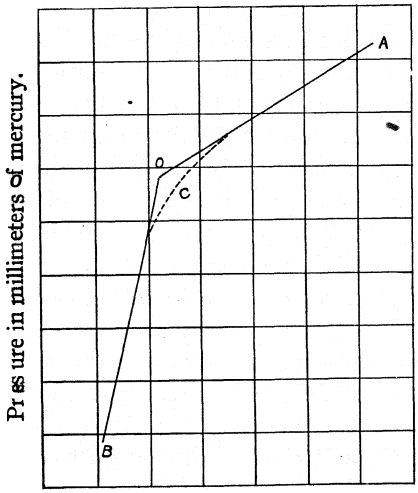

Fig. 1.

If, however, some of the vapor is adsorbed by the glass surface as the temperature is lowered, it is evident that the pressure will decrease more rapidly than is required by the gas laws, so that the curve will appear as shown in Fig. 1, ACB. The dotted line represents the portion of the curve where adsorption is taking place. From these considerations, it is clear that if adsorption occurs as the dew point is approached, there will be a gradual and more or less pronounced rounding off of one part of the curve into the other. The amount of this rounding off depends entirely upon the extent to which adsorption has occurred and from it the maximum pressure decrease due to such adsorption can readily be obtained by an inspection of the curve.

Now, if the decrease in pressure due to adsorption of a unimolecular film is known, it is only necessary to divide the total pressure decrease due to adsorption by this number in order to obtain the molecular thickness of the adsorbed film. As already stated, the volume and inside area of the adsorption bulb, together with the temperature and pressure at the point of maximum adsorption (that is, the dew point) are known, as are also the approximate molecular diameters of the substance worked with. By assuming that each molecule adsorbed is spherical and that it occupies an area on the glass surface included in a square whose side is the same length as the molecular diameter, it is a simple matter to calculate the pressure decrease caused by the adsorption of a unimolecular layer of such molecules. The thickness of the absorbed layer can then readily be calculated as already noted.

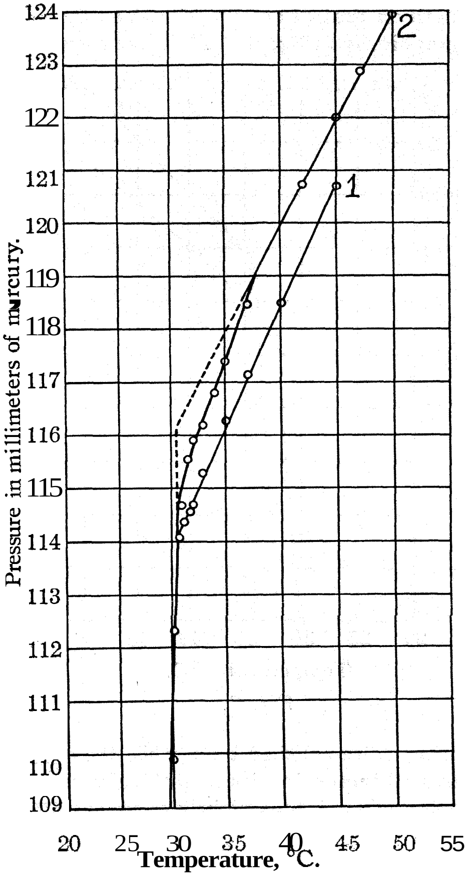

Fig. 2.

For the vapors and bulbs used during this work, the decrease in pressure caused by the adsorption of a unimolecular film varied from 0.01 to 0.04 mm., depending upon the size of the molecule.

Having thus pointed out the method by which the amount of adsorption was obtained, we can now turn to an examination of the experimental data.

The adsorption of acetonitrile vapor was first investigated. As already stated, both fire-polished and acid-treated bulbs were used. When the pressure-temperature data from measurements with a fire-polished bulb were plotted graphically, Curve 1, Pig. 2 was obtained. With the same vapor but after treating the bulb with acids and water, the measurements gave data which are shown graphically in Curve 2, Fig. 2.

Curve 1, Fig. 3, shows graphically the data obtained from measurements with nitromethane in a fire-polished bulb, while in the same figure Curve 2 is the corresponding one for an acid-treated bulb. The non-coincidence of the two vapor pressure curves is due to the fact that Curve 2 has been moved up vertically from its normal position in order to get both curves on the same graph.

The work of Frazer, Patrick and Smith with toluene was next repeated as a check both on that piece of work and on the present one. The data thus secured are shown graphically in Fig. 4. The curve shown as a solid line represents the data from the run using a fire-polished bulb, while the curve obtained from measurements with an acid-treated bulb coincides with this almost throughout except at points near the saturation point, where it falls slightly below, as shown in the dotted line. This was to be expected from the work done by Frazer, Patrick and Smith and also from the theory of this method.

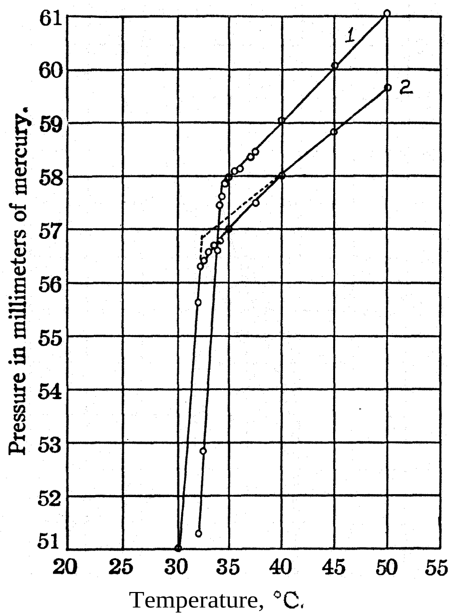

Fig. 3.

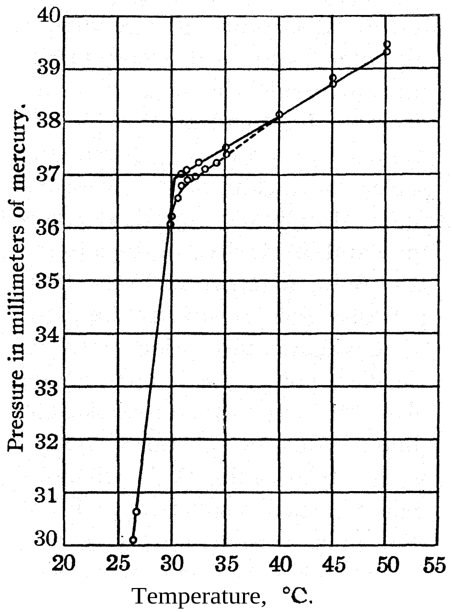

Fig. 4.

After an examination of the curves obtained (Figs. 2–4) it seemed that the amount of "rounding off" of the two parts of the several curves into each other was rather small-somewhat less than had been anticipated from the work of Frazer, Patrick and Smith. Accordingly, it was decided to make several experimental runs using different vapors in bulbs which also contained a small amount of activated silica gel. The bulbs themselves were of fire-polished glass. It was thought that since in this case we could be certain that adsorption was taking place strongly, the type of curve obtained would be interesting and instructive and might be of value in aiding one to interpret correctly the other curves. Two runs were made. One was made with 0.0003 g. of activated silica gel in a fire-polished bulb containing nitromethane as well in the vapor phase.

The other was run using the same amount of silica gel in a similar bulb with toluene vapor. The experimental results are shown graphically in Fig. 5 (for nitromethane) and in Fig. 6 (for toluene).

When we come to an examination of the experimental curves (Figs. 2–6), we see at once that in every case where a fire-polished bulb has been used, the pressure-temperature curve for the substance in the gaseous state is a straight line, and that where the two parts of the experimental curve intersect, there is a sharp break, with not the slightest trace of rounding off. On the other hand, wherever an acid-treated bulb has been used, the two parts of the curve do not intersect sharply but round off into each other more or less. Moreover, the curve for the substance in the form of vapor is not a straight line, but shows a pronounced tendency to round off near the saturation point. These facts can only be ascribed to adsorption on the acid-etched surfaces. Any other cause would show the same effect on each bulb.

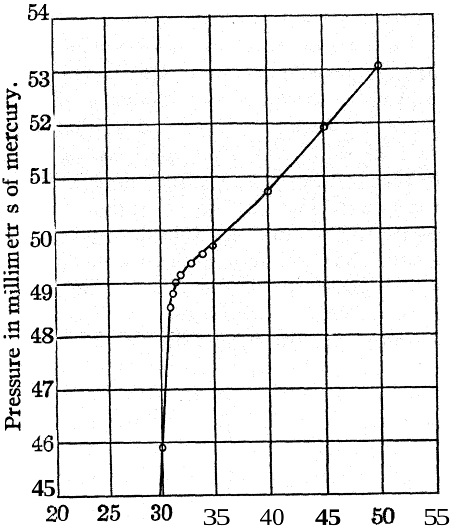

Fig. 5.

Since the pressure-temperature curves of the vapor are straight lines, it is permissible to calculate the number of moles of vapor present in the bulbs by means of the perfect gas laws. From this, together with the volume, area of the bulb, the temperature and pressure, the thickness of the adsorbed film of vapor can be calculated, as we have already indicated. These calculations have been made for each vapor. The results indicate that the adsorbed film is from 30 to 60 molecules thick at saturation pressures and temperatures on acid-treated glass, and not greater than unimolecular on fire-polished surfaces. The polar compounds appear to be somewhat more strongly adsorbed than toluene. This fact is indicated both in the character of the curves for these substances and in that for nitromethane and toluene in presence of activated silica gel.

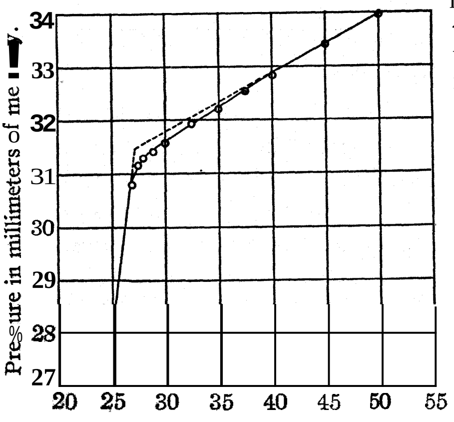

Fig. 6.

The calculation of the thickness of the adsorbed film was very simple. It was assumed that the film was of uniform thickness and that it covered the entire surface of the glass exposed to the vapor. The slopes of the curves obtained experimentally were in each case measured, and the theoretical slopes were calculated by means of Equation 1. The experimental and theoretical slopes agreed closely with the exception of those of the curves for nitromethane in presence of silica gel; this might have been expected. The dotted lines in the figures are prolongations of the straight portions of the curves and have the approximate theoretical slopes. These dotted portions represent the curves which would have been obtained had there been no adsorption at these points. Hence, the maximum distance, measured on the pressure axis, between the experimental and the dotted part of the curves is the maximum pressure decrease due to adsorption. This divided by the pressure decrease due to adsorption of a unimolecular layer gives directly the thickness of the adsorbed film.

In the case of the measurements with toluene and nitromethane in presence of silica gel, a calculation of film thickness is obviously out of the question, since the adsorption was presumably confined to the gel in the bulb, and the area of this is unknown. However, if we assume the adsorption to have taken place uniformly on the surface of the bulb as in the other experiments, the data for the run with toluene and 0.0003 g. of silica gel indicate a thickness of forty molecules for the adsorbed film, a result very closely agreeing with the other data. The curve (Fig. 6) bears a very marked resemblance to the curve for toluene vapor in an acid-treated bulb. These facts lead one to believe that it is not unreasonable to suspect that 0.0003 g. of silica may be formed on the glass by treatment with acids and water. In the case of the curve for nitromethane (Fig. 5) the similarity to that for the same vapor in an acid-treated bulb is not so clear; the adsorption of the vapor by the silica gel seems somewhat greater, especially at higher temperatures, than in an etched bulb, and also stronger than with toluene. It also seems from the curve that the silica gel was saturated with the nitromethane vapor just before condensation took place at the dew point.

It should be noted that this method does not and cannot show that there is no adsorbed film on fire-polished glass surfaces through the temperature range of 50 to 25°. It does, however, show that no additional adsorption occurs as the temperature is lowered—that is, none greater than a unimolecular layer. Calculation shows that adsorption of such a film causes a decrease in pressure within the bulb of from 0.01 to 0.04 mm., depending upon the vapor used. The pressure measurements made with the cathetometer were not accurate to more than 0.05 mm. Consequently, the method is not sufficiently sensitive to show the presence of a unimolecular layer but can detect anything essentially greater than that.

The Adsorption of Water Vapor upon Amalgamated Platinum and Silver Surfaces

After the conclusion of the adsorption experiments with glass surfaces, an attempt was made to prepare a plane metallic surface upon which the adsorption of water vapor could be studied. A platinum bulb upon the inner surface of which a film of mercury was deposited electrolytically seemed to offer hope of such a surface. Accordingly, such a bulb was prepared, similar in shape and size to those of glass already described. This bulb was sealed into a piece of clean soft glass tubing and was then filled with a solution of mercurous nitrate containing a few drops of nitric acid. Using the bulb as the cathode, the solution was electrolyzed by a current from two dry cells in series. Preliminary experiments had shown that upon clean platinum surfaces a thin mercury film could be deposited electrolytically and that this film would stay on during washing of the surface with water, subsequent drying and other handling incidental to preparing the bulb for measurements. When such a film attained greater thickness, it showed a marked tendency to break and to form globules of mercury which would fall off of the surface.

After electrolysis of the solution the bulb was carefully cleaned by washing repeatedly and gently with conductivity water. It was then dried at room temperature while it was evacuated for five hours and examined Its inner surface appeared to be evenly covered with a film of mercury. (The inside surface of the bulb was not polished but was used just as it came from the makers, with a somewhat roughened appearance. It was cleaned with hot nitric acid before deposition of the mercury film.) The bulb was at once sealed into the same apparatus used for the glass bulbs, all glass-blowing being done through phosphorus pentoxide. During sealing, the bulb was not allowed to become heated (the glass tube attached to the bulb made this possible).

Water vapor was admitted to the bulb so prepared (having previously been carefully freed from all traces of air). The measurements of pressure as the temperature was gradually lowered were made in the same manner as for glass bulbs. Necessarily this procedure required that a small portion of glass surface of the glass tubing connected to the bulb be exposed to the water vapor in order that the cathetometer could be used in reading the height of the mercury. The method used by McHaffie and Lenher in their work on platinum (that is, using a sensitive voltmeter and dry-cells connected to bulb and to mercury in the reservoir to indicate contact of mercury with the bottom of the bulb) was tried in this work but was abandoned because of troublesome sticking of the mercury when it touched the bulb, so that no dependence could be placed on this method of obtaining a constant level of mercury in the bulb.

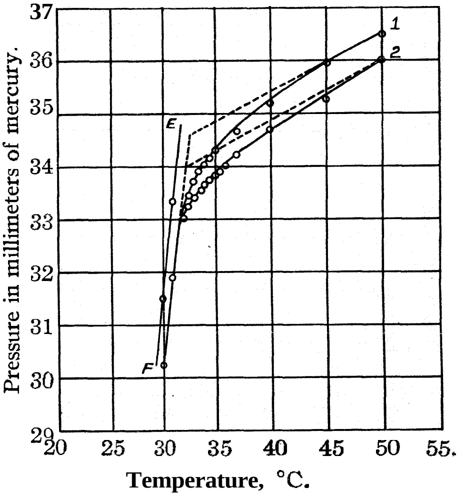

Fig. 7.

The data obtained during two runs using this apparatus and procedure are shown graphically in Fig. 7. Curve 1 was first obtained. The bulb was then evacuated, mercury was raised into it to fill it entirely for twenty-four hours, and after lowering the mercury out of the bulb again another sample of water vapor was introduced and a second run was made, with the results shown graphically in Curve 2 (Fig. 7).

It is evident from these curves that the mercury-platinum surfaces we are dealing with here adsorb water vapor strongly. The molecular thickness of the adsorbed film, calculated in the usual manner from Curve 1, is 28 molecules, and that from the second curve (2, Fig. 7) is **33** molecules. These two values may, on account of the approximate character of the calculations, be considered as a check.

It is interesting to point out here the fact that the parts of these curves which represent the vapor pressures of the condensed water do not coincide with the vapor pressure curve of water; the vapor pressure curve of water in this range is shown as EF, Fig. 7. This may be due to capillary effects in the surface or to the thin film of water, which would have a lower vapor pressure, as indicated in the experimental curves. These results obtained with amalgamated platinum are similar to those recently obtained by John William Smith, *J. Chem. Soc.*, 2045 (1928).

Having failed to obtain a plane surface with mercury-covered platinum, it was next decided to make a series of measurements with water vapor and a silver bulb upon the inner surface of which a film of mercury had been deposited as before. It was hoped that such a bulb would present a plane surface for the study of adsorption of water vapor. A silver bulb was prepared having a platinum band attached to its narrow neck so that it could be sealed into glass tubing and thus into the apparatus. The bulb, after careful cleaning by heating in a flame and repeated washing with conductivity water, was filled with a solution of mercurous nitrate within the case of the platinum bulb and was used as the cathode while the solution was electrolyzed. The solution was renewed twice during electrolysis. The bulb was then carefully cleaned with conductivity water, dried at room temperature and evacuated for five hours. Upon examination the inner surface appeared to be evenly amalgamated. The bulb was sealed into the apparatus without becoming heated, and a run was made with it, using water vapor as the substance to be studied. The resulting curve is shown in Fig. 8.

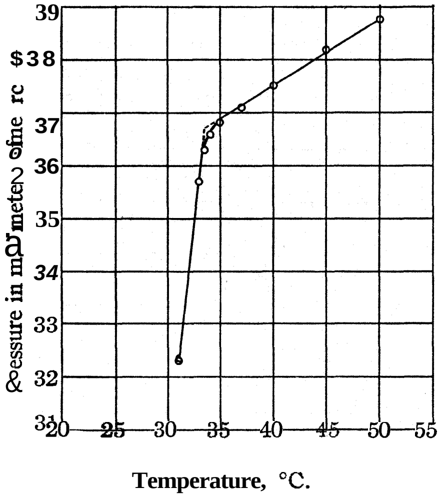

Fig. 8.

The upper part of this curve (that is, the curve for the pressure change with temperature for the water in the gaseous state) has the same slope as the theoretical value calculated for this amount of vapor from the gas laws and, as can be seen from the figure, is a straight line except for a very slight rounding off into the vapor pressure curve of the condensed vapor. This rounding off is, however, confined to the immediate temperatures at the dew point, and is very slight compared to the same phenomenon in the previous curves. Moreover, the slight adsorption may be explained by the fact that, as already stated, during the measurements a small amount of glass surface was exposed to the vapor as well as the silver amalgam surface. This was a necessary consequence of the way in which measurements were made. Moreover, this glass surface had been in contact with liquids and was undoubtedly not plane, so that it probably adsorbed vapor to the same extent that etched surfaces did in the previous work by McHaffie and Lenher, Frazer, Patrick and Smith and the author. If, then, the adsorption indicated in the curve (Fig. 8) is considered as upon the glass surface exposed only, calculation shows that the thickness of the adsorbed film upon the silver-mercury surface cannot be greater than unimolecular. If we are to consider that adsorption occurs only on surfaces that are not plane, then we are justified in considering the silver-mercury surfaces as plane, while those of platinum-mercury are not plane.

In conclusion, the author of this paper wishes to express his appreciation to Dr. J. C. W. Frazer and to Dr. W. A. Patrick who suggested this study and under whose direction it was performed.

Summary

1. The work of McHaffie and Lenher and of Frazer, Patrick and Smith has been continued, using various vapors and both glass and metallic surfaces.

2. Soft glass which has been thoroughly melted and cooled without coming in contact with anything except dry air may be considered as offering a plane surface for adsorption measurements, but acid-treated surfaces of such glass cannot be considered as plane from the standpoint of adsorption measurements.

3. The thickness of the adsorbed vapor film on fire-polished glass surfaces is not essentially greater than unimolecular for either polar or non-polar substances.

4. With acid-treated glass surfaces, the thickness of the adsorbed film appears to be about fifty molecules for both polar and non-polar substances investigated.

5. Platinum surfaces upon which mercury has been deposited electrolytically adsorb water vapor quite strongly. The thickness of the adsorbed layer appears to be approximately thirty molecules.

6. Silver surfaces amalgamated electrolytically may be considered as plane. The thickness of the film of water vapor adsorbed upon such a surface is never greater than unimolecular.

BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE JOHNS HOPKINS UNIVERSITY]

AN APPLICATION OF THE RULE OF DULONG AND PETIT TO MOLECULES[1,2]

BY DONALD H. ANDREWS AND ELLIS HAWORTH

RECEIVED SEPTEMBER 29, 1928 PUBLISHED NOVEMBER 6, 1928

A little over one hundred years ago Dulong and Petit[d] announced the empirical rule that the heat capacity per gram atom is about the same for all solid elements. Since that time the theoretical significance of this rule has been made apparent and the exceptions to it explained by the development of classical kinetic theory and quantum theory. For solids other than the elements, however, very little progress has been made in accounting for the heat capacities. With the hope of throwing some light on this latter problem, particularly for the compounds of carbon, the senior author and his associates have been measuring the heat capacities of a number of compounds. The results for the series of halogen derivatives of benzene presented here seem to show that the principles, of which the rule of Dulong and Petit is a part, can be applied to complicated molecules when the nature of the molecule is sufficiently understood.

The Calorimetric Measurements

The measurements of heat capacity were made in a calorimeter which operates on the principle of calibrated heat conduction, described in a paper by Andrews[4] where a general description of the method may be found.

The Calorimeter used for these observations embodies a number of improvements over the one previously described. As shown in Fig. 1 the inner vessel, which contains the substance to be studied, is a gold-plated copper can equipped with vanes to facilitate the conduction of heat throughout the material. This can is supported by four adjustable wooden pegs inside a heavy copper cylinder, also gold-plated. Both inner and outer can are equipped with covers not shown in the figure.

Temperature is measured by means of thermocouples of No. 30 constantan wire attached to the inner and outer cans.[5] There is a heating coil of the same wire wound on the outside of the outer can.

The Method.—The calorimeter is placed in a gallon Dewar and liquid air is poured on it until the whole apparatus is at constant temperature at about 90°K. Then a current is passed through the heating coil of such strength that the whole apparatus is

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[1] In memory of Ira Remsen.

[2] From the dissertation submitted by E. Haworth in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[3] Dulong and Petit, *Ann. chim. phys.*, **10, 395 (1819).**

[4] Andrews, THIS JOURNAL, 48, **1287 (1926).**

[5] The calibration of the thermocouples is described in a paper by Andrews, *J. Franklin Inst.*, **206, 285 (1928).** Measurements made with the thermocouple junction directly in the material studied as compared with those where the junction was soldered to the walls of the container indicate that errors of temperature measurements due to poor thermal conductivity of the material are not appreciable.

warmed at the rate of about half a degree a minute until 50° is reached. The heat capacity at different temperatures is calculated from the rate of heating of the inner can and the temperature head between the two cans, the constants for heat conduction of this particular apparatus being determined by calibration with hydroquinone.[6]

The Materials.—The substances which were studied were secured from the Eastman Kodak Co. The freezing point curves[7] indicate less than 1% impurity in every case.

The Results

The values of the heat capacity for mono-, di-, tetra- and hexachlorobenzene and for mono- and dibromobenzene are given in Table I. The relative accuracy seems to be about 1 or 2%. The absolute accuracy may not be quite as good as this in certain measurements because of uncertainties in the temperature scale. Comparison with the very limited data available from other sources indicates that at any rate the errors are not large enough to affect appreciably the conclusions drawn from the data.

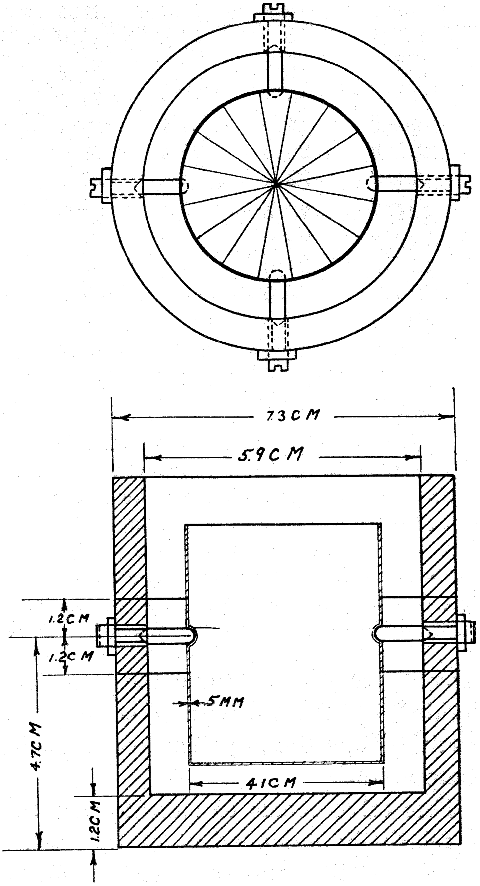

Fig. 1.—The calorimeter.

Conclusions

The principal interest in these two groups of compounds centers in the values we may secure for the heat capacity of the halogen atoms attached to the benzene ring. The rather complicated factors entering into the heat capacity of the ring itself have been discussed by Andrews.[8]

It seems very likely that since the heat capacity of the hydrogen atoms is practically negligible, the ring itself always has about the same heat capacity regardless of the groups attached to it. This conclusion is substantiated by the data in Table II, where the difference between the heat

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[6] Values taken from Andrews, ref. 4, in which paper the details of calibration may be found.

[7] Andrews, Kohman and Johnston, *J. Phys. Chem.*, *29*, 914 (1925).

[8] Andrews, *Verslag. Kgl. Akad. Wetenschappen Amsterdam*, *29*, 744 (1926).

TABLE I

C_p PER GRAM MOLE IN CALORIES PER DEGREE[a]

Temp., °K.	C_6H_6, calcd.	$C_6H_4Cl_2$	p-$C_6H_2Cl_4$	1,2,4,5-$C_6H_2Cl_4$	C_6Cl_6	C_6H_5Br	p-C_6H_4Br
101.2	11.6	13.3	15.6	20.8	20.5	14.2	17.5
125.7	13.4	15.4	17.6	22.9	30.3	16.1	19.9
147.1	15.1	17.4	19.9	25.6	33.9	18.1	21.9
166.4	16.7	19.3	22.0	27.8	36.3	19.7	23.8
184.3	18.2	21.1	24.1	30.1	39.2	21.2	25.6
201.0	19.5	23.1	26.4	32.2	41.5	23.0	27.5
216.8	20.8	25.4	28.9	34.3	44.3	25.5	29.6
231.7	22.1		28.1	37.1	47.8	30.5	32.1
246.1	23.5		30.0	39.5	50.9		34.4
259.8	24.9		34.9	41.3	53.3		36.4
273.1	26.2		37.5	43.3	56.1		38.0
286.3	27.5		39.2	45.8	58.9		39.8
299.8	28.7		41.1	48.4	61.6		41.7
311.7	30.0		44.7	50.5	64.5		43.6
323.9	31.4		51.0	52.7	68.0		46.0
335.8	32.8			55.4	71.8		48.7

[a] J. Narbutt, Z. Electrochem., 24,339 (1918), has measured the mean heat capacity of p-$C_6H_4Cl_2$ and p-$C_6H_4Br_2$ between various temperatures (—78 to 80°) and 0° by the method of mixtures. He finds, for example, the heat capacity at 217°K. to be 26.8 for $C_6H_4Cl_2$ and 27.8 for $C_6H_4Br_2$, and at 273°K., 32.4 and 33.0. The difference between these values and the authors' is probably due to the different methods employed, Narbutt's being below and the authors' above the true values. It is believed, however, that the accuracy of the authors' measurements, especially relative to one another, is amply sufficient to justify the conclusions drawn from the data.

capacity of the ring[g] and the heat capacity of each compound is shown divided by the number of substituent groups in the compound. The result is thus the apparent heat capacity per halogen atom in each of the compounds.

This table seems to indicate that the heat capacity per halogen atom is relatively independent of the *number* of halogen atoms attached to the ring. The apparent lack of effect on the heat capacity of *position*, that is, *rut-*, *p-*, etc., has been pointed out before.[4]

The fact that the values approach 6 cal. per degree at about room temperature suggests that Dulong and Petit's rule may be applicable. The plausibility of this may be shown in the following way. We believe that

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[9] The values of the heat capacity of the ring are those calculated from the infrared frequencies as explained in the paper by Andrews, ref. 8. These differ slightly from the observed values for benzene, but were used instead of the latter because of the uncertainty of the observed values in the neighborhood of the melting point and the obvious lack of observed values for the solid above the melting point. For a somewhat similar reason the term for the work of expansion (see reference above) is taken for hydroquinone rather than for benzene. The accuracy of the heat capacity of the ring so calculated should suffice, however, for the present purpose.

TABLE II

Cpd.	100°K.	140°K.	180°K.	220°K.	260°K.	300°K.
	C_p per Chlorine Atom					
C_6Cl_6	2.5	3.0	3.5	4.0	4.7	5.5
$C_6H_2Cl_4$	2.2	2.5	2.9	3.5	4.2	5.0
$C_6H_4Cl_2$	1.9	2.4	3.0	3.9	5.2	
C_6H_5Cl	1.5	2.6	3.0			
Calcd. from infra-red	1.6	2.7	3.4	3.9	4.3	4.6
	C_p per Bromine Atom					
$C_6H_4Br_2$	3.0	3.2	3.7	4.5	5.7	6.1
C_6H_5Br	2.5	2.6	3.1			
Calcd. from infra-red	1.8	2.8	3.5	4.1	4.4	4.7

the halogen atom is attached to the ring by a normal non-polar or so-called homopolar bond. There is considerable evidence[10] that all bonds of this type are of almost identical nature and strength even when in such apparently different circumstances as joining H—H, C—C, or C—Cl. Now one of

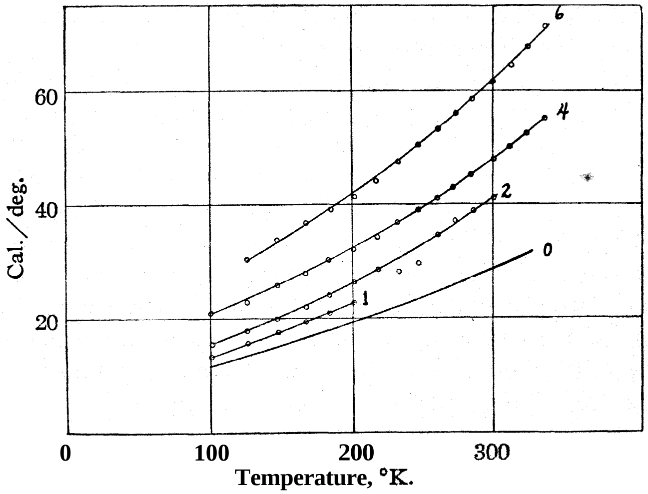

Fig. 2.—C_p for (0) C_6H_6, (1) C_6H_5Cl, (2) $C_6H_4Cl_2$, (4) $C_6H_2Cl_4$, (6) C_6Cl_6.

the characteristics of this type of bond is its spring-like nature. We may indeed think of the chlorine atom as joined to a carbon atom of the ring by a short spiral spring. In this case there should be two characteristic frequencies of vibration; one for motion parallel to the direction of the bond, which stretches the bond directly; the other perpendicular to this, which bends the bond without directly stretching it. This latter type of motion should involve a smaller restoring force than the first type and should have a lower frequency.

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[10] Bates and Andrews, *Proc. Nat. Acad. Sci.*, *14,* 124 (1928).

The values of frequencies such as these can be secured from absorption spectra, as both Salant[11] and Andrews[8] have shown. Thus Ellis[12] has found characteristic absorption in the infra-red corresponding to fundamental frequencies of 1.79 X 10^{13} sec. for C—Cl and 1.74 × 10^{13} sec.^{-1} for C—Br. Now it seems quite likely by analogy with other compounds that this is the frequency of motion parallel to the bond. If we assume as a very rough first approximation that the ratio of parallel frequency to perpendicular frequency is the same for C—Cl, or C—Br as for C—C, namely,[8] 1470/568, we get values for the frequency perpendicular which are $\theta = 334$ and $\theta = 325$ for C—Cl and C—Br, respectively, expressed in the notation for use in the Einstein specific heat equation for harmonic oscillation. The values for the frequency parallel are $\theta = 856$ and $\theta = 845$. Using these values we can calculate with the help of the Einstein equation what the heat capacity of the halogen atom is if these conditions are all fulfilled. The results of this calculation are given in the last rows of Table II. The agreement is certainly as good as can be expected and shows that atoms attached to a heavy group like the benzene ring do approach the Dulong and Petit value in a manner similar to the elements.

It is a little venturesome to draw conclusions as to what this picture of the molecule will tell about chemical activity, but it seems worth pointing out that since the effective masses are about the same for all the C—Cl vibrating systems, the values of the frequency and consequently of the heat capacity must depend only on the strength of the bond in each case. Since the heat capacities are so nearly the same in all cases we must conclude that the strengths of the bonds are also about the same. Thus, though changes occur in the molecule as we increase the number of substituent groups, such as changes in directive influence to produce different chemical activity, there is no evidence that these changes have any marked effect on the actual mechanical strength of the bonds.

Summary

Measurements have been made of the heat capacities of mono-, di-, tetra- and hexachlorobenzene and of mono- and dibromobenzene. The heat capacity per halogen atom in these compounds seems to approach the Dulong and Petit value of 6 cal. per degree at room temperature in a way predictable from optically observed frequencies in the infra-red. The strength of the carbon–halogen bond in every case seems to be about the same, there being no evidence of directive influence upon it.

BALTIMORE, MARYLAND

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[11] Salant, *Proc. Nat. Acad. Sci.*, *12,* **334, 370 (1926).**

[12] Ellis, *Phys. Rev.*, **28, 25 (1926).**

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

THE REFRACTOMETRIC ANALYSIS OF SOLUTIONS OF PURE COMPOUNDS

BY FRANK URBAN AND V. W. MELOCHE

RECEIVED APRIL 12, 1928 PUBLISHED NOVEMBER 6, 1928

I. Telluric Acid

Instrumental analysis continues to play an ever increasing role in the field of analytical chemistry. The reason for this probably lies in the fact that it quite often combines a satisfactory degree of accuracy with a substantial saving of time. Some of the methods of instrumental analysis have, in spite of their excellence, gained favor only slowly. Analysis by means of the immersion refractometer may be given as an example. When one reviews the interesting applications of this method of analysis to the determination of the concentration of solutions of pure compounds, its value becomes more apparent. In addition to the analysis of solutions containing only one pure compound as the solute, it has been possible to analyze mixtures of two salts in solution, one known and one of unknown concentration, mixtures of two salts in solution, both of unknown concentration and the mixtures of three salts in solution, one of known and two of unknown concentration.[1] Of equal interest is the application of the immersion refractometer to the analysis of blood serum,[2] sugar solutions, alcohols, oils, fats and waxes. Still wider application of analysis by means of the immersion refractometer is encouraged by the fact that if there is only a very small sample available, the immersion refractometer may be converted into an Abbé of high precision by an auxiliary prism which is provided with the instrument.

No rigorous relationship has been shown to exist between the refractive index and the molecular weight of the solute, the concentration and the temperature.[3] It is therefore necessary to represent the change of refractive index with concentration by such tables as are illustrated by the publications of Wagner.[4]

In this contribution, we are submitting additional data which we hope will give the immersion refractomcter still wider application in the laboratory. This is intended for the analysis of solutions of the materials mentioned and not for a ready reference for refractive indices.

Preparation of Materials

Although telluric acid of a high degree of purity can be prepared by the

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[1] J. A. Clemens, *Ind. Eng. Chem.*, 13, 813–816 (1921).

[2] J. Becka, *Physiol. Chem.*, 121, 288 (1922).

[3] C. Chéneveau, *Compt. rend.*, 138, 1493, 1578 (1900); 139, 361 (1900); *Ann. chim. phys.*, [8] 12, 145–228, 289–293 (1907).

[4] B. Wagner, "Tabellen, Sonderhausen," sold by Carl Zeiss, Jena, 1907.

direct application of Staudenmaier's[5] chromic acid oxidation to the nitric acid solution of crude tellurium dioxide, the acid used in this research was prepared from pure elemental tellurium, which in turn was obtained from tellurium basic nitrate and tellurium dioxide.

Tellurium Basic Nitrate.--Crude tellurium dioxide containing about 95% of tellurium dioxide together with sodium sulfate and traces of iron, copper and selenium, was dissolved in concentrated hydrochloric acid. Thii solution was then saturated with sulfur dioxide and the precipitated selenium removed by filtration. The filtrate was diluted so that the concentration of the hydrochloric acid was 8 to 10% and sulfur dioxide was again passed into the solution until the tellurium was completely precipitated. After washing repeatedly by decantation, the precipitate was transferred to a Biichner funnel and the washing continued until the filtrate was shown to be free of chlorides. The moist tellurium was then dissolved in dilute nitric acid (1:1) and the characteristic crystals of tellurium basic nitrate were obtained by evaporation and subsequent cooling of the saturated solution.

Tellurium Dioxide.——Tellurium basic nitrate was heated at a temperature of 500° for five hours. The material obtained was anhydrous tellurium dioxide of a very high degree of purity.

Elemental Tellurium.—Tellurium dioxide was dissolved in concentrated hydrochloric acid, diluted until the acid concentration was 8–10%, and the solution saturated with sulfur dioxide. The precipitated tellurium was washed by decantation and finally transferred to a Büchner funnel, where it was further washed until free from chlorides. This slightly moist elemental tellurium was used for the preparation of telluric acid without further drying.

Telluric Acid.[5]—**Elemental** tellurium was dissolved in an excess of dilute nitric acid (1:1). An excess of chromic acid was added and the solution concentrated by evaporation until crystals began to form. Upon cooling this solution the impure brown crystals of telluric acid were deposited. Although eight recrystallizations of the product from distilled water were sufficient to remove the chromic nitrate and free nitric acid, the crystals used were from a portion which had been prepared for conductance measurements and had been recrystallized twenty-four times. The white, air-dried crystals which contained a small amount of occluded water were ground to eighty-mesh and dried further in a calcium chloride desiccator.

Analysis

In order to establish the purity of the dried telluric acid, it was analyzed for water and tellurium. The water content was determined by passing a current of dry air over a weighed sample which was heated at 450° in a porcelain tube. The water which was evolved was collected in a U-tube which contained concentrated sulfuric acid. Tellurium was determined by the Lenher-Homberger[6] method in which elementary tellurium is precipitated from a hydrochloric acid solution of telluric acid by the addition of sulfur dioxide and hydrazine hydrochloride. The following results offer reasonable evidence of the purity of the telluric acid.

Anal. Calcd. for H_6TeO_6: Te, 55.54; H_2O, 23.55. Found: Te, 55.58; H_2O, 23.50.

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[5] Staudenmaier, *Z. anorg. Chem.*, 10, 189 (1895).

[6] Lenher and Homberger, THIS JOURNAL, 30, I, 387 (1908).

Method

Since temperature was an important limiting factor in the use of the immersion refractometer, precautions were taken to keep it constant, The refractometric examination of the telluric acid solutions of various concentrations was made in a constant temperature bath at 25 ± 0.03°, while the temperature of the room was 22.5 ± 0.3°. In order to correct the scale readings for possible realignment of the prism of the instrument with respect to the scale in the ocular, the zero of the instrument was determined at least once and sometimes twice for each twelve readings. The reference value for distilled water was taken as 13.20 scale divisions at 25°.

Inasmuch as the analysis of the acid indicated that it was relatively pure and free from occluded water, requisite amounts of the dry acid

TABLE I

TELLURIC ACID, H_6TeO_6

The values given in the table were taken from a curve which was prepared by plotting concentraton values against their corresponding scale readings of the immersion refractometer. Zero for distilled water, 13.20 at 25°. Values in grams per 100 cc. of solution.

	0.0	0.1	0.2	0.3	0.4	0.6	0.6	0.7	0.8	0.9
15	0.656	0.694	0.730	0.768	0.804	0.841	0.878	0.916	0.952	0.990
16	1.026	1.062	1.100	1.136	1.174	1.210	1.246	1.284	1.320	1.358
17	1.394	1.430	1.466	1.502	1.538	1.574	1.610	1.646	1.682	1.718
18	1.754	1.790	1.824	1.860	1.894	1.930	1.966	2.000	2.036	2.070
19	2.106	2.144	2.182	2.220	2.258	2.296	2.334	2.372	2.410	2.448
20	2.486	2.522	2.558	2.594	2.630	2.666	2.702	2.738	2.774	2.810
21	2.846	2.882	2.920	2.956	2.994	3.030	3.066	3.104	3.140	3.178
22	3.214	3.250	3.286	3.322	3.358	3.394	3.430	3.466	3.502	3.538
23	3.574	3.612	3.648	3.686	3.722	3.760	3.798	3.834	3.872	3.908
24	3.946	3.982	4.020	4.056	4.094	4.130	4.166	4.204	4.240	4.278
25	4.314	4.350	4.388	4.424	4.460	4.498	4.534	4.570	4.606	4.644
26	4.680	4.716	4.754	4.790	4.826	4.864	4.900	4.936	4.972	5.010
27	5.046	5.084	5.122	5.160	5.198	5.236	5.274	5.312	5.350	5.388
28	5.426	5.460	5.494	5.528	5.562	5.596	5.630	5.664	5.698	5.732
29	5.766	5.802	5.838	5.874	5.910	5.946	5.982	6.018	6.054	6.090
30	6.126	6.162	6.198	6.234	6.270	6.306	6.342	6.378	6.414	6.450
31	6.486	6.522	6.558	6.594	6.630	6.666	6.702	6.738	6.774	6.810
32	6.846	6.882	6.916	6.952	6.998	7.024	7.058	7.094	7.130	7.164
33	7.200	7.238	7.274	7.312	7.350	7.388	7.424	7.462	7.500	7.536
34	7.574	7.610	7.648	7.684	7.720	7.758	7.794	7.830	7.866	7.904
35	7.940	7.977	8.013	8.049	8.086	8.123	8.159	8.196	8.233	8.269
36	8.306	8.340	8.376	8.412	8.448	8.482	8.516	8.552	8.586	8.622
37	8.654	8.692	8.728	8.766	8.802	8.840	8.878	8.914	8.952	8.988
38	9.026	9.064	9.100	9.138	9.176	9.214	9.250	9.288	9.326	9.362
39	9.400	9.436	9.474	9.510	9.546	9.584	9.620	9.656	9.692	9.730
40	9.766	9.804	9.840	9.878	9.916	9.952	9.990	10.026	10.064	10.102
41	10.140	10.177	10.214	10.250	10.287	10.324	10.360	10.397	10.434	10.470
42	10.506	10.542	10.578	10.614	10.650	10.686	10.722	10.758	10.794	10.830
43	10.866	10.902	10.938	10.974	11.010	11.046	11.082	11.118	11.154	11.190
44	11.226									

were weighed, dissolved in distilled water and diluted to the proper volume in flasks which had been previously calibrated at 25°. It was found that the use of the conventional type of trough did not afford a uniform temperature. Additional circulation was then provided by pumping water from a constant temperature bath through a glass tube which contained a series of openings and was laid on the bottom of the trough. The excess of water was allowed to drain through the overflow. The refractometer was suspended with the prism immersed in the liquid to be examined a few minutes before a reading was attempted. After the instrument had acquired the temperature of the bath, the reading was taken. Each scale reading reported for a single concentration was the mean of several independent settings of the instrument. Each scale reading used to locate a point in the graphical representation of the data was the result of the examination of two independent solutions for each concentration. Between each set of readings, the prism of the refractometer was washed with distilled water and polished with lens paper. Since this operation changed the temperature of the prism, it was again necessary to suspend the instrument with the prism in the liquid to be examined and allow a few minutes for the temperature to become uniform. In the course of the experiments, it was found that two observers using two different instruments for the examination of the same solutions could obtain an agreement of scale readings of ±0.025 scale divisions. An excellent definition of the border was obtained when the temperature of the bath was uniform.

II. Selenious Acid

Preparation of Selenium Dioxide.—Crude selenium dioxide was dissolved in 10% nitric acid and the insoluble material removed by filtration. The solution was evaporated to dryness and the selenium dioxide sublimed by heating the residue in a six-inch evaporating dish and collecting the sublimed oxide on the sides of a five-inch funnel which was placed over the evaporating dish. The sublimation was repeated three times. Due to the hygroscopic character of selenium dioxide, the product always contained a small amount of water but was otherwise pure.

Method of Analysis

The concentration of the stock solution prepared from the selenium dioxide was determined by analysis for elementary selenium. The method used included the conventional separation of elementary selenium by hydroxylamine hydrochloride, filtration, drying the selenium at 105° and weighing as such. The results were calculated in terms of grams of selenium dioxide per hundred cubic centimeters of solution.

Procedure

The manipulation of the refractometer was identical with that already described for telluric acid. Since the solid selenium dioxide has a pronounced affinity for water, it was desirable to prepare the series of solutions from a standardized stock solution rather than attempt to weigh individual samples of selenium dioxide. The stock solution was measured in a calibrated buret and diluted to the desired volume in calibrated flasks at a temperature of 25°.

TABLE II

SELENIOUS ACID

The values given in the table were taken from a curve which was prepared by plotting concentration values against their corresponding scale readings of the immersion refractometer. Values are grams of SeO_2 per 100 cc. of solution.

	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
16	0.758	0.786	0.814	0.843	0.873	0.902	0.932	0.960	0.989	1.019
17	1.048	1.078	1.107	1.136	1.167	1.198	1.229	1.260	1.289	1.319
18	1.348	1.378	1.407	1.437	1.468	1.498	1.52%	1.559	1.588	1.619
19	1.649	1.678	1.709	1.740	1.769	1.799	1.828	1.858	1.888	1.918
20	1.948	1.978	2.009	2.040	2.071	2.099	2.127	2.155	2.185	2.214
21	2.242	2.272	2.301	2.329	2.358	2.388	2.419	2.450	2.479	2.508
22	2.538	2.567	2 597	2.627	2.656	2.685	2.715	2.744	2.774	2.803
23	2.833	2.862	2.890	2.920	2.949	2.979	3.008	3.039	3.068	3.098
24	3.127	3.157	3.186	3.216	3.245	3.275	3.304	3.334	3.364	3.395
25	3.423	3.451	3.480	3.508	3.537	3.567	3.596	3.625	3.655	3.684
26	3.714	3.743	3.773	3.802	3.832	3.861	3.891	3.920	3.949	3.979
27	4.008	4.038	4.067	4.097	4.128	4.159	4.189	4.220	4.250	4.279
28	4.310	4.339	4.372	4.403	4.434	4.462	4.491	4.521	4.550	4.579
29	4.609	4.638	4.668	4.697	4.727	4.756	4.786	4.815	4.845	4.874
30	4.905	4.936	4.967	4.997	5.027	5.056	5.086	5.115	5.145	5.174
31	5.204	5.233	5.263	5.292	5.320	5.348	5.376	5.404	5.433	5.460
32	5.489	5.517	5.546	5.576	5.605	5.634	5.664	5.693	5.723	5.752
33	5.780	5.809	5.836	5.865	5.893	5.921	5.950	5.980	6.009	6.038
34	6.068	6.097	6.125	6.154	6.182	6.210	6.238	6.268	6.295	6.325
35	6.353	6.381	6.410	6.440	6.468	6.496	6.525	6.555	6.584	6.614
36	6.643	6.673	6.701	6.729	6.758	6.788	6.817	6.843	6.876	6.906
37	6.935	6.964	6.994	7.023	7.053	7.082	7.112	7.141	7.171	7.200
38	7.230	7.259	7.289	7.318	7.347	7.377	7.407	7.436	7.464	7.492
39	7.522	7.551	7.580	7.610	7.640	7.669	7.698	7.728	7.757	7.787
40	7.816	7.846	7.875	7.905	7.934	7.963	7.993	8.022	8.052	8.081
41	8.111	8.140	8.170	8.199	8.229	8.258	8.288	8.317	8.346	8.375
42	8.405	8.435	8.462	8.494	8.523	8.553	8.582	8.612	8.641	8.671
43	8.700	8 730	8.759	8.788	8.818	8.847	8 877	8.906	8.936	8.965
44	8.995	9.024	9.054	9.083	9.113	9.142	9.172	9.201	9.230	9.260
45	9.289	9.319	9.348	9.378	9.407	9.437	9.466	9.496	9.525	9.555
46	9.584	9.614	9.643	9.672	9.702	9.731	9.761	9.790	9.820	9.849
47	9 880	9.911	9.940	9.970	9.999	10.030	10.060	10.090	10.120	10.150
48	10.180	10.209	10.238	10.267	10.297	10.326	10.356	10.385	10.415	10.444
49	10.474									

III. Potassium Ferrocyanide

Preparation and Analysis.—Ordinary "chemically pure" potassium ferrocyanide was recrystallized three times from aqueous solution and the resulting product pulverized and finally dried in a calcium chloride desiccator. The dry material was then analyzed for potassium and iron.

Potassium.—A 0.5g. sample was digested with concentrated sulfuric acid until the cyanide was destroyed. The sample was treated with water until the acid strength was about 10% and the iron was removed by double precipitation with ammonium hydroxide. The combined filtrates from the precipitated ferric hydroxide were evaporated to dryness and the residue was heated at 450°. The resulting potassium sulfate was weighed and the results were calculated to per cent. of potassium.

Iron.—For this determination the sample was dissolved in 10% sulfuric acid and **the** ferrous iron titrated with $N/10$ potassium permanganate, following the details of the potentiometric method described by Kolthoff,[7] and Hostetter and Roberts.*

Anal. Calcd. for $K_4Fe(CN)_6$: K, 42.46; Fe, 15.16. Found: K, 42.40; Fe, 15.13.

Procedure

Solutions of the concentrations desired were prepared by dissolving weighed samples of the dry material in water and diluting to the proper volume in calibrated flasks, maintaining the temperature at 25°. The same precautions were followed in the use of the refractometer as have been described for telluric acid.

TABLE III

POTASSIUM FERROCYANIDE—$K_4Fe(CN)_6$

Scale reading	G. of $K_4Fe(CN)_6$ in 100 cc. of solution	Scale reading	G. of $K_4Fe(CN)_6$ in 100 cc. of solution	Scale reading	G. of $K_4Fe(CN)$ in 100 cc. of solution	Scale reading	G. of $K_4Fe(CN)_6$ in 100 cc. of solution
15.7	0.466	36	4.388	56	8.302	76	12.236
17.0	0.704	37	4.584	57	8.496	77	12.432
18	0.898	38	4.774	58	8.692	78	12.620
19	1.092	39	4.964	59	8.888	79	12.808
20	1.286	40	5.154	60	9.086	80	13.004
21	1.480	41	5.334	61	9.284	81	13.200
22	1.674	42	5.540	62	9.484	82	13.388
23	1.868	43	5.736	63	9.684	83	13.576
24	2.058	44	5.934	64	9.882	84	13.764
25	2.256	45	6.132	65	10.080	85	13.968
26	2.448	46	6.330	66	10.276	86	14.164
27	2.640	47	6.528	67	10.472	87	14.360
28	2.834	48	6.728	68	10.668	88	14.552
29	3.028	49	6.928	69	10.864	89	14.744
30	3.222	50	7.128	70	11.060	90	14.938
31	3.416	51	7.328	71	11.256	91	15.132
32	3.610	52	7.524	72	11.452	92	15.324
33	3.804	53	7.718	73	11.648	93	15.516
34	3.998	54	7.914	74	11.844		
35	4.192	55	8.108	75	12.040		

Discussion

The results recorded were obtained by the graphical method of interpolation. Scale readings were plotted against concentrations, the concentration being given in terms of grams of solute per 100 cc. of solution.

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[7] Kolthoff, *Rec.* trav. *chim.*, 41, 343 (1922).

[8] Hostetter and Roberts, THIS JOURNAL, 41, 1337 (1919).

Forty to fifty points were plotted to establish the slope of each curve. In the range of concentrations given in the tables, there are no apparent irregularities. A change of concentration of telluric acid corresponding to 0.1 of a unit in scale divisions is equivalent to about 0.037 g. per 100 cc. of solution. Likewise for selenious acid, a change of concentration corresponding to 0.1 of a unit in scale divisions is equivalent to 0.029 g. of selenium dioxide per 100 cc. of solution. For potassium ferrocyanide, 0.1 of a unit in scale divisions is equivalent to 0.019 g. of the salt per 100 cc. of solution. As has been previously noted, two individuals can obtain readings whose mean values are within a range of ±0.025. It is therefore believed that a proper control of the method assures rapid analysis with reasonable precision for solutions of the materials mentioned.

The writers wish to acknowledge the kindness of Bausch and Lomb in providing one of their new instruments for this work.

Summary

1. The results in Table I correlate the scale readings of an immersion refractometer and the concentration of aqueous solutions of telluric acid thus making possible a rapid and reasonably accurate determination of the concentration of telluric acid solutions of unknown strength.

2. The results in Table II for selenious acid and those in Table III for potassium ferrocyanide also afford a rapid and accurate means of determining the concentration of these solutions.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF STANFORD UNIVERSITY]

THE INCOMPATIBILITY BETWEEN ANY THEORY OF COMPLETE DISSOCIATION AND MIGRATION DATA FOR DIVALENT IONS

BY JAMES W. MCBAIN AND PIERRE J. VAN RYSSELBERGE

RECEIVED JUNE 13, 1928 PUBLISHED NOVEMBER 6, 1928

In 1814 Porrett electrolyzed solutions of mixtures of "prussides" **and** observed that the potassium and the iron moved in opposite directions, the iron going toward the anode. Ever since, the ferrocyanide ion has been the model of a complex anion. The use of migration is, on account of its simplicity and unambiguity, one of the most powerful tools of the physical chemist in the cases where it can be applied. We wish to adduce it in deciding the rival claims of incomplete and complete dissociation in solutions containing divalent ions.

The object of this communication is to present experimental data which show that all divalent ions take part to a certain extent in such phenomena as those illustrated in extreme form by the prussides above, and familiar to us since Hittorf in the behavior of cadmium iodide. The new data show that all divalent ions, even the simplest, such as magnesium ion and sulfate ion, can form complex anions in such appreciable amount that the ordinary migration of the cation is completely submerged.

When to a **0.05** M solution containing a divalent ion sufficient quantity of anion is added, the divalent ion forms a complex anion, and we have the striking and highly significant result that the usual movement of the cation toward the cathode is suppressed or even reversed. Thus when an excess of sulfate ion is added to a **0.05** M solution of magnesium or cadmium sulfate, the magnesium or cadmium migrates toward the anode. Such facts constitute a disproof of the applicability of any hundred per cent. dissociation hypothesis to solutions containing divalent ions.

The almost non-conducting mercuric cyanide has never been included in the hundred per cent. hypothesis, and the same remark applies to the mercuric halides and cadmium iodide. The cadmium of cadmium iodide exhibits a migration to the cathode in dilute solution of +0.45 equivalents per faraday of current, but upon the addition of sufficient iodine ions, or indeed upon merely concentrating the cadmium iodide, the cadmium reverses the direction of its movement and now goes to the anode. Thus the migration of cadmium in a molar solution of cadmium iodide is −0.22. This has always been taken as incontrovertible evidence of the formation of complex ions such as CdI_3^-, whose movement carries more cadmium toward the anode than is simultaneously being carried by cadmium ions proper toward the cathode.[1] Since solutions of cadmium iodide are poor conductors, even in such dilutions as 0.1 M, and since their activity is correspondingly small, it is evident that much of the cadmium iodide is undissociated and that the undissociated molecules are capable of uniting with iodine ion to form complex anions.

The present communication shows that all of the divalent salts differ only in degree. Thus in a **0.05** M solution of magnesium chloride to which a sufficient concentration of chlorine ions has been added, the magnesium goes to the anode just like the cadmium and presumably for the same reason—certainly not because it is hundred per cent. dissociated into simple magnesium ions. The two ions, magnesium ion and sulfate ion, have been specially chosen for study because they are the simplest known divalent cation and anion, respectively, and if even they must be regarded as forming appreciable amounts of undissociated molecules and of complex anions, it is futile to extend any hypothesis of hundred per cent. dissociation to polyvalent ions. The result is not in conflict with the conception of interionic attraction but it is at once a disproof of the unwarranted assumption of hundred per cent. dissociation and a recognition of the molecules and ions really present.

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[1] See, for example, McBain, Z. *Elektrochem.*, **11**, 215–223 (1905); THIS JOURNAL, **34**, 1134–1137 (1912).

Experimental

The results here communicated consist of measurements of migration of cadmium, magnesium, lithium, potassium and calcium in 0.05 *M* solutions of one of their salts containing at feast one divalent ion. In each case there is added a large amount, usually 0.95 *M*, of a sulfate or chloride. The movement of the element present to the extent of 0.05 M in the mixture is measured. The analysis gives the actual direction, whether toward anode or cathode, unequivocally. A calculation of the distribution of the current between the two salts from known conductivity data gives an approximate value for the migration number. The important fact is that the movement is usually toward the anode. The actual numerical value is of far less interest.

The apparatus was that used and described by McBain and Coleman.[2] It is made of borosilicate glass, has an internal diameter of about 2 cm. and a capacity of 190 cc. The anode is of copper and the cathode of platinum. A very large hollow tap in the middle serves to separate the anode and cathode compartments; the solution just on the anode side of the tap served as middle portion. The current was measured with a silver coulometer.

The first experiment was carried out on 0.05 *M* cadmium sulfate in the presence of 0.95 M magnesium sulfate. This particular mixture is of interest because Brönsted[3] showed that the e.m.f. of the cell

$$\text{Cd amalgam}\ \left|\begin{array}{cc}\text{CdSO}_4, & \text{MgSO}_4\\ c_1 & 2-c_1\end{array}\right|\begin{array}{cc}\text{CdSO}_4, & \text{MgSO}_4\\ c_2 & 2-c_2\end{array}\right|\ \text{Cd amalgam}$$

could be calculated by the ordinary Nernst formula $E = k \ln c_1/c_2$, where c_1 and c_2 represent various dilute solutions of cadmium sulfate, the total concentration being 2 M. This was adduced as evidence in support of the 100% dissociation theory.[4]

In these experiments the solutions taken for analysis were not weighed (the only strictly correct method) but were measured by volume, making the assumption that the total volume in the cathode compartment was the same as that originally measured in. Cadmium deposited on the cathode was dissolved with a little sulfuric acid before the analysis, which was made by titration with $N/10$ ferrocyanide. There was less total cadmium in the cathode compartment after the experiment than before, showing that the net movement was toward the anode and that the cadmium was largely in other forms than positively charged cadmium ion. A previous experiment determining cadmium as cadmium sulfide, not quoted in the tables, gave a migration value of —0.34, that is, again toward the anode.

Having determined that the net movement toward the anode amounted to **1.22** mg. during the passage of 198.5 coulombs of current it is necessary to decide what fraction of the current has been carried by the cadmium sulfate in the mixture, We have done this as a first approximation by assuming that the amount of current carried by each constituent is proportional to its concentration multiplied by the specific conductivity which it exhibits when alone in 1.0 M solution. For the present mixture this fraction is $(19.8 \times 0.05)/[(19.8 \times 0.05) + (21.4 \times 0.95)] = 0.0484$. The final migration number is therefore $(96500 \times 0.00122)/(198.5\ X\ 0.0464\ \text{X}\ 56.2) = -0.227$, where 56.2 is the equivalent weight of cadmium.

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[2] McBain and Coleman, *Trans. Faraday Soc.*, *15*, Part I, 2747 (1919).

[3] Bronsted. *Medd. Vetensksakad. Nobelinst.*, No. 25, 1–19 (1919).

[4] Ebert, "Jahrbuch Radioakt. Elektronik," 18, 134–196 (1921).

Since the vital consideration was not the accurate determination of the migration but the demonstration of the movement of these supposed cations in the wrong direction, a direct comparison was made in most of the other experiments between the amounts of the element in question contained in a definite volume of the original compared with the same volume of solution drawn from the anode or cathode compartment after thorough mixing within that compartment. A diminution in the analytical value in the cathode compartment and a similar increase in the analytical value in the anode compartment meant movement away from the cathode toward the anode Finally, experiments were carried out in which the solutions were all determined by weight and based upon the amount of water actually present before and after electrolysis. Kahlbaum's or Baker's purest chemicals were used throughout. The current was passed for between three and four hours.

The experimental data are collected in Table I. Magnesium was determined as pyrophosphate, potassium as cobaltinitrite, lithium as sulfate (after evaporation of the ammonium sulfate present in the mixture) and calcium as oxalate Cadmium and copper are not precipitated in the phosphate method on account of the solubility of their phosphates in ammonia. The phosphate precipitates were allowed to settle for from four to twelve hours before filtration and the filter was put into the crucible when wet, before calcination. The cobaltinitrite method for potassium could be used in the presence of magnesium and copper sulfates and it was always carried out under strictly comparable conditions. The reagent was prepared by dissolving **220** g. of sodium nitrite in **440** cc. of water, then dissolving **113** g. of cobalt acetate in **300** cc. of water and **100** cc. of glacial acetic acid. The two solutions were mixed just before using

TABLE I

ANALYTICAL DATA FOR MIGRATION OF THE CATION OF A SALT CONTAINING DIVALENT ION IN 0.05 *M* SOLUTION IN THE PRESENCE OF A LARGE AMOUNT OF ADDED SULFATE OR CHLORIDE

Concn. of mixture, moles per liter	Middle %	Change	
		Cathode, mg.	Anode, mg.
0.05 $CdSO_4$ + 0.95 $MgSO_4$	+0.6	−1.22 Cd	....
0.05 $CdSO_4$ + 0.95 $MgSO_4$	+0.1	−0.83 Cd	....
0.05 $MgSO_4$ + 0.95 $(NH_4)_2SO,$	\$ 0 5	−1.71 Mg	+1.88 Mg
0.05 $MgSO_4$ + 0.95 K_2SO_4[a]	<+0.1	−1.88 Mg	+1.68 Mg
0.05 $MgSO_4$ + 0.95 $CdSO_4$	....	...	Approx. +0. 74 Mg
0.05 $MgSO_4$ + 0.95 $CuSO_4$	<+0.2	−0.86 Mg	(+0.23) Mg
0.05 $MgSO_4$ + 0.95 $CuSO_4$ by wt.	<+0.8	−0.55 Mg	+0.84 Mg
0.05 Li_2SO_4 + 0.95 $(NH_4)_2SO_4$	−0.2	+0 19 Li	....
0.05 K_2SO_4 + 0.95 $MgSO_4$	<−0.5	...	−18.6 K
0.05 K_2SO_4 + 1.95 $MgSO_4$	<−0.7	\$4.72 K	−4.25 K
0.05 K_2SO_4 + 2 95 $MgSO_4$	+1.0	+7.25 K	−5 09 K
0.05 $MgCl_2$ + 1 9 NH_4Cl	−0 6	40.677Mg	−0.535 Mg
0.05 $MgCl_2$ + 3.9 NH_4Cl	−0.3	−0.76 Mg	+1.15 Mg
0.05 $MgCl_2$ + 3 9 NH_4Cl	+0 2	...	+0.46 Mg
0.05 $CaCl_2$ + 4NH_4Cl	+0 4	0.00 Ca	0 00 Ca

[a] Plus a few drops ot H_2SO_4 to dissolve the K_2SO_4 hence the sign but not the numerical value of the migration number can be found

the reagent and the nitrogen peroxide was removed by thorough stirring The reagent was used in large excess, the precipitate allowed to settle for over an hour before filtering on a weighed filter, washed with aqueous acetic acid, dried and weighed by difference.

Discussion

The results of the migration determinations are collected in Table II and the more they are studied the less compatible do they appear with any assumption of 100% dissociation into simple independent ions.

TABLE II

MIGRATION DATA TO SHOW THE PRESENCE OF MOLECULES AND COMPLEX IONS IN SOLUTIONS CONTAINING DIVALENT IONS

Concn of mixture, moles per liter	Element	Obs.[a] migration, n	Remarks
0.05 $CdSO_4$ + 0.95 $MgSO_4$	Cd	−0.23	Cd to anode
0.05 $CdSO_4$ + 0.95 $MgSO_4$	Cd	− .20	Cd to anode
0.05 $MgSO_4$ + 0.95 $(NH_4)_2SO_4$	Mg	− .60	Mg to anode
0.05 $MgSO_4$ + 0.95 K_2SO_4[b]	Mg	Negative	Mg to anode
0.05 $MgSO_4$ + 0.95 $CdSO_4$	Mg	−0.25	Mg to anode
0.05 $MgSO_4$ + 0.95 $CuSO_4$	Mg	− .20	Mg to anode
0.05 $MgSO_4$ + 0.95 $CuSO_4$	Mg[c]	− .13	Mg to anode
0.05 Li_2SO_4 + 0.95 $(NH_4)_2SO_4$	Li	+ .06	Li to cathode
0.05 K_2SO_4 + 0.95 $MgSO_4$	K	+ .36	K to cathode
0.05 K_2SO_4 + 1.95 $MgSO_4$	K	+ .11	K to cathode
0.05 K_2SO_4 + 2.44 $MgSO_4$	K	+ .12	K to cathode
0.05 $MgCl_2$ + 1.9 NH_4Cl	Mg	+ .1	Mg to cathode
0.05 $MgCl_2$ + 3.9 NH_4Cl	Mg	− .36	Mg to anode
0.05 $MgCl_2$ + 3.9 NH_4Cl	Mg	− .38	Mg to anode
0.05 $CaCl_2$ + 4NH_4Cl	Ca	± .00	Ca neither

[a] 0.05 salts when alone give $CdSO_4$ +0.37; $MgSO_4$ +0.36; Li_2SO_4 +0.39; K_2SO_4 +0.49; $MgCl_2$ +0.39; $CaCl_2$ +0.40.

[b] Plus a few drops of H_2SO_4 to dissolve the K_2SO ; 0.0017 g. moved to the anode.

[c] Complete measurements of all constituents results based upon absolute amount of water.

The result is to show that in the majority of cases more of the metal studied is being carried to the anode than is migrating as simple ion to the cathode. This proves the presence of complex anions in relatively large amount. The complex anions have been formed by adding to such a solution as 0.05 M $MgSO_4$ or 0.05 M $MgCl_2$ a large excess of sulfate ions or chlorine ions, respectively. Thereupon these ions have combined with the $MgSO_4$ or $MgCl_2$ to produce the complex ions, showing the presence of the undissociated molecules with which they are thus combining.

For the last five or six years the complete dissociation of strong electrolytes has been generally assumed, and a fundamental separation has thus been made between strong and weak electrolytes. The weak electrolytes consist of weak acids and bases and a few individual salts such as mercuric chloride and cyanide. Acids of every degree of strength up to hydrochloric acid are, however, still recognized. In concentrated solution of sulfuric acid it is customary to explain formation of persulfuric acid on electrolysis as due to combination of two of the incompletely dissociated ions, HSO_4^-. All hypotheses, including that of Arrhenius, agree that in sufficiently dilute solution the dissociation is complete. In the development of the Debye and Hückel theory[5] of interionic attraction, the degree of dissociation α was, for lack of definite evidence, assumed to be unity. The present results indicate that the real value of α is less than unity and that the numerical values of the coefficients must be altered accordingly. Indeed, a sound physical explanation of the different coefficients introduced in that theory for higher concentrations is lacking.

The recent widespread use of activity coefficients has induced many scientists to leave the problem of the true degree of dissociation of strong electrolytes completely unsolved, although activity coefficients are completely empirical and their numerical values depend upon arbitrary conventions. It must remain a primary aim to determine the actual molecular species present and their real concentrations.

Recently Nernst[6] has rightly argued that some strong electrolytes must be incompletely dissociated because their heats of dilution are of the opposite sign to that predicted from interionic attraction alone. He even suggests a degree of dissociation for strong electrolytes which agrees with the mass law. His hypothesis, however, is not yet completely developed. Fajans[7] deduces from optical measurements that neutral molecules and complex ions are present in solutions of strong electrolytes. Several writers[8] have adduced migration data to show that 100% dissociation, even if it occurs for some salts, cannot be general. For solutions of different salts with a common ion at any definite molality, the product of the conductivity (μ) and the transference number of the common ion (n) must be the same for all the salts if they are completely dissociated. In this way MacInnes and Cowperthwaite showed that even if alkali chlorides are assumed to be completely dissociated in 0.1 N solution, such nitrates as those of sodium, potassium and silver must be incompletely dissociated or at least their ions must be partly paired or associated in Bjerrum's sense. Tables III and IV show similar calculations for the sulfate and chlorine ions, using the data of Landolt-Börnstein.

Deficient conductivity might be explained in terms of "associated ions"

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[5] Debye and Hückel, *Physik. Z.*, 24, 185, 305, 334 (1923); 25, 97 (1924).

[6] Nernst, *Z. Elektrochem.*, 33, 428 (1927); Naude, *ibid.*, —; Nernst and Orthmann, *Ergebnisse der exakten Naturwissenschaften*, 6, 155 (1927).

[7] Fajans, *Trans. Faraday Soc.*, 23, 357 (1927).

[8] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, 1923, p. 321; MacInnes and Cowperthwaite. *Trans. Faraday Soc.*, 23, 400–404 (1927).

TABLE III

"100%" MOBILITIES $n\text{Cl}^-$

Salt	In 0.01 M	In 0.05 M	Salt	In 0.01 M	In 0.05 M
NaCl	60.0	56.0	$BaCl_2$	58.5	52.6
KCl	60.4	56.6	$MgCl_2$	57.5	51.6
LiCl	61.0	57.4	$CaCl_2$	57.1	48.4
$(NH_4)Cl$	60.7	56.3	$SrCl_2$	57.9	52.2
HCl	61.4	57.9	$CdCl_2$	41.6	28.5

TABLE IV

"100%" MOBILITIES, $n\text{SO}_4^{--}$

Salt	In 0.01 M	In 0.05 M	Salt	In 0.01 M	In 0.05 M
Na_2SO_4	55.8	48.4	$MgSO_4$	41.6	31.2
K_2SO_4	56.0	48.4	$ZnSO_4$	42.8	28.2
Li_2SO_4	..	42.2	$CuSO_4$	..	27.4
H_2SO_4	51.25	40.0	$CdSO_4$	37.2	26.4

if one desired to deny the existence of undissociated molecules, but this does not appear to be adequate to explain the new migration data of Tables I and II, where the outstanding effect is the ready movement toward the wrong electrode. A new kind of "association" of ions in clusters containing one kind of ion in excess might be assumed, but this new assumption is of little value until, firstly, it is proved to be a legitimate possibility; secondly, the further consequences have been faced; and, thirdly, it has been shown capable of explaining the migration data.

The first thing is to demonstrate that it does not contradict existing knowledge of solutions and the laws of electricity. In other words, it has to be shown that such clusters of ions can be formed stably in relatively large amount and remain in stable units when placed in an electric field in which the constituent ions will travel together although pulled in opposite directions. Further, there is no reason apparent for explaining why clusters merely of three ions should occur. If ternary clusters can form in large amount, then larger ones would seem to be possible up to indefinite sizes, up through colloidal dimensions to complete crystals, in solution far from saturation. Indeed the conception is difficult to harmonize with solubility data (compare, for example, $ZnSO_4$, $MgSO_4$ and $BaSO_4$).

The second thing is to realize the consequences of denying undissociated molecules and true complex anions in favor of clusters of ions. It is obvious that since by hypothesis such clusters are largely broken down into independent ions by thermal vibration, they are less stable in an electric field where the components are pulled in opposite directions. The strain must increase with the slope of potential. Hence we must deduce that the transference numbers should change with the voltage applied—a possibility, although not yet recorded. If the voltage were high enough this conception would therefore seem to predict a reversal of direction of the movements observed, and a return to migration data such as are characteristic of ordinary dilute solutions A similar influence of voltage would be expected in conductivity measurements, which might afford an easier method of testing the existence of such an effect.

A third consequence of the conception, which shows that the occurrence or non-occurrence of ionic "association" is in general irrelevant to our main inquiry, is the fact that it predicts almost equal numbers of positively and negatively charged clusters. This is because the same Coulomb's Law and the same ionic radii or distances are used alike in calculating the electrostatic forces acting in a cluster of two positive with one negative as in a cluster of two negative with one positive ion.[9] The attractive forces and the repulsive forces are substantially identical in the two cases, thus giving cationic and anionic clusters in equal numbers—whose effects on migration would almost cancel each other, whereas the proportion of anionic clusters would have to be overwhelmingly greater than that of the cationic clusters if the observed data are to be accounted for.

Professors Parks, Bray and Latimer in conversation have suggested to us the possibility that the assumption of excessive hydration of all the cations might explain our results, and save recourse to recognizing complex anions.[10] Usually hydration has an almost negligible effect, but here its effect is multiplied about 19-fold, since 0.05 M salt is studied in presence of a 19-fold higher concentration of the other salt. For this purpose it is necessary to assume that each cation is much more hydrated than the sulfate or chloride ion; that is, that the cations actually take along with them large quantities of water during migration. Suppose, for example, a divalent cation carries ten molecules of bound water more than the anion. During migration this water is carried to the cathode, thus displacing the whole solution bodily toward the anode. Hence for each faraday of current carried by the divalent cation, there would be an apparent movement toward the anode of the amount of each constituent contained in one-half of 10 moles or 90 g. of water. For the 0.05 M salt (divalent) this would be $2 \times 0.09 \times 0.05$ equivalents = only 0.009 equivalents change

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[9] This becomes evident for ions whose charges are central or symmetrical when one draws three circles in contact, with centers lying on a straight line, the two outer circles representing ions of charge opposite to that of the ion between them. The opposite ions need not be of the same size.

[10] Such large movement would be readily tested by experiments such as those of Nernst, Washburn and others One of us (J. W. M.) carried out such measurements at the University of Toronto in 1904 with cadmium sulfate, using acetone as reference substance [see McBain, *Z. Elektrochem.*, 11, 216 (1905), also *Proc. Wash. Acad. Sci.*, 9, 7 (1905)], where the general formulation is discussed. Unfortunately the result was to show that the sulfate ion is *more* hydrated than cadmium ion, an experimental finding in the opposite direction from that required for the hydration explanation. If necessary one can arbitrarily discount this by saying that acetone cannot have been a suitable reference substance but must have combined with the cadmium ion, and that the uncombined acetone may have been moving in the opposite direction, of course to a less extent.

in apparent migration. But this is reduced in proportion to the migration number of the 0.95 molar cation, and then increased by the approximate 19-fold, because the whole movement of the 0.05 M cation is referred to the current carried by the 0.05 *M* salt. For 0.95 *M* $CuSO_4$ the migration number of the copper is 0.30. Hence the approximate effect on 0.05 M $MgSO_4$ in its presence would be 19 X 0.30 $\times$ 0.009 = 0.05. This is wholly inadequate to explain our results, where a ten times larger correction would be required to explain them away. This cannot be done, for we have already assigned nearly one-fifth of the total water to the excess hydration of copper ion (and similarly for Mg^{++}, Cd^{++}, Cu^{++}; K^+ and NH_4^+) above that of SO_4^{--} or Cl^-. Hence even if *all* the water in the aqueous solution were combined with the cation, the effect on the migration observed would be only half that required to explain away our results.

It is less forced to admit that we are here dealing with complex ions, particularly when it is universally admitted that numerous complex ions such as the silver cyanide ion $Ag(CN)_2^-$, are to be taken for granted.

Lastly, if undissociated molecules and complex ions are present in such large amounts under the conditions obtaining in our experiments, it must be admitted that they cannot be considered as negligible in much more dilute solutions. A similar conclusion follows from an inspection of graphs of migration numbers of divalent cations plotted against the logarithm of the concentration. This will be illustrated in a further communication dealing with cadmium salts.

Summary

It is shown that when a sufficient excess of chlorine ions or sulfate ions is added to 0.05 M solutions of salts containing a divalent ion, the migration of the anion is suppressed or often reversed, showing that the sulfate or chlorine ions have combined with undissociated molecules to form complex ions. Such migration is incompatible with the assumption that salts containing polyvalent ions are completely dissociated, except in extreme dilution.

STANFORD UNIVERSITY, CALIFORNIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BUCKNELL UNIVERSITY]

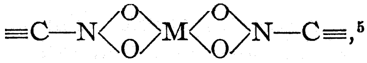
THE QUANTITATIVE DETERMINATION OF PALLADIUM BY MEANS OF 6-NITROQUINOLINE

BY S. C. OGBURN, JR., AND A. H. RIESMEYER[1]

RECEIVED JULY 19, 1928 PUBLISHED NOVEMBER 6, 1928

The use of certain organic complexes in the formation of stable coordinated salts with metals of the platinum group is well known. Those of the oximes, aromatic nitroso-amines and hydroxyquinolines are of great value in the quantitative removal of these metals from solution. This is particularly true with platinum and palladium.[2]

Bargallini and Bellinois[3] state that in the case of the hydroxyquinolines, the condition $\equiv C-O-M-N=$ (where M is one metallic equivalent and in which the ring is closed by a secondary valence) must be met. Thus the metal replaces the hydrogen of the hydroxyl (which must be in the eighth position) and is connected with the N of the quinoline molecule.

One of us[4] found that other substituted quinolines would also act with the formation of coordinated salts with palladium. The best of these is 6-nitroquinoline. The metallic grouping formed in this case is not with the nitrogen of the quinoline structure, but with the nitrogen of the nitro group. The structural condition here is  $\equiv C-N\langle{}^{O}_{O}\rangle M\langle{}^{O}_{O}\rangle N-C\equiv$,[5] in which the metal, palladium, exhibits a coordination number of four. This compound has been found to be so stable and so insoluble in aqueous solutions that it may be used as a means of quantitatively removing palladium. As it has no precipitating effect on solutions of ruthenium, rhodium, osmium, iridium and platinum, it may also be used in separating palladium from the entire platinum metal group.

Experimental Part

Preparation of Palladium Chloride Solution.—To insure the purity of the palladium chloride used, a few grams of the dry c. p. salt as purchased from a leading supply house was dissolved in hot water acidulated with hydrochloric acid. The metal was precipitated from this solution by the addition of previously tested pure zinc dust. The spongy metal

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[1] This paper is based upon a thesis submitted by A. H. Riesnieyer 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, 2507 (1926).

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

[4] Ogburn, THIS JOURNAL, 48, 2493 (1926).

[5] This grouping is in accord with Lowry's (*J. Soc. Chem. Ind.*, 42, 462 (1923)) interpretation of the structural formula for the precipitate of nickel with dimethylglyoxime, except that in this case nickel has a coordination number of six.

was washed free from chlorides and dissolved in freshly prepared *aqua regia* (1:3). After evaporating this solution to dryness and extracting with hydrochloric acid, several repeated evaporations with the latter reagent were carried out in order to expel all nitrogen oxides. The dihydrate, $PdCl_2 \cdot 2H_2O$, thus obtained was dissolved in a small quantity of distilled water and the palladium precipitated as $Pd(C_4H_7O_2N_2)_2$ by means of a 1% alcoholic solution of dimethylglyoxime in the *cold*.[6] After stirring, this bright yellow precipitate was filtered, washed with a small quantity of cold water containing a few cubic centimeters of alcohol and dried in an electric oven at 105°. It was then carefully ignited in air, heated for twenty minutes at red heat in a stream of hydrogen, cooled and the metallic palladium thus obtained weighed. A definite quantity (**4.780** g.) of this metal was subsequently dissolved in aqua *regia* and the solution evaporated to dryness. The residue was taken up with hydrochloric acid; this was followed by several evaporations with the latter reagent to remove all nitrogen oxides, and the solution diluted to one liter. The resulting palladium chloride solution, which was only slightly acid, was analyzed for its metal content per cubic centimeter by treating a known portion with zinc dust until all color was removed from the solution. (The colorless solution gave no precipitate with dimethylglyoxime, hydrogen sulfide, mercuric cyanide or 6-nitroquinoline—thus the absence of palladium was assured.) Excess zinc was dissolved in dilute hydrochloric acid and the spongy palladium was filtered, washed free from chlorides, dried, heated at red heat in a stream of hydrogen, cooled and then weighed. Results of two such determinations were

Weight of boat plus metal, g.	3.2723	3.2724
Weight of boat, g.	3.2484	3.2485
Weight of metal, g.	0.0239	0.0239
Amount of solution used, cc.	5.0	5.0
Weight of metallic Pd per cc., g.	0.00478	0.00478

This solution was used in the following work.

Preparation of 6-Nitroquinoline Solution.—In the analytical determinations recorded below, a hot saturated aqueous solution of this reagent was used.

The Removal of Palladium from a Solution of Palladium Chloride.—A measured amount of palladium chloride solution was heated to boiling and treated with a hot saturated solution of 6-nitroquinoline. After stirring, the mixture was allowed to boil for about five minutes. More of the reagent was then added until no further precipitation was observed. After standing for fifteen to twenty minutes, the thick, flocculent yellow precipitate was filtered. (A small portion of the filtrate was treated with

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[6] To prevent any platinum from being precipitated.

more reagent to assure the complete precipitation of the palladium.) The precipitate was washed with distilled water until free from chlorides (as ascertained by the silver nitrate test), dried, ignited carefully in air, then heated for thirty minutes at a red heat in a stream of hydrogen, cooled[7] and the metallic palladium weighed. The results were as follows:

Weight of boat plus metal, g.	8.0769	5.9559	6.8619
Weight of boat, g.	8.0531	5.9322	6.8524
Weight of metallic Pd, g.	0.0238	0.0237	0.0095
Amount of $PdCl_2$ solution used, cc.	5.0	5.0	2.0
Weight of metal per cc., g.	0.00476	0.00474	0.00475
Weight of metal per cc. (theoretical)	0.00478	0.00478	0.00478

These results show conclusively the accuracy which is attained by the use of 6-nitroquinoline as a reagent for the removal of palladium from solutions of its salts in which there is present only a small amount of the metal.

The Removal of Palladium from a Solution of All the Platinum Metals.—Solution number 1 below was made to contain 95% by weight of palladium and 1% of each of the other platinum metals, that is, ruthenium, rhodium, osmium, iridium and platinum. The solutions of each of these used were those of the chlorides of the metals which were prepared in this Laboratory directly from the pure metal, except in the case of the osmium, which was prepared from pure crystalline OsO_4. Solution number 2 below was made to contain equal quantities of each of the six metals. The procedure of analysis was followed as shown above. The results obtained were as follows:

	Solution No. 1		Solution No. 2	
Weight of boat and metal, g.	3.2686	3.1350	3.6574	3.3210
Weight of boat, g.	3.2476	3.1262	3.6359	3.3123
Weight of metallic Pd, g.	0.0210	0.0088	0.0215	0.0087
Amount of $PdCl_2$ solution used, cc.	5.0	2.0	5.0	2.0
Weight of metal per cc. (recovered), g.	0.00420	0.00440	0.0043	0.00435
Weight of metal per cc. (theoretical), g.	0.00478	0.00478	0.00478	0.00478

These determinations, while showing a slight influence of the other metals of the platinum group on the removal of palladium from such a mixture by means of 6-nitroquinoline, are sufficiently close to indicate its usefulness as a quantitative procedure. With larger quantities of metals present it could, in all probability, be made more accurate.

The Separation of Palladium from Platinum.—As platinum is the most common metal of this group which is prevalent with palladium both in nature and in commerce, it would seem important to know whether large amounts of this particular metal would influence this separation. Also, it is with platinum, especially, that most of the organic coordinated salts are formed.

[7] Cooling the spongy metal in carbon dioxide is preferable to cooling in hydrogen.

Solution number 1 below was made to contain 20% of palladium and 80% of platinum, while solution number 2 was made to contain 80% of palladium and 20% of platinum. Following the above procedure, the results were

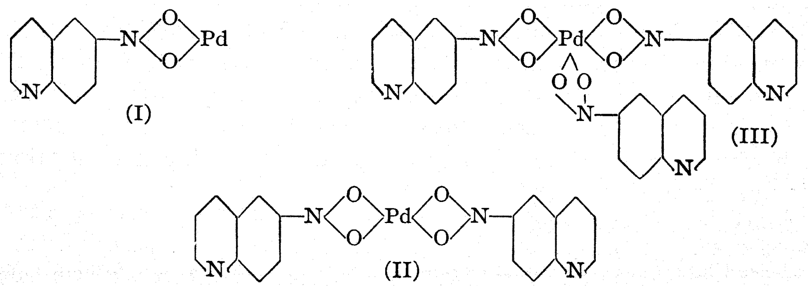
	Solution No. 1		Solution No. 2	
Weight of boat and metal, g.	**3.1352**	**3.2534**	**3.3326**	**3.5449**
Weight of boat, g.	**3.1260**	**3.2487**	**3.3096**	**3.5359**
Weight of metallic Pd, g.	**0.0092**	**0.0047**	**0.0230**	**0.0090**
Amount of $PdCl_2$ solution used, cc.	**2.0**	**1.0**	**5.0**	**2.0**
Weight of metal per cc. (recovered), g.	**0.0046**	**0.0047**	**0.0046**	**0.0045**
Weight of metal per cc. (theoretical), g.	**0.00478**	**0.00478**	**0.00478**	**0.00478**

These determinations show that platinum does not interfere with the quantitative removal of palladium by this reagent.

The Determination of the Empirical Formula **of the** Palladium Compound.—With such organic substances, palladium forms either an additive (double) salt or a coordinated (inner) one. If the precipitated compound formed in the above determinations should contain chlorine, it would indicate an additive compound. If no chlorine were found, the indications would point strongly toward a coordinated one.

Sufficient fuming nitric acid was added to a small quantity of the compound, *which had been washed free from chlorides* from the precipitating mixture, to insure its solution.[8] Excess nitrogen oxide was removed by boiling. When the solution had attained a clear straw yellow color, it was diluted and a portion taken and treated with silver nitrate. No trace of silver chloride precipitate was observed. This process was repeated on several samples of the compound with the same result.

Three possible structural formulas were then considered. These represented the palladium with coordination numbers of two, four and six, and were as follows: $Pd \cdot C_9H_6NNO_2$ (1), $Pd \cdot (C_9H_6NNO_2)_2$ (2) and $Pd \cdot (C_9H_6NNO_2)_3$ (3).



(I)

(III)

(II)

The molecular weights of these compounds are as follows: (1) 280.813, (2) 454.926 and (3) 629.039. Their percentage composition with respect to palladium, carbon and hydrogen is

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[8] **Concentrated hydrochloric acid has no effect on the compound.**

	(1)	(2)	(3)
Palladium, %	37.99	23.45	16.96
Carbon, %	38.47	47.50	51.53
Hydrogen, %	2.16	2.66	2.88

An analysis of the yellow compound was then made which included determinations for palladium, carbon and hydrogen.

The palladium content was obtained by the reduction of the compound at red heat in a stream of hydrogen, after it had been previously washed, dried and ignited carefully in air. After cooling the spongy metal was weighed.

The carbon and hydrogen were determined by the usual combustion method,[9] in which the complete oxidation of the organic compound was attained with the formation of carbon dioxide and water, which were collected separately and weighed.

Six such determinations were made. A typical pair of analyses gave

Palladium, %	23.45	23.42
Carbon, %	43.79	44.33
Hydrogen, %	2.58	2.62

By comparing these results with the percentage composition of the three compounds immediately above, it is readily seen that number two, representing the formula $Pd(C_9H_6NNO_2)_2$ is identified.

The gravimetric factor for palladium in this compound is 0.2345. Instead of reducing the precipitate in a stream of hydrogen, it may be more conveniently washed free from chlorides, dried and the percentage of the metal calculated by the use of this factor.

Summary

A new quantitative method for the determination of palladium is given. The metal is removed from a chloride solution by means of a saturated solution of 6-nitroquinoline. The composition of the compound formed is $Pd(C_9H_6NNO_2)_2$, a coordinated salt in which palladium exhibits a coordination number of four. By use of the gravimetric factor, 0.2345, the percentage content of palladium may be had by direct weighing of the precipitate. The reagent does not react with the other metals of the platinum group, hence it may be used in effecting a separation of palladium from these metals.

LEWISBURG, PENNSYLVANIA

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

[CONTRIBUTION FROM THE DEPARTMENT OR CHEMISTRY, UNIVERSITY OR CALIFORNIA]

SOLUBILITY. XI. SOLUBILITIES OF LIQUID STANNIC IODIDE IN SEVERAL LIQUID PARAFFINS

BY MIRIAM E. DICE AND J. H. HILDEBRAND

RECEIVED JULY 23, 1928 PUBLISHED NOVEMBER 6, 1928

Stannic iodide has been shown by Dorfman and Hildebrand[1] to have a sufficiently high internal pressure to cause incomplete miscibility in the liquid state with paraffin hydrocarbons. Since cases of incomplete miscibility are not numerous among non-metallic liquids of low polarity, and accurate data concerning such systems are lacking, a study of this sort seemed very desirable. We wished, first, to determine the way in which internal pressure varies among the paraffin homologs; second, to study the relation between the solubility of stannic iodide in the liquid and in the solid state in the light of methods recently proposed by the senior author[2] for dealing with deviations from the ideal solution laws.

Purification of Materials

Chemically pure stannic iodide was distilled twice under reduced pressure and then crystallized several times from hot carbon tetrachloride. As a further check, another sample of stannic iodide was prepared according to the method of McDermott.[3] A solution of c. p. resublimed iodine in pure carbon tetrachloride and an excess of c. p. tin were heated together. The stannic iodide solution resulting was decanted through a folded filter and crystallized three times from hot carbon tetrachloride. After each crystallization, the crystals were rinsed free from mother liquor on a small-holed Biichner funnel without filter paper. The crystals were finally dried by heating them under reduced pressure to a temperature slightly above their melting point.

The melting point of each preparation was found to be 143.6°, which agrees well with the value of 14'3.5" found in the "International Critical Tables." The purity was further checked by analysis. The stannic iodide was converted into hydrated stannic oxide by hydrolysis with ammonium hydroxide in the presence of ammonium sulfate. After standing overnight, the solution was neutralized with dilute nitric acid, methyl orange being used as an indicator, and was filtered through a Gooch crucible which had previously been ignited to constant weight. The crucible was then placed on a nichrome triangle in a large nickel crucible and heated to a red heat to drive off the water of hydration. The ratios of stannic iodide to stannic oxide were found to be for preparation I, 4.156, 4.161; and for preparation II, 4.155, 4.149, 4.158. The averages are 4.159 and 4.154, agreeing well with the theoretical value of 4.157.

The tin used in the above preparation was obtained as analyzed sticks containing, as impurity, a very small percentage of lead. This tin was further purified by electrolysis, using the tin sticks as electrodes and a slightly acid solution of stannic chloride as the electrolyte. The current density used was such that the tin was deposited at the cathode in the form of long crystals, the lead remaining at the anode.

Ammonium hydroxide was prepared by passing ammonia gas into distilled water. Carbon tetrachloride was purified by shaking it with sodium hydroxide to remove all

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

[2] Hildebrand, *Proc. Nat. Acad. Sci.*, 13,267 (1927).

[3] McDermott, THIS JOURNAL, 33, 1963 (1911).

acidic constituents and then by distilling it from phosphorus pentoxide. The normal hexane used was from Kahlbaum, prepared from propyl iodide; the octane, from the same source, had been prepared from normal butyl iodide from butyl alcohol. The *iso*-octane, 2,2,4-trimethylpentane, was obtained from the Ethyl Gasoline Corporation. The preparation and properties of this substance were described by Edgar.[4] Dr. Lachman, of this Laboratory, had tested our sample for the presence of butyl alcohol and unsaturated bodies, finding them practically absent. The constancy of boiling point also showed the liquid to be sufficiently pure for all ordinary purposes. The heptane was from a supply of high purity prepared for a previous investigation in this Laboratory.[5] All of the liquids used were distilled using a fractionating column and the middle fractions only were taken. All gave boiling points in close agreement with the values in the "International Critical Tables."

Experimental Procedure

Pyrex glass tubes were closed at one end, drawn out into a capillary for subsequent sealing and opened into a funnel at the other end. A tube was weighed, an appropriate amount of stannic iodide was placed in the funnel, melted into the closed end of the tube and weighed. The liquid paraffin was then added so as nearly to fill the tube below the constriction; the tube was then cooled in liquid air, sealed off and the sealed tube weighed along with the rejected portion. From these weights the mole fractions of stannic iodide given in Table I were calculated.

These tubes were rocked back and forth in an oil-bath in an electric oven

TABLE I

SOLUTION TEMPERATURES OF STANNIC IODIDE

SnI_4, mole fraction	Temp., °C.	SnI_4, mole fraction	Temp., °C.	SnI_4, mole fraction	Temp., °C.
n-Octane		0.4573	136.7	0.3225	146.4
		.4745	136.3	.3714	148.8
0.3602	127.3	.4776	136.9	.4526	148.7
.3824	129.4	.4861	136.7	.5344	145.4
.4454	131.1	.5142	136.4	.5916	138.2
.4541	131.2	.5209	136.3		
.5418	132.3	.5606	135.4	iso-Octane	
.5832	131.5	.5700	135.9		
.6297	130.2	.5847	134.8	.3029	183.4
.6430	129.4	.5945	134.7	.3146	185.4
		.6105	131.5	.3692	191.6
n-Heptane		.6240	132.0	.4592	194.9
		.6548	128.9	.4758	194.9
.2836	127.6	.6818	127.2	.5193	195.4
.3220	130.9			.5380	194.9
.3434	131.6	n-Hexane		.5920	193.6
.3595	134.1			.6253	188.1
.3720	134.8	.2531	138.1	.6256	191.6
.4340	136.4	.2887	143.4	.6604	187.5
				.6922	181.5

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[4] Edgar, Ind. *Eng. Chem.*, 19, 145 (1927).

[5] Westwater, Frantz and Hildebrand, Phys. *Rev.*, 31, 135 (1928).

equipped with small glass windows and illuminated from the rear. The rate of heating and cooling was regulated by varying the resistance in the circuit. A sufficiently slow rate was maintained so that the mean of the readings taken at the point where the two liquid phases disappeared and of those taken where they appeared agreed, in every case, within 0.2°. At least six observations were made upon each tube, the averages being recorded in Table I. These observations seldom differed from one another by more than 0.4°.

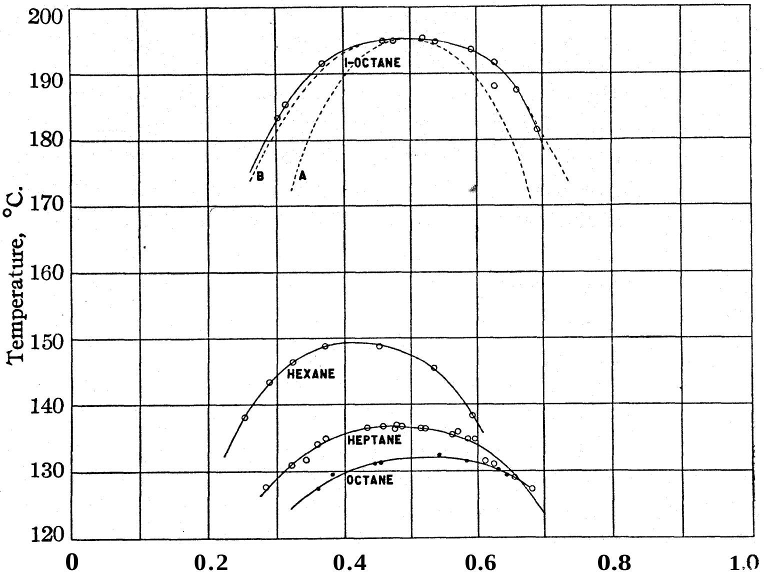

Fig. 1.—Mole fraction of stannic iodide.

From these values mole fraction–temperature curves were plotted, as shown in Fig. 1. It was impossible to determine the shape of the curves at much lower temperatures than those given, due to the crystallization of the stannic iodide. The maxima give the critical mixing temperatures recorded in Table II.

TABLE II

CRITICAL SOLUTION TEMPERATURES OF STANNIC IODIDE

Second liquid	*i*-Octane[a]	n-Hexane	n-Heptane	*n*-Octane
SnI_4, mole frac.	0.50	0.42	0.48	0.52
Crit. temp., °C.	195.3	149.4	136.8	132.0

[a] 2,2,4-Trimethylpentane.

Discussion

We may note, first, that the order of critical temperatures is in rather good agreement with such data as we have regarding internal pressures. For estimating the latter, we have only the boiling points, t_b, using a relation previously given by the senior author[a] $(5200 + 30t_b)/v$, where v is the molal volume of the liquid at 20°. For the liquids here employed, we have the data in Table III.

TABLE III

RELATIVE INTERNAL PRESSURES

	Density at 20°	Molal vol.	B. p., °C.	$(5200 + t_b)/v$	t_c
i-Octane	0.690	165.5	99.3	49.4	195.3
n-Hexane	0.660	130.5	69.0	55.7	149.4
n-Heptane	0.683	146.5	98.4	55.6	136.8
n-Octane	0.701	162.8	124.6	59.4	132.0
Stannic iodide	4.16	150.7	340	102	...

The figures in the next to the last column for relative internal pressures agree with the order of critical solution temperatures repeated in the last column except for the minor difference between hexane and heptane. In view of the lack of accurate figures for the heats of vaporization, it is believed that the critical temperatures best represent the true order of the internal pressures. We may note, further, that heptane does not quite fall midway between hexane and octane, although the difference is so small that it may not be significant. It is especially striking that the iso-octane has an internal pressure much lower than n-octane. The generally lower boiling points of iso-paraffins indicate that their internal pressures will probably be found lower than those of the corresponding normal paraffins. These trends in internal pressure may be expected to determine rather accurately the general solubility relations of the paraffins.

In a paper by the senior author now in preparation, there is set forth a method for calculating mutual solubility curves for non-polar liquids. As a first approximation, the equation

$$\log \frac{1 - N_1'}{N_1'} = \frac{k}{T}(1 - 2N_1') \qquad (1)$$

has been derived, where N_1' is the mole fraction of component 1 in one phase, T the absolute temperature and k a constant depending, in part, upon the difference in internal pressure of the two components. The mole fraction of component 2 in this phase is $1 - N_1'$, while in the second phase the two mole fractions are interchanged. This equation applies to symmetrical systems only, that is, to those whose critical composition is 0.5. When the critical composition is not 0.5, an additional constant must be used and two simultaneous equations are obtained whose solution is mathematically very laborious. Consequently, we will illustrate the treatment by using the curve for iso-octane, which is practically symmetrical. The dotted curve in Fig. 1, marked A, represents Equation 1, using $k = 407$. In solving this equation arbitrary values are assigned to N_1', and the equation is solved for T, since the reverse procedure would

[6] Hildebrand, "Solubility," Chemical Catalog Company, New York, 1924, p. 108.

require a method of successive approximations. It is seen that Curve A is too steep; however, the equation is of such a nature that slight changes in k greatly affect the spread in N, and it is known from other systems as well as from theoretical considerations that k is likely to diminish with increasing temperature.

A determination of the solubility of solid stannic iodide in this *iso*-octane, to be presented in the paper now in preparation, has given a value of k of 503 at 25°. If we represent the variation of k with temperature by the equation $k = 671 - 0.565\ T$, we get the dotted curve, B, Fig. 1, which agrees excellently with the experimental points, although this makes k vary only 2% in 15°.

In the case of heptane, we have not carried through the troublesome calculations, since the curve is unsymmetrical, but it is evident from a few figures that the rate of change of k necessary to give the value obtained from the solubility of stannic iodide, 130° lower, also gives the proper spread to the liquid solubility curve.

Summary

1. Critical solution temperatures of stannic iodide have been obtained with liquid paraffins as follows: n-octane, 132.0°; n-heptane, 136.8'; n-hexane, 149.4'; i-octane (2,2,4-trimethylpentane), 195.3°.

2. The mole fractions of stannic iodide at the critical solution temperatures are, respectively, 0.52, 0.48, 0.42 and 0.50.

3. The internal pressures increase for the normal hydrocarbons in the order of increasing molecular weight.

4. The normal octane has a higher internal pressure than the *iso*-octane used; this difference between a normal and an iso-paraffin is probably general.

5. The form of the liquid–liquid solubility curve has been calculated.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE PHYSICO-CHEMICAL LABORATORY OF THE POLYTECHNIC INSTITUTE OF COPENHAGEN]

THE DETERMINATION OF REACTION AFFINITY IN SYSTEMS OF SOLID SALTS

BY J. N. BRÖNSTED AND W. T. RICHARDS

RECEIVED AUGUST 2, 1928 PUBLISHED NOVEMBER 6, 1928

1. A Thermodynamic Relation for Partially Saturated Solutions[1]

If $\pi_0, \pi_1, \ldots\ldots$ indicate the chemical potentials of the components K_0, $K_1, \ldots\ldots$, and $n_0, n_1, \ldots\ldots$ indicate the number of gram molecules of each in a homogeneous solution, the Gibbs equation for this solution reads

$$n\,d\pi_0 + n_1 d\pi_1 + \ldots\ldots = 0 \qquad (1)$$

If the potentials $\pi_2, \pi_3, \ldots\ldots$ are held constant, $d\pi_2 = d\pi_3 = \ldots = 0$, and consequently Equation 1 becomes merely

$$n\,d\pi_0 + n_1 d\pi_1 = 0 \qquad (2)$$

Equation 2 is applicable to homogeneous mixtures of $K_0, K_1 \ldots$ when saturated with the pure solid components $K_2, K_3, \ldots$ It has often been applied to simple binary mixtures. According to the above, however, it retains its validity when the binary mixture is saturated with an arbitrary number of solid substances while the concentration n_1/n_0 varies.

In order to define n_0 and n_1 in a solution saturated with other substances $K_2, K_3 \ldots$ it is necessary to remove the latter from the solution so far as is stoichiometrically possible. The solution will then consist stoichiometrically of K_0 and K_1 only. This is also true if one or several of the saturating substances are molecular compounds of K_0 or K_1.

By means of Equation 2 it is possible to calculate, from vapor pressure measurements of the solvent, the free energy change of reaction of solid salts. The principle of this method is described in section 2.

2. The Principle of the Affinity Measurement

Where the reaction, in the solid state, is the formation of a double salt from its components as A + B ⟶ AB, the affinity of the process equals the chemical potential of A in the solid system A + AB minus the potential of A in the solid system B + AB. Representing these systems by (1) and (2), respectively, the affinity may, therefore, be expressed, $\pi = \pi_{A\,(1)} - \pi_{A\,(2)}$, or $\pi = \pi_{B\,(2)} - \pi_{B\,(1)}$. With water present as a solvent, when the amount of A in the solution is gradually changed from saturated solution (1) to saturated solution (2) while equilibrium with the solid AB is maintained, we have, $\pi = -\int_1^2 d\pi_A$, where $d\pi_A$ indicates the increase in chemical potential for A in the solution corresponding to a small increase in n_A. Introducing equation (2), we obtain

$$\pi = \int_1^2 \frac{n_0}{n_A}\,d\pi_0 \qquad (3)$$

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[1] J. N. Bronsted, *Kgl. Dansk. Vid. Selsk. Medd.*, *1*, *Nr.* **5** (1918).

where n_0 refers to the solvent. In order to integrate this expression, π_0 must therefore be known as a function of n_0/n_A from (1) to (2). Or, since $\pi_0 = RT\ln p_0$, we must know the vapor pressure of the solution over this interval. It is of value to note in the construction of this vapor pressure curve that, contrary to the case of simple binary mixtures, $d\pi_A/dn_A$ is finite for $n_A = 0$, owing to the existence of A in solutions containing only AB in a stoichiometrically pure state.

If the reaction considered is one between four solid salts, A + B $\longrightarrow$ C + D, the affinity is measured by a method which is entirely similar, the stable salt pair C + D fulfilling the function of the double salt in the example considered above, and (1) and (2) therefore corresponding to the two triads A + C + D and B + C + D, respectively. The affinity is therefore obtained by integration of Equation (3) between these two limits on the basis of vapor pressure measurements in a solution saturated with C + D, the amount of A or B varying from one triad solution to the other.

To test this relation experimentally, a distinction must be made between two possible cases, which may be called the congruent and the incongruent, respectively.[2] When a saturated solution of A + AB and B + AB may be made by means of positive amounts of these respective salts, the solution is congruent. If, however, the solution saturated with B + AB can be made by positive quantities of A and AB, the solution is incongruent, and a saturated pure double salt solution will be unstable.

The latter case, which is the simplest experimentally, is illustrated by Fig. 1, n, the number of moles of A per mole of water, being taken as abscissas and p, the vapor pressure of the saturated solution, being ordinates. The point AB on this diagram corresponds to a solution saturated with double salt and points AB + B and AB + A to saturation with each of the indicated solid systems. Starting with the solution saturated with AB + B and evaporating off water, p will remain constant as long as two solid phases are present, but will finally begin to fall when all solid B has been converted into solid AB. On further evaporation of water the pressure will fall until AB + A is reached, when solid A will separate and p will again become constant. When the original amounts of AB, B and water are known, and the amount of water evaporated has been determined, a curve for vapor pressure as a function of concentration between AB + B and AB + A may be constructed of the type necessary for the calculations outlined above.

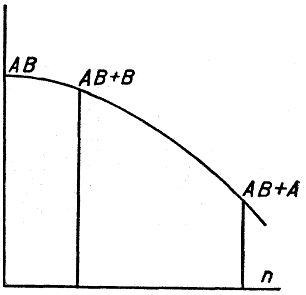

Fig. 1.

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[2] Meyerhoffer, *Sitz. Aknd. Wiss. Wien*, *104*, IIb (1895); Neyerhoffer and Saunders, *Z. physik. Chem.*, 28, 471 (1899).

In the congruent case, which has been treated experimentally in this communication, much the same reasoning applies. Here, however, the evaporation of water from a single solution containing AB + B will be insufficient to give the desired solution saturated with AB + A. From Fig. 2 it may be seen that a determination of the concentration–vapor pressure function involves, in this case, the evaporation of water from two separate solutions saturated with AB which contain small amounts of A and B, respectively. Here p will fall increasingly with increasing concentration of A or B until the two points A + AB and B + AB are reached, where constancy of p will in each case be attained. A knowledge of the amount of water, double salt and single salt present, and of the vapor pressure of each of the two solutions is therefore necessary in order that the affinity may be computed for the double salt.

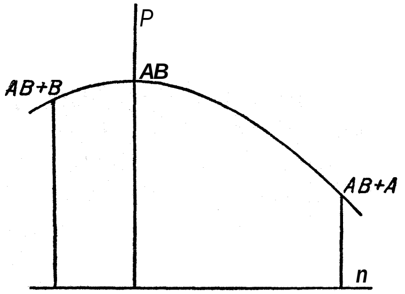

Fig. 2.

3. Apparatus and Procedure

The apparatus used is illustrated in Fig. 3. It consisted, in essence, of two flasks A and B, a condensing bulb M, and a manometer H, these being connected by a system of stopcocks which enabled each part of the apparatus to be evacuated separately. A Gaede pump, the connection for which only is shown in the drawing, was used for evacuation. The flasks, mounted together on a strong support which gave them a motor-driven horizontal agitation of about 3 cm., were connected to the bulb M and the mano-

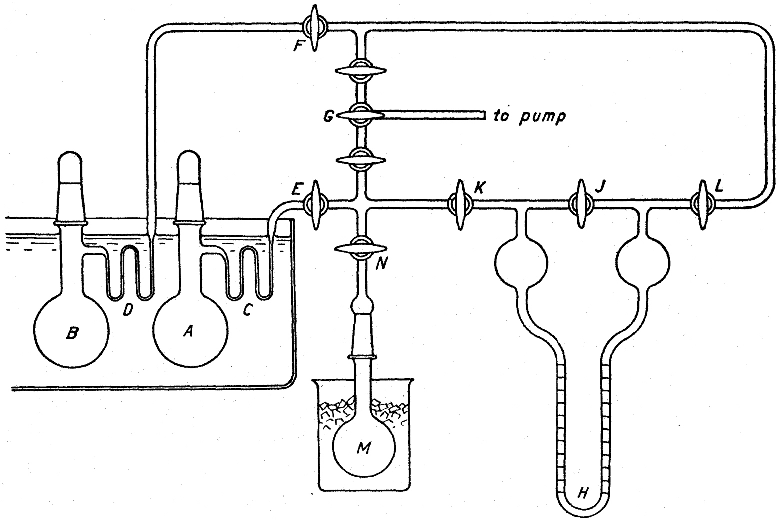

Fig. 3.

meter system by the long, thin-walled glass tubes, or springs, C and D, sufficiently elastic to permit the agitation. They were immersed to their necks in a thermostat giving a temperature of 19.93 ± 0.01°. The rest of the apparatus was at room temperature, care being taken to prevent the condensation of water vapor on the walls of the tubes. Flask **A** contained the solution the vapor pressure change of which with changing concentration was under observation. Flask B contained a saturated reference solution of constant vapor pressure. The saturating component used in all experiments in this communication was ammonium chloride. The spring C and the stopcock E were made of as large a bore as possible to permit the ready passage of water into the condensing bulb M.

In operating the apparatus the oil in the manometer, β-bromonaphthalene, was first carefully freed from air by warming and prolonged evacuation. The flasks were then appropriately filled and freed from air by prolonged evacuation and agitation. The remainder of the system was then evacuated with the stopcocks E and F closed. After about five minutes the solutions had come to temperature equilibrium after evacuation, and the stopcocks in the bridge G were closed and, with K, J and I, open, E and F were opened. J was then closed and the difference of level in the manometer H read with a lens and recorded when it had become constant. The process of evacuation and measurement was repeated to constancy of the vapor pressure difference between the two solutions, when air had adequately been removed from the system. With K closed, about 2 cc. of water was then transferred from **A** into the ice-cooled bulb M by distillation. N was then closed and M weighed to determine the quantity of water transferred, after which M was dried and reattached to the apparatus. With E and K closed M was again evacuated, and the pressure difference between the two solutions again determined. Thus, by successive small increments, the concentration of the single salt in the saturated double salt solution was made to approach saturation. Finally a point was reached where the solid single salt separated from the solution and further evaporation of water caused no further decrease in vapor pressure. When this point was clearly established the experiment was discontinued and the contents of the flask A were analyzed by one of several methods given hereinafter in order to find the amount of water present at the start. If the solution became inconveniently thick, the experiment was discontinued before the double point had been reached and more water and weighed single salt were added. The process of measurement and concentration was then repeated. From the data so obtained was calculated the vapor pressure of the solution as a function of its concentration.

A few precautions deserve brief note. Obviously, for instance, the apparatus must not be evacuated during the progress of a determination since this would entail an indeterminate loss of water. Again, after the removal of water by condensation there was, in the presence of much solid salt, a lag in the attainment of equilibrium which often necessitated a wait of two hours. Finally, the stopcocks K and L were kept closed when the apparatus was not in use to prevent the solution of water in the oil of the manometer H.

4. Measurements

Preliminary experimentation having demonstrated that carnallite was unsuitable for the purposes of measurement, the double salt $CuCl_2 \cdot 2NH_4Cl \cdot 2H_2O$ was finally selected as having convenient properties. Measurements were made with and without NaCl as an additional saturating component of constant potential. The following reference points were then determined.

The saturated ammonium chloride solution used throughout in the reference flask B had a vapor pressure, at 19.93°, of 12.32 cm. of oil or 13.65 mm. of mercury. The last of these two figures is based on a pycnometric determination of the density of β-bromonaphthalene, which showed it to be 0.1108 that of mercury at room temperature.

The vapor pressures of the saturated points of the systems under investigation were found to be:'

Saturating salts	p, mm. of Hg
$CuCl_2 \cdot 2H_2O + CuCl_2 \cdot 2NH_4Cl \cdot 2H_2O$	11.80
$NH_4Cl + CuCl_2 \cdot 2NH_4Cl \cdot 2H_2O$	13.63
$CuCl_2 \cdot 2H_2O + CuCl_2 \cdot 2NH_4Cl \cdot 2H_2O + NaCl$	10.80
$NH_4Cl + CuCl_2 \cdot 2NH_4Cl \cdot 2H_2O + NaCl$	12.11
$CuCl_2 \cdot 2NH_4Cl \cdot 2H_2O$	14.75
$CuCl_2 \cdot 2NH_4Cl \cdot 2H_2O + NaCl$	12.73

These points serve as the integration limits for the equation developed above. The concentrations of the salts at the various points were determined analytically, as described below.

The purity of the salts prepared commercially for analytical purposes was found sufficient for the experiments. Proof of this is, of course, the constancy of the double-point vapor pressures on the evaporation of successive increments of water. That the double salt (which was prepared from its single constituents recrystallized together from solution in stoichiometric proportions), the ammonium chloride and the copper chloride contained, in the solid state, no more than their theoretical amount of crystal water was demonstrated by gravimetric analysis to 0.1%.

The four sets of measurements, which are summarized below, were then made. Actual readings of vapor pressure and concentration have been omitted in the interests of space conservation, the figures in the several tables having been obtained from curves constructed in each case from separate concordant series of observations. The initial amounts of double and single salts, which were always weighed before their introduction, and the different methods of obtaining the initial water content are recorded in each case to give a complete picture of the measurements.

In the tables **Ap** signifies the difference in vapor pressure, in cm. of oil, between the solution under observation and the saturated ammonium chloride reference solution, gH_2O indicates the number of grams of water present in the solution at each reading, p indicates the vapor pressure of the solution in mm. of mercury, $\log_{10} p$ the logarithm of this quantity, **and** n_1/n_0 the ratio of moles of single salt to moles of solvent at each vapor pressure.

Determination I.—Copper chloride, 4.826 g.; double salt, 9.63 g.

The amount of water present at the double point was found to be 9.77 g. by adding a weighed quantity of water to the salt–water mixture after the conclusion of the determination, and analyzing the resulting solution for ammonium content by distillation and for chlorine content by a standard silver nitrate solution.

TABLE I

RESULTS OF DETERMINATION I

Δp	H_2O, g.	p	$\log_{10} p$	m_1/m_0
−1.67	2.64	11.80	1.0719	0.1931
1.45	2.97	12.04	1.0806	.1709
1.14	3.48	12.39	1.0930	.1464
0.87	3.98	12.69	1.1035	.1280
.63	4.48	12.95	1.1123	.1136
.32	5.23	13.30	1.1239	.0958
.11	5.98	13.53	1.1312	.0853
+ .12	6.98	13.78	1.1393	.0731
.41	8.48	14.10	1.1492	.0598
.55	9.48	14.26	1.1541	.0539
.74	11.98	14.47	1.1605	.0426
.81	14.48	14.55	1.1629	.0352
.85	16.98	14.59	1.1641	.0300
.87	19.48	14.61	1.1647	.0262
.88	21.98	14.63	1.1653	.0232
..	...	14.75	1.1688	0

Determination 11.—Ammonium chloride, 0.9153 *g.*; double salt, 9.96 g. The amount of water present at the double point was found to be 8.10 g. by saturating a solution with ammonium chloride and double salt and analyzing for ammonium and chlorine concentration as in Determination I. From these data the weight of water present when the double point is reached with 0.9153 g. of ammonium chloride was calculated. In this determination, therefore, the weight of double salt present during the vapor pressure measurements played no part since it was saturated throughout.

TABLE II

RESULTS OF DETERMINATION II

Δp	H_2O, g.	p	$\log_{10} p$	n_1/n_0
−0.02	8.10	13.63	1.1345	0.1193
+ .25	9.38	13.93	1.1439	.1029
.47	10.88	14.17	1.1514	.0888
.55	11.88	14.26	1.1541	.0814
.65	13.38	14.37	1.1575	.0722
.74	15.88	14.47	1.1605	.0610
.81	18.38	14.55	1.1629	.0526
.85	20.88	14.59	1.1641	.0463
.89	23.38	14.64	1.1656	.0415
.92	25.88	14.67	1.1664	.0374
.96	28.38	14.71	1.1676	.0341
..	...	14.75	1.1688	

Determination 111.—Sodium chloride, **18.13** g.; copper chloride, **11.147 g.;** double salt, **4.940** g.; **10.33** g. of water was present at the double point. In this case, owing to the large amount of sodium chloride present, chemical methods were out of the question and the flask **A (Fig. 3)** was cut from the apparatus at C and weighed when a determination was finished. It was then emptied, dried and reweighed. These data permit the calculation of the desired quantity.

TABLE III

RESULTS OF DETERMINATION III

Δp	H_2O, g.	p	$\log_{10} p$	n_1/n_0
−2.57	10.33	10.80	1.0334	0.1140
2.22	12.58	11.19	1.0488	.0937
1.93	15.08	11.51	1.0611	.0783
1.71	17.58	11.75	1.0700	.0612
1.54	20.08	11.94	1.0770	.0587
1.46	21.58	12.03	1.0803	.0546
1.42	22.58	12.08	1.0821	.0522
1.32	25.08	12.19	1.0860	.0469
1.26	27.58	12.25	1.0882	.0427
1.22	30.08	12.30	1.0899	.0392
1.18	32.58	12.34	1.0913	.0362
1.13	35.08	12.40	1.0934	.0336
1.09	37.58	12.44	1.0948	.0314
..	...	12.73	1.1048	...

Determination IV.—Sodium chloride, **19.40** g.; ammonium chloride, **1.5096** g.; double salt, **4.843** g. The amount of water present at the double point, **31.19** g., was ascertained exactly as in Determination III.

TABLE IV

RESULTS OF DETERMINATION IV

Δp	H_2O, g.	p	$\log_{10} p$	n_1/n_0
−1.39	6.50	12.11	1.0832	0.0782
1.25	8.23	12.26	1.0885	.0618
1.15	9.73	12.37	1.0923	.0523
1.08	10.73	12.45	1.0952	.0464
1.01	12.23	12.53	1.0980	.0416
0.93	14.73	12.62	1.1011	.0345
.89	17.23	12.66	1.1024	.0295
.88	19.73	12.67	1.1028	.0258
.87	22.23	12.68	1.1031	.0229
.87	24.73	12.68	1.1031	.0206
.87	27.23	12.68	1.1031	.0187
..	...	12.73	1.1048	

5. Computation of the Affinity of Formation

The results given in the tables of the preceding section permit the calculation of two values for the affinity of formation of the double salt $CuCl_2\cdot$-

$2NH_4Cl \cdot 2H_2O$, one in the presence of sodium chloride as a saturating component of constant activity, and the other in its absence. The necessary integration is most easily effected by throwing Equation (3) into the form

$$A = \frac{RT}{0.4343}\int_0^n \frac{d \log p}{n}$$

where n = (n_1/n_0). Then Determinations I and III may be integrated by the relationship

$$\log p_0 - \log p = \alpha n^2 + \beta n^3$$

and Determinations II and IV by the expression

$$\log p_0 - \log p = \alpha n^2$$

where α and β are constants for each determination and p_0 refers to the saturated double salt solution. The values for these constants are:

Detn. **no.**	I	II	III	IV
α	7.05	2.4	10.7	3.75
β	−22.5	...	−46.0	..

Integration yields the following results

Detn. **no.**	I	II	III	IV
A in cal.	**1960**	**767**	**2060**	**785**

The two concordant values for the affinity of formation follow directly

$$A_{(\text{abs. NaCl})} = 2A_{\text{ii}} + A_{\text{i}} = 3494 \text{ cal.}$$
$$A_{(\text{pres. NaCl})} = 2A_{\text{iii}} + A_{\text{iv}} = 3630 \text{ cal.}$$

The average value for the affinity of formation of one molecule of double salt from its solid components, that is, the change in free energy by the reaction

$$CuCl_2 \cdot 2H_2O_{\text{solid}} + 2NH_4Cl_{\text{solid}} \longrightarrow CuCl_2 \cdot 2NH_4Cl \cdot 2H_2O_{\text{solid}}$$

is **3560** cals.

Summary

1. **A** thermodynamic relationship for the dilution affinities of partially saturated solutions has been advanced.

2. The change in vapor pressure with changing concentration of single salt in the systems $CuCl_2 \cdot 2NH_4Cl \cdot 2H_2O + CuCl_2 \cdot 2H_2O$, $CuCl_2 \cdot 2NH_4Cl \cdot 2H_2O + NH_4Cl$, $CuCl_2 \cdot 2NH_4Cl \cdot 2H_2O + CuCl_2 \cdot 2H_2O + NaCl$, and $CuCl_2 \cdot 2NH_4Cl \cdot 2H_2O + NH_4Cl + NaCl$, saturated with double salt and NaCl, has been determined by means of a differential tensimeter of novel design.

3. The validity of the principle desired has been demonstrated within experimental error, a free energy of formation of **3560** cal. being found for the double salt in question.

COPENHAGEN, DENMARK

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF STANFORD UNIVERSITY AND OF THE UNIVERSITY OF CALIFORNIA]

THE VAPOR DENSITY OF FORMIC ACID

BY H. C. RAMSPERGER[1] AND C. W. PORTER

RECEIVED AUGUST 31, 1928 PUBLISHED NOVEMBER 6, 1928

Papers on the vapor density of formic acid have been published recently by Wrewsky and Glagoleva[2] and by Coolidge.[3] In a paper entitled "The Ultraviolet Absorption Spectrum of Formic Acid," published by Ramsperger and Porter in May, 1926,[4] the vapor densities of formic acid at temperatures between 25 and 80° were reported. Since, in the title of this paper, no reference was made to vapor density, it was overlooked by Coolidge who credits Bineau and Pettersson and Ekstrand with the only earlier work in this field.

The purpose of this communication is to make a graphical comparison of all the data on this subject. Equilibrium constants for the reaction $(HCOOH)_2 = 2HCOOH$ have been calculated from the data of Pettersson and Ekstrand,[5] of Wrewsky and Glagoleva,[2] of Coolidge,[3] and of Ramsperger and Porter.[4] The equilibrium constant is given by the expression $K = p_m^2/p_b$, where p_m is the pressure in atmospheres, due to the unimolecular form, and p_b is the pressure of the bimolecular form.

In Fig. 1 $R \ln K$ is plotted against $1/T$. The line drawn approximately through the experimental points of Wrewsky and Glagoleva is the graph of an equation given by Willard Gibbs[6] which he found would fit the experimental values of Bineau[7] fairly well, and it is seen that it also fits most of the data of Wrewsky and Glagoleva. The recent, very accurate determinations of Coolidge do not fit this equation at all. Constants have not been calculated for all of the large number of experiments of Coolidge. We have selected those having about the same pressures at low temperatures as were used in our own work. At the higher temperatures his lowest pressures experiments were chosen so as to minimize errors due to deviations from the gas laws. The straight line drawn through his points is also the best straight line through the points obtained by Ramsperger and Porter. The slope of this line corresponds to a heat of dissociation of 14,100 cal. per mole, which is identical with the average value published by Ramsperger and Porter. The equation of Gibbs gives a heat of dissociation of 17,400 cal. per mole, and Pettersson and Ekstrand's data give 16,000 cal. per mole.

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[1] National Research Fellow in Chemistry.

[2] Wrewsky and Glagoleva, *Z. physik. Chem.*, **133**, 370 (1928).

[3] Coolidge, THIS JOURNAL, **50**, 2166 (1928).

[4] Ramsperger and Porter, *ibid.*, **48**, 1267 (1926).

[5] Pettersson and Ekstrand, *Ber.*, **13**, 1194 (1880).

[6] Gibbs, *Am. J. Sci.*, **18**, 247 (1877).

[7] Bineau, *Ann. chim. phys.*, [3] **18**, 228 (1846).

Coolidge took very great precautions as to the purity of his formic acid. This is a matter of importance. In our early experimental work it was observed that considerably lower constants were obtained at low temperatures and at pressures approaching the saturation pressure than under other conditions. Adsorption on the glass walls could have been responsible for only a small part of this, since the addition of broken pieces of the same kind of glass gave only a small increase in density. An impurity such as a trace of stopcock grease greatly increased the apparent density. Our final results were obtained with a sample of Kahlbaum formic acid which was analytically pure. This was distilled in vacuum and was free from non-condensable gases. It was passed through glass wool which apparently helped to remove those impurities which favored incipient condensation on the walls. It seems very likely that traces of impurities were responsible for the lower constants of earlier investigators.

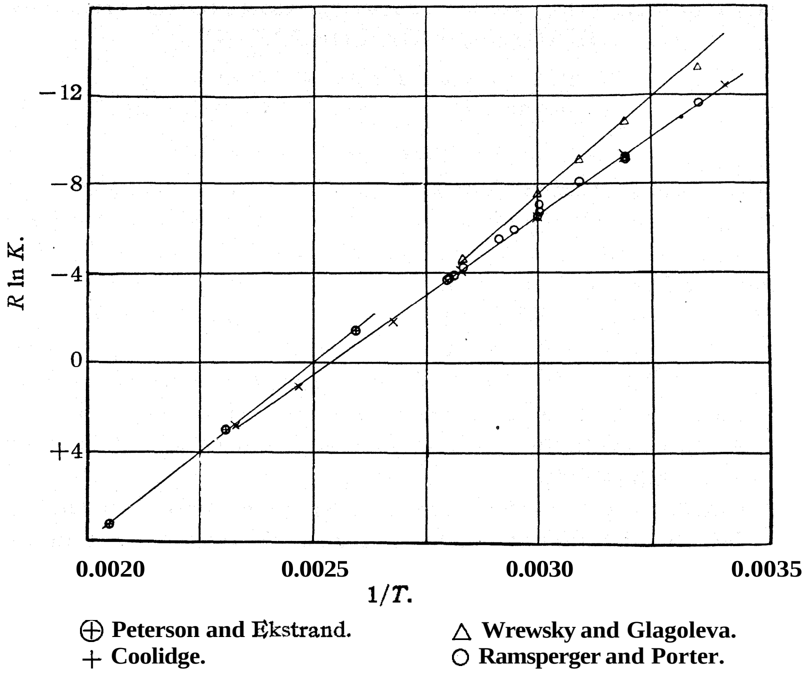

Fig. 1.

The experiments of Wrewsky and Glagoleva were made by a method in which the vapor density was determined by an analysis of air which had passed through liquid formic acid. The higher densities may have been due to small fog-like particles of liquid which were carried over with the vapor. Such particles are not easily eliminated.

Summary

A survey has been made of all existing data on the vapor density of formic acid. There is complete agreement between the measurements made by Coolidge and those of Ramsperger and Porter. Traces of impurities were probably responsible for the discordant results of the earlier investigators.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WASHINGTON UNIVERSITY]

SOME PROPERTIES AND TRANSFORMATIONS OF ORTHO-DICHLORO-4-NITROBENZENE[1,2]

BY L. MCMASTER AND A. C. MAGILL

RECEIVED JUNE 18, 1928 PUBLISHED NOVEMBER 6, 1928

Introduction

Beilstein and Kurbatow[3] found that 4-nitro-o-dichlorobenzene formed in two modifications when o-dichlorobenzene was treated with fuming nitric acid. They describe a semi-fluid mixture from which the solid part settles out and can be crystallized from alcohol in long needles of m. p. 43° and b. p. of 255–256°. Holleman[4] has studied the nitration of the dichlorobenzenes and found that when the ortho compound is dropped into nitric acid cooled to 0 or 30° the 1,2-dichloro-4-nitrobenzene is the principal product along with small amounts of isomers. His work on its physical constants agrees with thosd of Beilstein and Kurbatoff but he makes no mention of a liquid form.

In connection with some work to prepare o-chloro-p-nitraniline, we found that the nitration of o-dichlorobenzene always gave us a mixture of the liquid and solid forms of o-chloro-4-nitrobenzene. Since Beilstein and Kurbatoff give no information regarding any changes of the one form into the other and since the literature records no other nitro-o-dichlorobenzenes as liquids we decided to make a study of some of the properties and transformations of o-dichloro-4-nitrobenzene.

Experimental

Purification and Nitration of *o*-Dichlorobenzene.—The o-dichlorobenzene used in this work was prepared from the commercial material supplied us by the Monsanto Chemical Works. It was first distilled to remove any mono- and trichlorobenzene, the fraction between 165 and 200° being retained. One liter of this fraction was then cooled to −15° so that any of the para compound present would crystallize out and could be

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[1] In memory of Ira Remsen.

[2] Presented before the Organic Chemistry Division of the American Chemical Society at the St. Louis Meeting, April, 1928.

[3] Beilstein and Kurbatow, *Ann.*, 176, 41 (1875).

[4] Holleman, Rec. trav. *chim.*, 23, 357 (1904).

filtered off. The filtrate was distilled, the fraction boiling between 174 and 180" being collected and cooled to −15°. This procedure was repeated and the fraction boiling between 177 and 180° was found to be free from the para isomer[6] by sulfonating a portion of the liquid with fuming sulfuric acid and pouring the mixture into water. By this process the ortho only is sulfonated. Any *p*-dichlorobenzene present would be unchanged and separate out in the water. If the aqueous solution of the o-dichlorobenzenesulfonic acid is then steam distilled, the o-dichlorobenzene will pass over. After drying and distilling, it was water white and had a sp. gr. of 1 299 at 20°.

In order to purify the material further it was nitrated and distilled with steam. p-Dichlorobenzene does not readily nitrate and, if present, can be blown out with steam. The nitro compound was then reduced with tin and hydrochloric acid. The reduced product was not removed from the mixture but was diazotized at once and boiled with water and an excess of caustic soda. The o-dichlorobenzene separated out, was drawn off, dried and distilled. In order to replace the diazo group by hydrogen we found that alcohol and other reducing agents were not necessary. The crystallizing point of the compound was found to be −17.5". The "International Critical Tables" give it as −17.6°, whereas the Monsanto Chemical Works[6] have recently found it to be −16.7" on a sample prepared by a different method than just described.

One hundred and twenty-five cc. of the pure o-dichiorobenzene was nitrated, using 200 cc. of sulfuric acid of sp. gr. 1.84 and 175 cc. of nitric acid of sp. gr. 1.42. Nitration at 60° was easily effected in two hours with stirring. The nitro compound was separated, washed a number of times with water, dried over calcium chloride and distilled, the fraction between 254 and 257° being collected; yield, 95% of the theoretical. Nitration of 125 cc. of the o-dichlorobenzene was also accomplished in two hours at 60° by using 370 cc. of commercial mixed acid containing 57.3% of sulfuric acid and 33% of nitric acid; yield, 94% of the theoretical. A mixture of the liquid and solid forms was obtained.

Some Properties of **o-Dichloro-4-Nitrobenzene.**—The solid portion obtained above, when crystallized from alcohol or carbon tetrachloride, melts at 43°. When o-dichloro-4-nitrobenzene is kept at 15° the liquid form changes entirely to the solid form as long yellow needles of m. p. 43°. This would seem to indicate that no other isomer is present in the liquid form. We recognized the fact that a small amount of the *o*-dichloro-3-nitrobenzene (m. p. 62°) might be present. If, however, the material is kept at 25°, all of it changes to the liquid modification mentioned by Beilstein, the solid phase disappearing. Twenty g. portions of the material were kept for periods of eight hours each at various temperatures between 15 and 25". It was found that an appreciable amount of the liquid was present at 17°. At 22° the material appeared to be half liquid and half solid. At 24" a very small quantity of the solid remained. The portion at 22° was rapidly filtered and the solid weighed. The crystals obtained weighed 10.1 g. Apparently the solid and liquid are present in equal quantities at this temperature. When the crystals were allowed to stand at 22° they gradually changed until about 50% of liquid was present. When the liquid was allowed to stand at this same temperature about 50%

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[5] The b. p. of the o-compound is 179–180° and that of the para 172°.

[6] Carswell, *Ind.* Eng. *Chem.*, 20, 728 (1928).

of crystals formed. Of course the solubility of the solid form in the liquid is to be considered, but a number of experiments gave the same results. When the solid material was crystallized from alcohol or carbon tetrachloride, the crystals obtained did not change to the liquid modification. If some of the other o-dichloronitrobenzenes were liquids, it is quite possible that the liquid form of the 4-nitro compound would be a mixture of the solid form and the liquid dichloronitrobenzene, but such is not the case.

Action of Alcoholic Potash on o-Dichloro-4-Nitrobenzene.—There is no mention in the literature of the action of alcoholic potash on *o*-dichloro-4-nitrobenzene. Twenty g. of the liquid-solid mixture was refluxed with 40 g. of potassium hydroxide in 200 cc. of ethyl alcohol. When the reaction mixture reached 80°, a vigorous reaction set in and within five minutes was complete. The solution turned red and a dark red solid precipitated out. The solid, which proved to be 3,3′,4,4′-tetrachloro-azoxybenzene, was filtered off and recrystallized from carbon disulfide; 14 g. of crystals of m. p. 139° was obtained. The filtrate was poured into water and acidified with hydrochloric acid. A black, tarry mass formed. This was filtered off, warmed with caustic soda to dissolve the phenol and again filtered. The filtrate, when acidified with hydrochloric acid, had a very pronounced phenol odor. The liquid was extracted with ether and 0.5 g. of 2-chloro-4-nitrophenol, melting at 110°, was obtained. The residue obtained by heating the tarry mass with caustic soda was extracted with ether, from which was obtained 1.8 g. of 3,4-dichloro-aniline of m. p. 72°. The literature records 71.5°.

3,3′,4,4′-Tetrachloro-azoxybenzene was prepared by G. M. Kraay[7] by the oxidation in air of 3,4-dichloro-phenylhydroxylamine. He found the melting point to be 139–139.5°.

Action of o-Dichloro-4-Nitrobenzene with Sodium **Alcoholates.**—When o-dichloro-4-nitrobenzene is treated with solutions of various sodium alcoholates in the corresponding alcohol, ethers are formed, a chlorine group being replaced by O–R. In each case given in the adjoining table, 10 g. of o-dichloro-4-nitrobenzene was refluxed for two hours with the alcoholate, the mixture cooled and the solid which formed filtered off and washed with the corresponding cold alcohol. The solubility of the resulting ether in methyl alcohol, ethyl alcohol, benzene, ether and acetone was determined, as was also the melting point. A determination of the percentage of nitrogen in the compound also was made. Five g. of each nitro-ether was reduced with tin and hydrochloric acid. The resulting amine in most of the cases was diazotized and coupled with an alcoholic solution of β-naphthol, giving a dye.

We can find in the literature none of the ethers described except the

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[7] G. M. Kraay, "Dissertation," Amsterdam, 1926.

2-chloro-4-nitro-anisole which was prepared by Griess[8] by replacing the amino group of 2-amino-4-nitrophenyl methyl ether with chlorine. He records its m. p. to be 93–94°.

TABLE I

DATA ON THE ETHERS

Ether, 2-chloro-4-nitro-	Color and cryst. form	Yield, g.	Nitrogen, Calcd.	% Found	M. p., °C.	Color of amine dye
Anisole	Cream flakes	9.0	7.46	7.44	94	Purple
Phenetole	Dark brown cryst.	4.0	6.94	7.00	142	...
Isopropyl ether	Light brown flakes	4.5	6.49	6.45	128	Dark red
Phenyl-n-butyl ether	Brown flakes	8.4	6.10	6.10	136	Purple-red

The first of the above ethers is insoluble in cold or hot water, slightly soluble in ethyl alcohol and acetone and very soluble in these latter solvents when hot. It is also soluble in ether and benzene. The second ether is insoluble in water, cold ethyl alcohol and acetone but soluble in the last two when hot. The third ether is insoluble in water and slightly soluble in cold ethyl and isopropyl alcohols and acetone. It is also soluble in ether, benzene, hot ethyl alcohol and acetone. The last one is slightly soluble in acetone, soluble in ether and benzene and very much so in hot methyl and ethyl alcohols.

Summary

1. o-Dichloro-4-nitrobenzene was found to exist in a liquid and a solid modification, the two existing in approximately equal quantities at 22°.
2. Alcoholic potash on the compound gives mainly 3,3′,4,4′-tetrachloro-azoxybenzene and small quantities of 3,4-dichloro-aniline and 2-chloro-4-nitrophenol.
3. Four ethers of the compound were prepared, three of them for the first time. The 2-chloro-4-nitro-anisole had been previously prepared by a different method. Some of their properties are described. Three of these were reduced, diazotized and coupled with β-naphthol, giving red and purple dyes.

ST. LOUIS, MISSOURI

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[8] Griess, *Jahresber. Fortschritte Chem.*, 1866,459.

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 31]

THE REACTIVITY OF ATOMS AND GROUPS IN ORGANIC COMPOUNDS. VII. THE INFLUENCE OF CERTAIN SOLVENTS ON REACTION VELOCITY—ADJUVANCE

BY JAMES F. NORRIS AND SPENCER WARD PRENTISS[1,2]

RECEIVED JUNE 23, 1928 PUBLISHED NOVEMBER 6, 1928

It has long been known that the rate at which a reaction takes place in solution is markedly affected by the solvent. This fact has been studied by a number of investigators, but no adequate explanation has as yet been offered. The object of the work about to be described was not to attempt to solve this problem, but to get definite information in regard to the relative effects of the members of a series of alcohols on the rate at which a reaction took place in solutions in which the alcohols served as solvents.

In order to facilitate the consideration of the effects of solvents on reaction velocity, it seemed desirable to coin a new word which would serve to express this kind of action. The word adjuvance, from the Latin adjuvans from *adjuvare,* to help or to assist, has been found convenient in expressing the behavior of solvents from this point of view. For example, reactions, in general, take place more rapidly in nitrobenzene than in benzene; the adjuvance of the former is greater than that of the latter. It is impossible to measure the absolute adjuvance of a solvent but the word can be used in a derived sense to express quantitative relationships. We have found, for example, that the adjuvance of nitrobenzene is 26 times that of benzene when the reaction involved is that between pyridine and ethyl iodide. This means that the rates at which the reaction takes place in the two solvents are in the ratio of 26 to 1.

The desirability of studying the adjuvance of aliphatic alcohols is evident from the following facts. In most of the determinations of the rates at which alcohols enter into reaction with other substances, the alcohol studied has been used in excess as the solvent. This is notably the case in the large amount of work on rates of esterification. The values obtained are specific and express the behavior of the alcohol under the conditions of the experiment. They cannot be used in making absolute comparison between any two alcohols. The velocity of esterification, when measured in the way just indicated, is determined by the nature of the alcohol and its adjuvant effect. If the adjuvance of methyl alcohol is different from that of ethyl alcohol, the observed velocity constants of esterification of these alcohols with the same acid cannot be used to express the relative quantitative behavior of the alcohols in esterification. It has been found

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[1] In memory of Ira Remsen.

[2] From the thesis of Spencer Ward Prentiss, submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1925.

by several investigators that reactions, in general, take place more rapidly in methyl than in ethyl alcohol. It is probable that this difference in adjuvance exerts its effect in reactions in which the alcohols serve as both reactant and solvent.

In 1887 Menschutkin[3] discovered the phenomenon of adjuvance when he was investigating the rates at which certain alcohols react with acetic anhydride. The reaction was carried out in an "indifferent" solvent, benzene. When xylene and hexane were used in place of the latter he was surprised to find that the rates observed were not the same as before. This led to a detailed study of the subject.[4]

No systematic study of the adjuvance of alcohols has been made. As such information was needed in the interpretation of the results of work being carried out in this Laboratory, eight alcohols were examined. In addition, the adjuvance of nitrobenzene, acetone and benzene were determined.

In order to reduce experimental difficulties to a minimum and obtain results that would probably be susceptible of interpretation, a comparatively simple reaction was first studied—the addition of ethyl iodide to pyridine.

Especial care was taken in the purification of the substances used. The effect of concentration of the reactants on the velocity constant was found to be small within the limits studied, 0.23 and **1.0** *M*. In Table **I** are given the results obtained.

TABLE I

SECOND ORDER VELOCITY CONSTANTS OF THE REACTION PYRIDINE + ETHYL IODIDE = ETHYL PYRIDONIUM IODIDE

Temp., 25.00". Time in hours

Solvent	Velocity constant	Relative values, Benzene = 1	Solvent	Velocity constant	Relative values, Benzene = 1
Benzene	**0.0028**	**1**	*n*-Propyl **alcohol**	**0.0031**	**1.11**
Nitrobenzene	.070	**25.0**	*n*-Butyl "	.0031	**1.11**
Acetone	.036	**12.8**	**Isopropyl** "	.0030	**1.07**
Methyl alcohol	.0070	**2.50**	*Sec.*-butyl "	.0028	1.00
Ethyl "	.0039	**1.40**	*Tert.*-butyl "	.0026	**0.93**

The results show that nitrobenzene and acetone have a high adjuvance relative to that of benzene. Menschutkin found in the study of the reaction between trimethylamine and ethyl iodide at 100° the value **10.4** for acetone, whereas with pyridine and ethyl iodide at 25° we find **12.8.** He did not study nitrobenzene.

Methyl alcohol has a distinctly higher adjuvance than ethyl alcohol, which in turn is higher than *n*-propyl alcohol. Further increase in molecular weight has little or no effect. It is a striking fact that the adjuvance

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[3] **Menschutkin,** *Z. physik.* **Chem., 1, 611 (1887).**

[4] **Menschutkin,** *ibid.,* **5, 589, and 6, 41 (1890).**

of tertiary butyl alcohol is so close to that of the isomer with the normal structure. The two alcohols differ widely in chemical properties. It is also noteworthy that the adjuvance of these oxygen compounds approaches so closely that of benzene. The facts suggest that adjuvance may be related more to physical forces set up between the molecules involved than to chemical attractions.

The only previously determined values with which the results here given can be compared are those obtained by Menschutkin. In his study of the reaction between trimethylamine and ethyl iodide at 100°, he used a variety of solvents, among which were benzene, methyl alcohol and ethyl alcohol. His values for these substances are, respectively, 1, 8.8 and 6.3. Results at 100° are not strictly comparable with those at 25°. Further, it is highly probable that at 100° a reaction fakes place between the alcohols and ethyl iodide, as a result of which hydriodic acid is liberated. Any ionizable iodine formed in this way would have been included in the analyses made and calculated as produced in the primary reaction. We are convinced that this error came into the work, because it has been found in this Laboratory that n-butyl bromide reacts at a measurable rate at 100" with n-butyl alcohol to form the ether and hydrobromic acid. The relative adjuvance of the two alcohols measured at different temperatures and by means of different reactions with the possible source of error just indicated are in the two sets of experiments 1 to 1.8 and 1 to 1.4.

No results have been reported in regard to the other alcohols with which ours can be compared. It is planned to study the adjuvance of these alcohols in a reaction of a different type to see to what extent the nature of the reaction affects the results. The values that have been obtained will be used in the interpretation of the results of experiments which will be published later.

Experimental Part

The determinations of the velocity constants were made in the following manner. Equimolecular quantities of the reactants were added to the amount of the solvent necessary to produce a solution of the desired concentration. Measured amounts of the mixture were then placed in ampules, which were sealed and put into a thermostat at 25.00° The time at which the second reactant was added was taken as zero. This was justifiable because the reaction was a very slow one and the temperature of the solutions before being placed in the thermostat was close to 25°. The first analyses made at the end of about half an hour showed that the reaction had taken place to less than 0.5%.

From time to time an ampule was broken under water. The solution was acidified with nitric acid, silver nitrate was added and the excess of the latter was titrated with a solution of potassium thiocyanate. Check titrations of solutions in different ampules frequently agreed to within 0.5%. All the measuring apparatus used was carefully calibrated and care was taken to prevent contamination from the moisture of the air.

Second order velocity constants were calculated in the usual way. It was found that the values obtained as the reaction proceeded slowly increased. In order to get the true constant these values were extrapolated to zero time, using the following method. The values of t and of k were separated into two groups as nearly equal as possible. The average values of *t* and k in each group were computed, and from the differences between the *t* value.: and between the *k* values was obtained a linear equation in *t* and *k*. The value sought is the value of *k* when *t* is placed equal to 0. This method will be seen to be the two point method of obtaining the equation of a straight line.

In Table II are given the data used in a typical experiment.

TABLE II

THE VELOCITY CONSTANT OF THE REACTION BETWEEN PYRIDINE AND ETHYL IODIDE DISSOLVED IN *n*-PROPYL ALCOHOL

$d_{4°}^{25°}$ = 0.7998. Time in hours

	Moles	G.	No	Time	Fraction converted	K
Propyl alcohol		34.998	(0)	0 6	0 002	. . .
Pyridine	0 0350	2 771	1	24	.054	0 00336
Ethyl iodide	.0350	5.459	2	24	055	,00342
		———	3	72	153	,00356
Solution		43 228	4	72	1.54	,00358
Density of solution		0 872	5	122	,253	.00394
Molality (per 1000 g. of			6	122	.246	.00378
solution)		1 000	7	168	.337	.00428
Moles of solvent		16 65	8	168	334	,00423
		0.706	9	216	.404	.00444
Weight of sample analyzed (average of 3)		2 864 g.	10	216	.405	.00446

CALCULATIONS

Average point from 1 to 6 $t_1 = 72.7$ $K_1 = 0.00361$

Average point from 5 to 10 $t_2 = 126.7$ $K_2 = 0.00419$

t = 960 K = 0.00058

Whence 0.00361 − 0.00000605 X 72.7 = $K = 0.00318$

In Table III are given the results of the several experiments. In the first column are the numbers of the experiments. In the second the solvents used are listed. In the third, values of the density of the solvent used and the best recorded density are given. In the case of benzene, for example, the figures $^{22}/_{36}$ signify that the density of the benzene used was 0.8722, whereas the most probable figure for the true density is 0.8736. In the fourth column (M) are given the molalities of the solutions expressed as moles of each solute per 1000 g. of the solvent. In the fifth column

(N) the normality is expressed as moles per 1000 cc. of solvent. In the sixth and seventh columns are the values of the velocity constants found.

TABLE III

SECOND ORDER VELOCITY CONSTANTS OF THE REACTION BETWEEN PYRIDINE AND ETHYL IODIDE IN THE SOLVENTS LISTED

Temperature, 25.00°. Time in hours

No.	Solvent	Density	M	*N*	*K*	Average *K*
1	Acetone	65/54	0.500	0.368	0.0387	0.039
2	Acetone	65/54	.500	.368	.0385	
3	Acetone	55/54	1.000	.695	.0352	.036
4	Acetone	55/54	1.000	.695	.0366	
5	Nitrobenzene	78/81	0.200	.231	.0691	.069
6	Nitrobenzene	78/81	.201	.232	.0694	
7	Nitrobenzene	78/81	1.002	1.004	.071	.071
8	Nitrobenzene	78/81	1.007	1.009	.070	
9	Benzene	22/36	0.500	0.404	.00250	.0028
10	Benzene	22/36	1.000	.769	.00277	
11	Benzene	22/36	1.004	.767	.00286	
12	Benzene	36/36	1.000	.767	.00292	
13	Methyl alcohol	76/67	1.000	.699	.00687	.0070
14	Methyl alcohol	76/67	1.000	.699	.00718	
15	Ethyl alcohol	51/51	1.000	.695	.00385	.0039
16	Ethyl alcohol	51/51	1.000	.695	.00387	
17	n-Propyl alcohol	98/98	1.000	.706	.00318	.0031
18	n-Propyl alcohol	98/98	1.000	.706	.00304	
19	Isopropyl alcohol	11/08	1.000	.690	.00313	.0030
20	Isopropyl alcohol	11/08	1.002	.691	.00296	
21	n-Butyl alcohol	58/57	1.004	.717	.00295	.0031
22	n-Butyl alcohol	58/57	1.009	.718	.00318	
23	*Sec.*-butyl alcohol	25/23	1.000	.706	.00275	.0028
24	*Sec.*-butyl alcohol	25/23	1.11	.706	.00285	
25	*Tert.*-butyl alcohol	07/06	1.000	.688	.00258	.0026
26	*Tert.*-butyl alcohol	07/06	1.002	.689	.00272	

In experiments numbered 1 and 2 a sample of acetone containing a trace of water was used. The constant is higher than that obtained in 3 and 4. Menschutkin found in his experiments that the presence of 8% of water in acetone increased the velocity constant about 46%.

The values obtained in Expts. 5, 6, 7 and 8 indicate that the effect on the constant of a change in concentration of the reactants is slight. From Expts. 11 and 12 it is seen that a sample of benzene having the density 0.8722 gave the same result as a sample with true density, 0.8736.

Since a knowledge of the purity of the substances used in the determination of velocity constants is of paramount importance, a brief account will be given of the methods employed in this research. The determinations of boiling points were made with thermometers which were checked against standards from the Reichsanstalt of Berlin. Fractional distillations were carried out with efficient columns. Densities were determined with a Sprengel pycnometer, capacity about 13 cc., provided with ground glass caps. A counterpoise was used and the weighings were reduced to vacuum.

Pyridine.—Eastman's White Label pyridine was converted into the ferrocyanide, which was washed with a mixture of water and ether containing enough alcohol to make a homogeneous liquid. Pyridine was liberated by potassium hydroxide and taken up in ether. The latter was removed by boiling, the residue dried over quick lime and fractionated. A fraction was obtained, 90% of which on redistillation boiled within 0.2' around 115.3°. The densities of the material used varied between 0.97753 and 0.97764 at 25°/4°.

Ethyl Iodide.—Eastman's White Label ethyl iodide was shaken with cold sulfuric acid (3 vols. c. p. concd. H_2SO_4 and 1 vol. H_2O), separated and distilled from a flask containing silver powder and a few small lumps of marble, after preliminary heating for an hour at 60". The distillation was carried out in an atmosphere of carbon dioxide. A fraction was obtained, 95% of which boiled on redistillation within 0.1" around 72.3°. The material was kept in the dark in a bottle containing carbon dioxide It remained colorless for a long time. The density of the samples prepared varied between 1.9234 and 1.9241 at 25°/4°.

Acetone.—Eastman's White Label acetone from the bisulfite compound was distilled from potassium permanganate. The process was repeated until a sample was obtained which did not give a precipitate with the permanganate after standing for twenty-five hours. The acetone was distilled off and allowed to stand with a small amount of c. p. anhydrous potassium carbonate. When there was no evidence of any action the acetone was distilled. A fraction was obtained that boiled on redistillation almost completely within 0.1° around 56.1'. The density of the sample was 0.7855 at 25°/4°.

Benzene.—A high grade sample of "reagent quality" benzene was purified by the method described by Richards.[5] The product melted sharply at 5.42°. Its density was 0.8736 at 25°/4°.

Nitrobenzene.—Eastman's Blue Label nitrobenzene was distilled under diminished pressure. The product was alternately partially melted and the liquid poured off. This process was repeated until a small amount was obtained which gave good melting and freezing curves; m. p. 5.75°; density, 1.1978 at 25°/4°.

The Alcohols.—The alcohols were purified in general by the procedures used in this Laboratory in previous investigations. The values for the densities obtained at 25°/4° were as follows: methyl, 0.7866; ethyl from 0.78507 to 0.78511; propyl, 0.78998; isopropyl, 0.7811; n-butyl, 0.8058; *sec.*-butyl, 0.8025; *tert.*-butyl, 0.7807 (m. p. 24.5°).

Summary

1. It is pointed out that the results of the determination of the velocity constants of reactions in which an alcohol serves simultaneously as a reactant and as a solvent cannot be correctly interpreted without a knowledge of the effect of the solvent on the rate at which the reaction takes place.

2. *Adjuvance* is suggested as a convenient word to be used in expressing the property possessed by liquids of affecting the rate at which reactions proceed when the liquids are present as solvents.

3. The velocity constants of the reaction between pyridine and ethyl

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[5] Richards and Shipley, THIS JOURNAL, 36, 1825 (1914).

iodide in a number of solvents have been determined. The relative values of the constants are as follows: benzene, 1; nitrobenzene, 25; acetone, 12.8; methyl alcohol, 2.5; ethyl alcohol, 1.4; *n*-propyl alcohol, 1.11; n-butyl alcohol, 1.11; isopropyl alcohol, 1.07; *sec.*-butyl alcohol, 1.00 and *tert.*-butyl alcohol, 0.93.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

CATALYTIC STUDIES ON ACETOACETIC ESTER[1,2]

BY F. O. RICE AND JOSEPH J. SULLIVAN

RECEIVED JUNE 27, 1928 PUBLISHED NOVEMBER 6, 1928

Ethyl acetoacetate was discovered in 1863 by Geuther[3] and since then has been the subject of research by numerous workers. One phase of this work has comprised the identification of the two forms, their preparation in the pure condition, the equilibrium ratio of the liquid and of solutions in various media, and, in a semi-quantitative way, the rate of change of one form into the other. The purpose of the present work was to make a quantitative research on the rate of attaining equilibrium of the ester when rigorously purified according to the best technique available, and also when definite amounts of known catalysts were present. In our experiments we used Martin's method of distillation without ebullition:[4] by keeping a high vacuum (10^{-5} mm.) in our apparatus, we had no difficulty in distilling the ester at room temperature; in this way no bumping occurred and there was slight, if any, decomposition. Before allowing air to enter the apparatus, it was first bubbled through sulfuric acid to remove traces of aminic impurities and water, and then filtered to remove dust particles and sulfuric acid mist. Various kinds of containers were used, Pyrex, quartz and soft glass, either etched by corrosive cleaning agents, or with their inner surfaces smoothed by heating almost to the point of collapse. Using this special technique, we found that we could prepare samples of the ester of high enol content, which had a stability far greater than heretofore obtained. Our best samples had a half life of about 500 hours, as compared with rates less than one-tenth of this value reported by previous workers. There are no indications that we have reached the limit of stability, since the lowest rates appear to be due, at least in part, to traces of catalytic impurities still remaining.

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[1] In memory of Ira Remsen.

[2] Taken from a thesis submitted by Joseph J. Sullivan to the Graduate Faculty of the Johns Hopkins University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[3] Geuther, *Jahr. der Chem.*, 1863, 325.

[4] Martin, *J. Phys. Chem.*, 24, 478 (1920).

Historical

As late as 1905, Brühl[5] considered the pure form of acetoacetic ester to be the keto form, although Wislicenus[6] had earlier proved that the two forms existed in dynamic equilibrium. Perhaps the most important point in this connection lies in devising an exact method of estimating the ratio keto/enol in samples of the esters. Methods involving some physical property or other[6] have been proposed, especially refractive index, which has been used by Knorr[7] and also by Meyer.[8] Of the chemical methods three may be mentioned. The first makes use of the formation of a purple enolate with ferric chloride,[9] and is really a colorimetric method. In the second method the enol form is titrated with a standard bromine solution, using ferric chloride, if desired, as indicator.[10] The third method is that perfected by Meyer and his collaborators[11] and takes place in the following steps: the ester, dissolved in alcohol, is treated with a slight excess of an alcoholic bromine solution, and the excess bromine is immediately removed by β-naphthol. The bromine adds quantitatively to the double bond of the enol, which then splits off hydrobromic acid giving the bromoketone. This is estimated by adding potassium iodide, warming slightly and titrating the liberated iodine by thiosulfate.

The analytical difficulties cleared, the next step was the preparation of the pure isomers. It had long been known that the freshly distilled ester contains from 20–25% enol,[12] and Meyer and his collaborators,[8,13] using a method of successive distillations *in vacuo,* finally obtained an ester of 99.8% enol. The last distillations were performed in a quartz apparatus, in which they found that only slight isomerization occurred. Other methods of preparing the pure isomers are extraction of the keto form with hexane,[14] and freezing out the keto form at −78° as employed by Knorr.[6]

But little quantitative work has been done on the rate of rearrangement. A sample of freshly distilled ester, at 15°, followed by Meyer[10] for forty hours, shows on calculation a half life of 24.2 hours. In dissociating solvents, such as alcohol, the rate increases about 100 times, but the rate in these solvents is not much affected by halogen acids. In non-polar sol-

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[5] Bruhl and Schroder, *Z. physik. Chem.,* 50, 1 (1905).

[6] Wislicenus, *Ahrens Sammlung,* 2, 230 (1898).

[7] Knorr and co-workers, *Ber.,* 44, 1138 (1911).

[8] Meyer and Schoeller, *Ber.,* 53, 1410 (1920).

[9] Knorr, *Ber.,* 44, 2772 (1911); Meyer, *Ber.,* 45, 2843 (1912).

[10] Meyer, *Ann.,* 380, 212 (1911).

[11] Meyer and Kappelmeier, *Ber.,* 44, 2718 (1911); *Ber.,* 45, 2852 (1912); Finkelstein, *Ber.,* 43, 1528 (1910).

[12] (a) Schaum, *Ber.,* 31, 1964 (1898); (b) Traube, *Ber.,* 29, 1720 (1896); (c) Hantzsch, *Ber., 43,* 3049 (1910).

[13] Meyer and Hopff, *Ber.,* 54, 579 (1921).

[14] Meyer, *Ann.,* 380, 231 (1911); Dimroth, *Ann.,* 377, 127 (1910).

vents the rate is practically the same as for the pure liquid, but traces of halogen acids increase the rate enormously in these solvents. Meyer and Schoeller[8] give one specimen of work showing absence of isomerization in the vapor phase. In Table I we have collected the results of previous workers. For ease of comparison we have calculated the rate of change of enol → keto according to the method given later in the paper. The half life is the time in hours taken by the pure enol to fall to 50%. In the first three cases we have assumed the initial enol content to be 25%.

TABLE I

PREVIOUS WORK ON RATE OF ISOMERIZATION

Observer	Change in enol	Hours obs.	k_1	Half life, hours	Remarks
Traube[12b]	1.0244–1.0247	24	0.170	4.2	Density
Schaum[12a]	1.0278–1.0287	6	0.685	1.1	Density
D. and M.[15]	1.0209–1.0213	0.5	2.1	0.35	Viscosity
Meyer[10]	18.5%–7.9%	40	0.032	24	In quartz
M. and S.[8]	0%– 3%	20	.023	32	In quartz
Rumeau[16]	43%–33%	2	.15	5	In quartz
	52%–33%	4	.13	6	In quartz
	83%–58%	28	.013	58	In Pyrex
	52%–52%	4	...		In Pyrex
	52%–50%	4	.011	74	In Jena
	83%–10%	0.5	6.5	0.12	Soft glass

Quantitative investigation on the catalytic effect of impurities on the rate of rearrangement is also meager. Meyer and Willson[17] use oxalic acid (a trace) and Meyer and Hopff[13] phthalic anhydride (a few mg.) to stabilize a mixture of the isomers against aminic impurities, but give no measurements showing a relative improvement of conditions by their use. Hydrochloric acid and hydrobromic acid catalyze enolization, especially in non-polar solvents;[10] quartz is non-catalytic, but soft glass brings a mixture to equilibrium in a few hours. Alkalies act instantaneously.[10] A recent paper by Rumeau[16] concurs with the above in general, but he finds that phthalic anhydride is not a stabilizer, nor is a residue from the distillation of an ester previously treated with oxalic acid. Yet he notes that oxalic acid is an energetic stabilizer.

Apparatus and Experimental Method

To obtain the aseptic conditions mentioned by Meyer and, if possible, to improve on them, we planned to distil the ester in accordance with the method first used by Martin. The final form of our apparatus is shown in Fig. 1. This simple form of apparatus gave quite as good results as very much more complicated forms in which elaborate precautions were taken to prevent any possible contamination of the ester. The tubes A and B were connected to the apparatus by pieces of Gooch tubing. The

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[15] Dunstan and Mussel, J. Chem. *Soc.*, 99, 566 (1911).

[16] Rumeau, Bull. *soc. chim.*, 35, 762 (1924).

[17] Meyer and Willson, *Ber.*, 47,832 (1914).

tubes could therefore be easily removed and transferred to a thermostat for rate measurements. Our distillations were performed at pressures of 10^{-3} to 10^{-5} mm. of mercury. By keeping tube B at −78° and tube A at room temperatures, or a little higher, satisfactory rates of distillation were obtained. When distillation was completed we allowed air to enter the apparatus, the air having first been bubbled through sulfuric acid and then passed through an asbestos filter to remove acid mist and other suspended particles.

Analytical and Materials.—We found the analytical procedure perfected by Kurt Meyer[11] very satisfactory and used it without any important modifications throughout the work. We avoided as far as possible the use of violent cleaning reagents on our glass apparatus; our usual method was to give a final rinse in distilled water followed by heating nearly to the melting point. The acetoacetic ester used in our experiments was a commercial sample which we washed several times with distilled water, dried with calcium chloride and anhydrous copper sulfate and distilled; only the middle portion was used in our work.

Calculation **of** Rates.—In order to compare the stability of samples of ester prepared in different ways, it was necessary to measure the velocity constant of the change enol ⟶ keto.[10] Let x be the mole fraction of enol in any mixture and $1 - x$ the mole fraction of keto. Let k_1 be the rate of change of pure enol and k_2 the rate of change of pure keto. Then in any mixture, we have

$$\text{rate of change of enol to keto} = k_1x, \text{ and}$$
$$\text{rate of change of keto to enol} = k_2(1 - x)$$

Therefore,

$$-\frac{dx}{dt} = k_1x - k_2(1 - x)$$

If we put $k_1/k_2 = \alpha$ and integrate, we obtain

$$k_1 = \frac{\alpha}{t(1 + \alpha)} \ln \frac{x_0 - 1/(1 + \alpha)}{x - 1/(1 + \alpha)}$$

Throughout our work we took $\alpha = \mathbf{11.82}$, so that this equation becomes

$$k_1 = \frac{2.12}{t} \log \frac{x_0 - 0.078}{x - 0.078}$$

For ease of comparison of different samples we found it convenient to calculate a quantity that we refer to as the "half life," namely, the calculated time taken for a sample of pure enol to become a mixture of 50% enol and 50% keto. This is given by the formula

$$t_{1/2} = \frac{0.72}{k_1}$$

Experimental Results

In our earlier experiments extreme precautions were taken to prevent contamination of the ester, even to the extent of building the apparatus of fused silica. We finally found that we could relax these precautions and, in particular, use Pyrex glass instead of silica. Our first quantitative experiments were directed toward testing out the velocity equation which we have developed in the previous section. A sample of the ester was distilled in the apparatus shown in Fig. 1. The distillate was placed in a thermostat and samples were withdrawn for analysis at noted time intervals. A few of the results are given in Table I. It will be seen that k_1 shows a fairly satisfactory constancy over a period of several hundred hours.

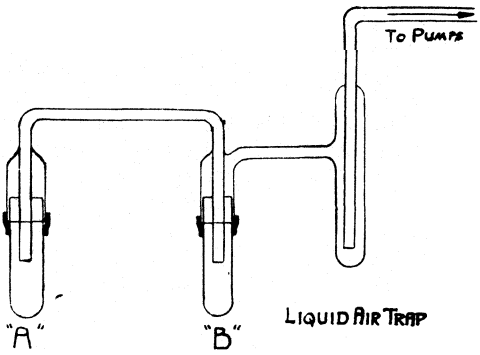

Fig. 1.

During this time, the tubes were opened many times to withdraw samples for analysis.

Our next experiments were directed toward finding if it were possible to transfer the ester from one container to another without contamination (Table II). The experiments usually show a fall in stability but the effect is not very great.

TABLE I

TABLE OF RESULTS

Sample A

Hours.......	0	43	47.3	71.5	74.5	142.5	185	236	286	330
Enol, %	36.4	30.1	30.4	28.6	27.6	23.7	20.3	17.7	15.8	14.2
$k_1 \times 10^{-4}$	..	53	46	41	45	38	41	41	41	42

Sample B

Hours.......	0	49.5	92.3	143.3	190.5	237.5	290.5	335	384
Enol, %	35.3	32.1	29.1	25.7	22.7	19.8	17	14.2	11.7
$k_1 \times 10^{-4}$	..	23	26	28	30	32	39	40	47

Sample C

Hours.......	0	71.8	145.5	215.8	264.3	333.3	383.5	478.3	506
Enol, %	36.6	27.7	21.5	17.4	15.2	13.0	12.1	10.6	10.0
$k_1 \times 10^{-4}$	..	47	47	47	47	47	46	45	47

Sample D

Hours.......	0	20.6	68.8	137.3	187.3	255.8	307.3	401.3
Enol, %	23.3	22.4	19.6	15.9	15.0	13.5	12.4	9.9
$k_1 \times 10^{-4}$	..	26	36	44	37	35	36	45

TABLE II

EFFECT OF TRANSFERENCE ON STABILITY OF ESTER

	Series A (Pyrex)				Series B (Quartz)			
Half life before transf.	175	175	175	175	131	131	131	131
Half life after transf.	156	161	151	158	108	124	116	150
Hours observed	17	17.5	18	18.5	545	470	470	640

In Series A the ester was transferred from a Pyrex container to four other Pyrex containers using a Pyrex pipet; in Series B from a Pyrex container to four quartz containers using a quartz pipet.

Series B is instructive because it shows that there is comparatively little difference in stability whether the ester is kept in quartz or Pyrex.

We made three runs in soft glass containers. The results are shown in Table III, which illustrates the great catalytic power of soft glass.

TABLE III

RATE OF CHANGE OF ESTER IN SOFT GLASS

Init enol, %	k_1	Half life	Hours obs
18.7	1 76	24 min.	1.4
18.7	2 66	16 min.	1.2
17.3	7.58	6 min.	0.8

From our experiments with different kinds of containers we concluded that any catalytic surface action in quartz or Pyrex was small compared to the effect of impurities dissolved in the ester. We therefore turned our attention to removing traces of dissolved impurities. Table IV shows the results obtained when we distilled a large portion of ester and examined the stability of the successive fractions.

TABLE IV

RESULTS ON FRACTIONATED ESTER

Frac.	Initial enol, %	k_1	Half life	Hours obs.
1	41.5	0.021	34	286
2	32.4	.032	21	165
3	22.6	.055	13	165
4	12.1	.140	5	20
5	38.4	,0014	515	335
6	34.8	.0058	124	424
7	32.0	.012	61	330
8	31.6	.004	180	422

It will be seen that the stability increases as the distillation progresses, with possibly a maximum at the middle portions. Our experiments so far indicate that more efficient fractionation would result in a considerably diminished rate of isomerization. The erratic results shown by fractions 4 and 7 (in this particular experiment) are probably due to accidental contamination of some kind or other.

We next turned our attention to the addition of substances to the ester with the hope of stabilizing it. Our experiments in this direction, however, did not meet with any success. The addition of small quantities of substances like phthalic anhydride, oxalic acid and acetyl chloride, whether before or after distillation, had the effect of increasing the rate of change instead of diminishing it. The observed rate of change is probably largely due to the presence of a minute trace (a few parts per million of ester) of aminic impurities, and a trace of acetyl chloride might be expected to remove these.[18] However, further consideration shows that a small trace

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[18] See Lowry and Magson, J. *Chem. Soc.,* 93,107 (1908).

of water present would hydrolyze the acid chloride probably at a faster rate than the latter would react with the aminic impurity. The removal of the last traces of water from a substance like acetoacetic ester is a difficult matter since violent dehydrating agents will decompose the ester. We tried the effectof activated silica gel on the ester, but there was obvious decomposition, the ester becoming brownish-red. The distillate from this had a half life of about one hundred hours.

In our final experiments we decided to add various substances in known amounts, and compare the rate of isomerization of the ester before and after this addition. The results are shown in Table V. The third column contains a list of the ratios of the rates k_2/k_1, where k_2 is the rate after addition of the catalyst, and k_1 is the rate before addition.

TABLE V

EFFECT OF CATALYSTS ON THE RATE OF ISOMERIZATION OF ACETOACETIC ESTER

Catalyst	Conc. × 10^{-5}	k_2/k_1	Catalyst	Conc. × 10^{-5}	k_2/k_1
Piperidine	4	11,400	Phthalic anhydride	40	6
Ammonia	4	4,000	Oxalic acid	1	3.2
Pyridine	4	264	Water	100	1
Quinoline	4	17	Dehydracetic acid	4	36
Bromine	4	>1,300	Residue	4	3
Acetyl chloride	4	157			

The extraordinary effectof small quantities of bases is at once apparent. Thus, one part in a million of piperidine increases the rate by three orders. It is somewhat surprising to find that bromine is an extremely good catalyst, being even more effective than some of the bases. Occasionally in the course of our work we would meet with very anomalous behavior which we may ascribe to accidental contamination since it is obviously very difficult to make quantitative measurements with materials so sensitive to small traces of basic substances.

We also made a study of the temperature coefficientof the rate of change of the liquid ester, since this does not seem to have been measured by previous workers. Measurements by Meyer[10] for aqueous solutions of the ester gave $k_{10}/k_0 = 3$, and by Meyer and Willson[17] for alcoholic solutions gave $k_{25}/k_0 = 1.3$. We made measurements on two samples at 25 and 35°, and obtained for k_{35}/k_{25} the values 4.9 and 6.3. Taking a mean value of 5.6 we obtain the value of 31,200 for the heat of activation. This is surprisingly large, especially when we compare it with the value for the aqueous solution.

Summary

1. We have made a quantitative study of the rate of isomerization of acetoacetic ester in the liquid condition. Distillations were carried out in high vacuum and every precaution was taken to prevent contamination of the ester.

2. The rate of change of the enolic form of the ester when prepared in this way was over 10 times slower than the (calculated) best values previously reported.

3. The velocity constants for the change have been measured in presence of known amounts of various substances.

BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WEST VIRGINIA UNIVERSITY]

FLUOSILICATES OF SOME ORGANIC BASES[1]

BY C. A. JACOBSON AND H. A. H. PRAY

RECEIVED JULY 11, 1928 PUBLISHED NOVEMBER 6, 1928

Introductory

It is well known that fluosilicic acid is a relatively strong acid which yields insoluble salts with most inorganic bases, a large number of which have been prepared. However, few attempts have been made to prepare the salts of this acid with organic bases. E. Ebler and E. Schott[2] have described a fluosilicate of hydrazine, $N_2H_4 \cdot H_2SiF_6$, and of hydroxylamine, $(NH_2OH)_2 \cdot H_2SiF_6$. On the other hand, a number of hydrofluorides of organic bases have been isolated and found to be well-defined, crystalline compounds. Weinland and Lewkowitz[3] report upon the hydrofluorides of aniline, aminophenol, aminophenetole, aminobenzoic acid, etc.

This paper describes the preparation and properties of fluosilicates of aniline, methylaniline and *o*-, *m*- and *p*-toluidine.

Experimental

For the preparation of the aniline salt, redistilled aniline, dissolved in about three times its volume of 95% ethyl alcohol, was treated with a 30% aqueous solution of fluosilicic acid in such a way that the aniline was kept in excess. The precipitated product was washed free from excess aniline with cold 95% ethyl alcohol. The precipitate was then recrystallized twice from hot 95% alcohol and dried, first in the air and finally in a desiccator over sulfuric acid.

The product thus prepared was found to be a snow-white powder composed of small plate-like crystals of irregular shape. Upon heating it sublimed, the sublimation being rapid at a temperature of about 230°. It was insoluble in absolute ethyl alcohol, methyl alcohol, acetone, carbon tetrachloride, chloroform, ethyl ether and carbon disulfide, slightly soluble in hot acetone, but extremely soluble in water. When heated a gas was evolved which when passed into water caused the precipitation of gelati-

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[1] In memory of Ira Remsen.

[2] Ebler and Schott, *J. prakt. Chem.*, [2] 78, 338 (1908); [2] 81, 552 (1910).

[3] Weinland and Lewkowitz, *Z. anorg. Chem.*, 45, 39–51 (1905).

nous silicic acid, thus indicating that the material was a fluosilicate. Inorganic fluosilicates behave in the same way. A further indication that the substance was a fluosilicate lies in the fact that in water solution it reacts quantitatively with a solution of sodium hydroxide as do the other fluosilicates.

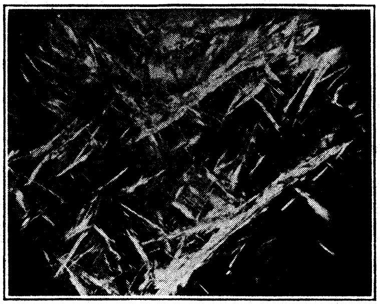

Fig. 1.—Di-aniline fluosilicate.

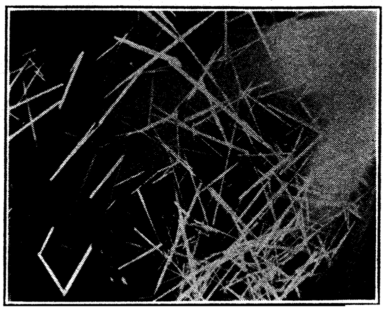

Fig. 2.—Di-methylanilinefluosilicate.

In order to arrive at the empirical formula of the compound, quantitative determinations of nitrogen by the Kjeldahl-Gunning-Arnold method, as well as quantitative determinations of the fluosilicic acid radical, by a method previously devised by one of us,[4] were employed. The latter method consists of the titration of a weighed quantity of the salt dissolved in hot water by a standard solution of sodium hydroxide. An electrometric titration showed the end-point to be within the range of phenol red; consequently, this indicator was used for the determinations of the acid radical part of the salts. These determinations show that the compound under investigation is a di-aniline fluosilicate whose formula is $(C_6H_5NH_2)_2 \cdot H_2SiF_6$.

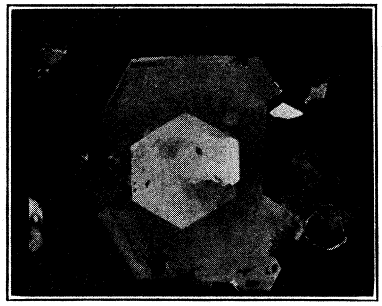

Fig. 3.—Di-o-toluidine fluosilicate.

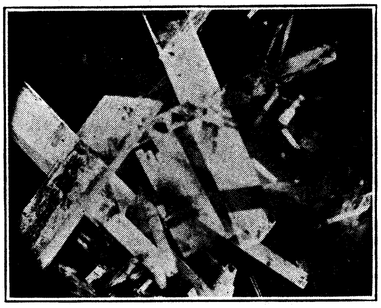

Fig. 4.—Di-m-toluidine fluosilicate.

Anal. Calcd.: N, 8.49; H_2SiF_6, 43.68. Found: N, 8.48, 8.60; H_2SiF_6, 43.60, 43.21.

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[4] Jacobson, J. Phys. *Chem.*, 28, 506 (1924).

It has already been mentioned that this di-aniline fluosilicate sublimes at a relatively low temperature, and it seemed of importance to learn if the composition of the sublimed product was the same as that of the recrystallized. The following nitrogen determinations show that the composition is not changed by sublimation.

Anal. Calcd.: N, 8.49. Found: N, 8.32, 8.33.

In a similar manner it mas shown that, unlike the fluorides, no other fluosilicate compound with aniline is obtained by precipitating with excess of the acid. A product so obtained showed the same composition and properties as described above.

The method of preparing and purifying the other salts of fluosilicic acid was identical with that described for the di-aniline fluosilicate. The following table gives the analytical data obtained for the five new salts prepared, together with their crystal forms.

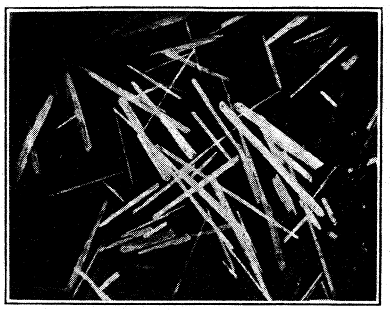

Fig. 5.—Di-*p*-toluidine fluosilicate.

Work is now in progress on other basic fluosilicates such as tolidine and urea. These two compounds are also obtained in nice crystalline form.

The di-p-toluidine fluosilicate (No. 3) is the most unstable. The crystals are at first pure white but in a few days they begin to turn yellow and after two or three months assume a deep brown color at the surface of the glass which has been exposed to diffused sunlight, and more and more yellow toward the center of the mass. The irregular outline of the crystals shown in Fig. 5 also indicates the unstable character of this compound.

TABLE I

ANALYTICAL DATA AND CRYSTALLINE FORM

No.	Fluosilicate	Nitrogen, % Calcd.	Nitrogen, % Found	H_2SiF_6, % Calcd.	H_2SiF_6, % Found	Crystal form
1	Di-aniline	8 49	8 48, 8 60	43 68	43.60 43.21	Irreg. plates
2	Di-methylaniline	7 82	7.85, 7.80	40.22	40.05, 39.97	Monoclinic needles sharp outline
3	Di-o-toluidine	7 82	7.68 7.69	40.22	40.14, 39.90	Orthorh. plates
4	Di-*m*-toluidine	7.82	7.73, 7.98	40.22	40.03, 40.18	Rect. plates
5	Di-*p*-toluidine	7.82	7.50, 7 59	40.22	39.90, 40.30	Needle-like, irreg. outline

Summary

Five new crystalline compounds have been made and analyzed. They are the fluosilicates of aniline, methylaniline, o-, *m*- and *p*-toluidine, and are the direct addition products of two molecules of the base with one of fluosilicic acid.

The physical properties of these salts have been investigated and microphotographs taken which depict a wholly different crystalline form for each one. The fact that the salts crystallized easily from hot alcohol enabled us to prepare them in very pure condition.

MORGANTOWN, WEST VIRGINIA

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

ALKYL ORTHOSILICATES[1]

BY A. W. DEARING[2] AND E. EMMET REID

RECEIVED JULY 24, 1928 PUBLISHED NOVEMBER 6, 1928

Though ethyl orthosilicate was discovered as long ago as 1846 by Ebelmen,[3] it has not been extensively studied. Khotinsky and Seregenkoff[4] found that one and only one of its ethoxy groups is exchanged for the radical of the Grignard reagent. It seemed desirable to learn more about the preparation and reactions of alkyl orthosilicates.

Results

The method of preparing ethyl orthosilicate has been improved, the yield being brought up to 70%. New esters were made from n-butyl, n-amyl, n-heptyl, n-octyl and β-chloro-ethyl alcohols, though the last two were impossible to purify as they are liquids which could not be distilled Attempts to obtain orthosilicates from secondary alcohols proved unsuccessful, the reaction taking another course. With mercaptan silicon tetrachloride reacts only partially, even when heated to 200° for twenty hours.

It has long been known that ethyl orthosilicate ethylates water and acetic acid. It has been found to yield diethyl phthalate with phthalic anhydride, according to this equation:

$$C_6H_4(CO)_2O + (C_2H_5O)_4Si \longrightarrow C_6H_4(CO_2C_2H_5)_2 + (C_2H_5O)_2SiO$$

Similarly ethyl acetate is obtained with acetanhydride. With sulfuric acid, diethyl sulfate is formed. Benzoic acid reacts with it very sluggishly but ethyl benzoate is formed. *p*-Nitrobenzoic acid could not be made to react. It could not be made to react with phenol, β-naphthol or thiophenyl. In the presence of aluminum chloride benzene is ethylated by it even up to hexa-ethylbenzene.

When ethyl, or methyl, orthosilicate reacts with water or acetic acid under the proper conditions, the silicic acid produced separates as a gel. This is of interest since it does not contain electrolytes which are so difficult

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[1] In memory of Ira Remsen.

[2] From the Ph.D. dissertation of A. W. Dearing, 1927.

[3] Ebelmen, Ann., 57, 334 (1846).

[4] Khotinsky and Seregenkoff, Ber., 41, 2948 (1908).

to wash out of the gel from sodium silicate. The silica obtained from methyl orthosilicate is 50% of the weight of the ester. The shrinkage of the gel prepared from this or the ethyl ester is only a fraction of that of the gel precipitated in the usual way from sodium silicate. This suggested the possibility of obtaining disks of silica gel which might be used for osmotic pressure measurements. Disks were obtained, best by the action of moist air on the ester. but none perfect enough for the desired purpose. In parallel experiments in which a mixture of the vapors of acetic acid and ethyl alcohol was passed over silica gel at 180°, the gel from ethyl orthosilicate proved to be decidedly more active than a carefully prepared specimen of the gel from sodium silicate. More recently, gel purified by Patrick by boiling with nitric acid has appeared to be about as active as our gel. As the gel from the alkyl orthosilicates can be made in benzene solution by the action of the calculated amount of water or acetic acid, a product is obtained the surface of which has never been wet by water. It was thought that such a gel might show different absorptive power from that precipitated in water solution. This did not prove to be the case.

Experimental

The difficulty in the preparation of alkyl orthosilicates is that four molecules of hydrogen chloride are eliminated for each molecule of silicon tetrachloride that reacts. The large evolution of gas causes a considerable loss of the volatile reactants. The method which proved to be best is to add the silicon tetrachloride, which must be free from higher boiling compounds, dropwise to the alcohol cooled in a freezing mixture. The alcohol must be perfectly anhydrous and is used in about 10% excess to insure the reaction of all of the chlorine. The escaping hydrogen chloride is led through a small amount of cold alcohol to recover the silicon tetrachloride that is carried off. After the reaction is judged to be complete, dry air is drawn through the product for several hours to rid it of hydrogen chloride. The ester is then fractionated in a vacuum with the careful exclusion of moisture. To avoid decomposition the esters of the higher alcohols must be distilled at very low pressures.

Ethyl orthosilicate was obtained in 70% yield. It boils at 165–167° at 760 mm. The properties of the new esters are given in tabular form.

TABLE I

ESTERS OF ORTHOSILICIC ACID

Alkyl	B. p., °C.	Press., mm.	Density		Silicon, %		
			0°/4°	25°/4°	Calcd.	Found	
n-Butyl	160–5	20	0.9353	0.9194	8.82	8.75	8.63
n-Amyl	145–50	3	.9117	.8933	7.53	7.45	7.49
n-Heptyl	200–15	3	.9097	.8958	5.79	5.99	6.03
n-Octyl	240	3	...	...	5.19	5.23	5.09

Phenylethyl alcohol reacted as was expected but the product could not be purified, as it decomposed when distillation was attempted even with a good vacuum. It was heated at 90° in a vacuum for some hours, which eliminated most of the excess of the alcohol but even then it was only about *88%* pure, as analysis for silicon showed 4.88 and 4.84% instead of the calculated 5.53. Its density is about 1.00.

Silicon tetrachloride was added to four equivalents of anhydrous ethylene chlorohydrin. Reaction took place as usual. As the products could not be distilled, it was purified by heating in a vacuum for some hours, which gave a product which analysis showed to be 94% pure.

This product was refluxed for several hours with an excess of aniline hydrochloride and a white amorphous material was obtained. This resembled silicic acid in appearance but is soluble in alcohol and ether. It could not be recrystallized and hence little weight can be attached to the analysis for silicon, which corresponded to the formula $(C_6H_5NHC_2H_4)_4Si$. Very similar products were obtained with dimethylanilinc and pyridine.

Silicon tetrachloride reacts vigorously with isopropyl alcohol but converts it to propylene and isopropyl chloride. With mercaptan it gave no reaction under the usual conditions. A mixture of mercaptan and silicon tetrachloride was heated at 200° in a sealed tube for twenty hours. The evaporation of the reactants left a small amount of liquid boiling at 125° but this still contained chlorine, which shows that the replacement takes place very slowly.

Ethyl orthosilicate was heated with one molecule of phthalic anhydride for eight hours at 160°. The ethyl phthalate formed was separated by fractionation in *vacuo* and identified by boiling point, density and saponification number. A similar experiment was tried with acetanhydride and ethyl acetate identified.

To a mixture of benzene and ethyl orthosilicate, aluminum chloride was added. A reaction took place at once. The mixture was heated for several hours, poured onto ice and extracted with ether. Hexa-ethylbenzene was identified by its melting point. The intermediate ethylated benzenes were present but not in sufficient amounts for separation.

Silica Gel from Ethyl Orthosilicate.—A shallow layer of the ester reacts with water vapor and finally sets to a gel, but more uniform results are obtained by adding the calculated amount of water to the ester diluted with 1.5 times its volume of alcohol. If too much alcohol is used the gel does not set properly.

A on-aqueous gel was prepared by refluxing a mixture of four parts of acetic acid to one of the ester for an hour and allowing it to stand overnight. The excess of acetic acid was gotten rid of by soaking the gel in dry benzene, which was poured off and replaced by fresh benzene every day for four days. The gel was then dried in a vacuum and the soaking and drying repeated every three or four days for three weeks. The gel prepared in this manner was excellent in appearance and proved to be an excellent catalyst for vapor phase esterification, but its absorption from water solution was practically identical with that of the regular gel.

A variation of this method was to dissolve the ester and the required amount of acetic acid in dry benzene and boil until. gel formation took place on cooling. Usually about eight hours' boiling was required. The gel formation seems to take place rather suddenly after long heating. In one experiment the mixture was boiled for seven and three-fourths hours and gave no appearance of gel formation on cooling. Further heating'for fifteen minutes caused it to become viscous and to set to a stiff gel on cooling. This gel was purified as described above and had the same properties.

Acids higher up in the acetic acid series were used for preparing the gel but these acids did not give as good a product. In one case paraffin wax was dissolved in the benzene with the idea that it might coat the gel and diminish its affinity for water.

In whatever way the gel was prepared it acted the same when put into water and showed the same absorption as the regular silica gel.

Esterification experiments similar to those of Milligan and Reid[5] were run to compare the special gel obtained as described above with the regular silica gel. The whole aim was to get comparative results. The sample of gel was contained in a tube surrounded by the vapor of boiling cyclohexanol. A mixture of equivalent amounts of absolute ethyl alcohol and acetic acid was dropped at the desired rate from a calibrated capillary tip into a bulb which served as a vaporizing chamber from which it passed into the catalyst tube. The products were condensed, weighed and titrated immediately. The results are given in the table below.

TABLE II

PERCENTAGE ESTERIFICATION OVER REGULAR AND SPECIAL SILICA GEL

Time of contact, sec.	Regular gel	Special gel	Time of contact, sec.	Regular gel	Special gel
11.3	20.5	29	26.4	34	46.5
11.3	28	29.5	26.4	35	49
11.3	29	29	123	49.3	82.5
11.3	29	30	123	50	78.5
26.4	43	47	123	53	89
26.4	33	46.5			

There are considerable irregularities in the results but the special gel shows decidedly greater activity at the slower rates.

Summary

The preparation of ethyl orthosilicate has been improved and a number of new orthosilicate esters have been prepared. The reactions of ethyl

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[5] Milligan, Chappell and Reid, J. Phyc. *Chem.*, **38,** 872 (1924).

orthosilicate have been investigated. It has been used to prepare silica gel free from strong electrolytes and some of the properties of such gel have been studied.

BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

SOME 1,2-DIALKYL CYCLOPENTANE DERIVATIVES[1,2]

BY FRANCIS H. CASE[3] AND E. EMMET REID[4]

RECEIVED JULY 24, 1928 PUBLISHED NOVEMBER 6, 1928

As cyclic hydrocarbons are found in some petroleums it is important to know more of the chemistry of this class. The derivatives of cyclopentane have not been extensively studied; it seemed desirable to synthesize more of them so as to extend our knowledge of the properties of the members of this group. The particular line chosen was the 1,2-dialkyl cyclopentanes. The reaction chosen for the preparation of these hydrocarbons led quite unexpectedly to the formation of the corresponding unsaturated hydrocarbons. Due to the expiration of the grant, time was not available for the reduction of the latter to the saturated derivatives, and it was deemed best to publish the results obtained.

The necessary intermediate for the study was a-ethyl-cyclopentanone. This compound is supposed to have been obtained by Best and Thorpe[5] by the hydrolysis of 2-cyano-2-methyl-cyclopentane-one-1. They described it as boiling at 149° at 756 mm. and gave the melting point of its semicarbazone as 177". This compound prepared by our method boils at 160–161° (755 mm.) corr. and its semicarbazone melts at 189° corr. We started with ethyl adipate (I), which was made to undergo an internal acetoacetic ester condensation to form the ethyl ester of α-carbethoxy-cyclopentanone (II). The sodium compound of this[6] reacted with ethyl iodide to give the ethyl derivative (111), which by the ketone splitting left a-ethyl-cyclopentanone (IV). By the Grignard reaction this ketone was converted to the tertiary alcohol (V). This was transformed into the iodide. It was intended to remove the iodine by reduction to obtain the 1,2-alkyl-ethyl-cyclo-pentane (VI). When this was attempted an unsaturated hydrocarbon was obtained.

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[1] In memory of Ira Remsen.

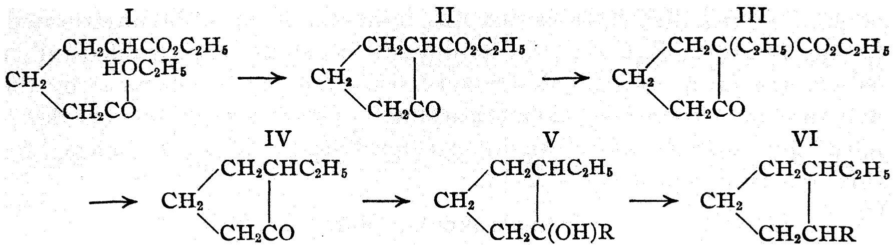
[2] This paper presents the results of an investigation of cyclopentane derivatives listed as Project 15 of the American Petroleum Institute. Financial assistance has been received from a research fund of the American Petroleum Institute donated by the Universal Oil Products Co. This fund is being administered by the Institute with the cooperation of the Central Petroleum Committee of the National Research Council.

[3] American Petroleum Institute Research Fellow.

[4] Director, American Petroleum Institute Research Project 15.

[5] Best and Thorpe, J. Chem. *Soc.*, **95**, 713 (1909).

[6] Rysselberge, Bull. *sci. acad. roy. Belg.*, [5] **12**, 171 (1926).



In the preparation of a-methyl-a-carbethoxy cyclopentanone, Bouveault[7] treated one mole of a-carbethoxy-cyclopentanone with one equivalent of sodium dissolved in absolute alcohol and added methyl iodide to the cooled mixture. Whereas the method was generally satisfactory for the methyl derivative, it sometimes miscarried, giving almost exclusively ethyl-a-methyl adipate. For higher alkyl groups such as the *iso*propyl, no reaction occurred unless heating in a sealed tube was resorted to. In this case a large amount of ethyl-α-*iso*propyl adipate was obtained. Indeed Bouveault was unable to prepare the isopropyl keto ester in a state of purity. It was prepared, however, by Kotz and Schüler[8] by treating a-carbethoxy-cyclopentanone with a finely divided alloy of sodium and potassium and refluxing the mixed salt thus formed for seventy hours with isopropyl iodide.

We have been able to prepare the various alkyl derivatives of a-carbethoxy-cyclopentanone in a reasonable time by adding the alkyl iodide to the sodium salt of the keto ester suspended in an aromatic hydrocarbon and refluxing. It was found that as the size of the alkyl group increases it is necessary to use a higher boiling solvent and to heat for a longer time. Thus an 82% yield of methyl derivative was obtained in three hours using benzene as solvent, 74% of ethyl keto ester in six hours in toluene and 59% of isopropyl in twelve hours in xylene.

The yields of substituted cyclopentanols obtained by the action of various Grignard reagents on a-ethyl-cyclopentanone were found to be very low, due perhaps to the steric effect of the ethyl radical in the α-position to the carbonyl group. In each case much of the ketone was recovered unchanged and much high boiling material was found. Thus, with ethyl magnesium bromide, the yield of 1,2-diethyl-cyclopentanol-1 (V) was 27%, with propyl magnesium bromide the yield of 1-propyl-2-ethylcyclo-ethyl-cyclopentanol-1 was only 8.5% and with *iso*propyl magnesium bromide no alcohol was obtained. In an attempt to prepare 1,2-diethyl-cyclopentane from 1,2-diethylcyclopentanol-1, the latter compound was converted to the iodide and this reduced with zinc and hydrochloric

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[7] **Bouveault,** *Bull. soc. chim.*, [3] **21,** 1019 (1899). **Bouveault and Locquin,** *ibid.*, [4] 3,432 (1908).

[8] **Kötz and** Schüler, *Ann.*, 350, **222** (1906).

acid. The resulting hydrocarbon was, however, shown to be unsaturated, having the formula C_9H_{16}. In its physical constants it resembled rather closely the unsaturated hydrocarbon C_9H_{16} prepared by Kishner[9] by the dehydration of diethyl-cyclobutylcarbinol. This hydrocarbon was designated by Kishner as 1,2-diethyl-cyclopentene-1, although evidence for this structure appears to be lacking.

Experimental Part

α-Carbethoxy-cyclopentanone.—The directions of von Rysselberge[6] were used.

α-Methyl-α-carbethoxy-cyclopentanone.—To 20.7 g. of sodium, finely divided by shaking in hot xylene, suspended in 400 cc. of benzene, 140 g. of α-carbethoxy-cyclopentanone was added with cooling and the mixture allowed to stand overnight. To the sodium salt thus formed, 131 g. of methyl iodide was added and the mixture refluxed for three hours. The sodium iodide was then filtered off and the benzene solution fractionated The yield of material boiling at 106–107° (17 mm.) corr. was 125 g., or 82%. The semicarbazone melted at 152–153° corr.

α-Ethyl-α-carbethoxy-cyclopentenone.—This was prepared in the same way as the methyl derivative except that toluene was used as solvent instead of benzene. The proportions used were 29.6 g. of sodium, 200 g. of a-carbethoxy-cyclopentanone, 500 cc. of toluene and 210 g. of ethyl iodide. The yield of material boiling at 100° (7 mm.) corr. was 174 g., or 74%; $d_4^0 = 1.0531$, $d_4^{25} = 1.0310$.

Anal. Calcd. for $C_{10}H_{16}O_3$: C, 65.17; H, 8.76. Found: C, 64.68; H, 8.74.

Semicarbazone.—The semicarbazone of or-ethyl-a-carbethoxy-cyclopentanone melts at 148–149° corr.

Anal. Calcd. for $C_{11}H_{19}O_3N_3$: C, 54.73; H, 7.94. Found: C, 55.13; H, 8.00

α-*Iso*propyl-α-carbethoxy-cyclopentanone.—To the sodium salt prepared by treating 14.7 g. of sodium suspended in 300 cc. of xylene with 100 g. of α-carbethoxy-cyclopentanone was added 100 g. of *iso*propyl iodide. The mixture was refluxed for twelve hours, the sodium iodide filtered off and the xylene removed by distillation. The yield of *iso*propyl keto ester boiling at 136–137 (34 mm.) corr. was 75 g., or 59%. The semicarbazone melted at 141–142° corr., which agrees with Bouveault's observations.

α-Ethyl-cyclopentanone.—A mixture of 100 g. of α-ethyl-α-carbethoxy-cyclopentanone, 200 cc. of water and 100 cc. of concd. sulfuric acid was refluxed for five hours. After cooling the mixture was extracted with ether and the ethereal extract washed with sodium bicarbonate solution. After removal of the ether, 39 g. of crude ketone, b. p. 161–164°, was obtained. The pure ketone boils at 160–161° (755 mm.) corr.; $d_4^0 = 0.9469$; $d_4^{25} = 0.9260$.

Anal. Calcd. for $C_7H_{12}O$: C, 74.93; H, 10.70. Found: C, 74.76; H, 10.71.

The semicarbazone melts at 189° corr.

Anal. Calcd. for $C_8H_{15}N_3O$: C, 56.76; H, 8.94. Found: C, 56.95; H, 9.29.

1,2-Diethyl-cyclopentanol-1.—To the cooled Grignard reagent prepared from 28.8 g. of magnesium and 160 g. of ethyl bromide, 120 g. of a-ethyl-cyclopentanone was slowly added with stirring. After several hours the mixture was decomposed with dilute acetic acid, extracted with ether and the ether solution washed with sodium bicarbonate solution. Alter removal of the ether, the resulting liquid was fractionated *in vacuo*. The lower boiling fraction was found to be unchanged ketone. The fraction

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[9] Kishner, J. *Russ. Phys.-Chem. Soc.*, **43**, 1149–1157 (1011).

boiling at 100–102° at 49 mm. was 41 g. This on redistillation boiled at 101–102° corr. at 46 mm. and proved to be the desired diethyl-cyclopentanol; yield, 27%. There was a higher boiling fraction which was not investigated; $d_4^0 = 0.9250$; $d_4^{25} = 0.9041$.

Anal. Calcd. for $C_9H_{18}O$: C, 75.98; H, 12.77. Found: C, 75.79; H, 13.24.

1-Propyl-2-ethyl-cyclopentanol-1.—To the cooled Grignard reagent from 28.8 g. of magnesium and 200 *g.* of n-propyl bromide, 100 g. of α-ethyl-cyclopentanone was added slowly with stirring. After four hours at room temperature, the mixture was decomposed with dilute acetic acid, extracted with ether and the ether layer washed with sodium bicarbonate solution. After removal of the ether, the mixture was fractionated several times in *vacuo*. A large low boiling fraction proved to be unchanged ketone. The fraction boiling at 112–115° at 48 mm. was 14 g. On redistillation, the pure alcohol boiling at 115–116° at 42 mm. corr. was obtained, yield, 8.5%; $d_4^0 = 0.9156$; $d_4^{25} = 0.8949$.

Anal. Calcd. for $C_{10}H_{20}O$: C, 76.84; H, 12.81. Found: C, 76.77; H, 13.12.

1,2-Diethyl-cyclopentene, C_9H_{16}.—1,2-Diethyl-cyclopentanol-1, 48 g., was saturated in the cold with hydrogen iodide. The resulting mixture was dissolved in 310 cc. of alcohol and 40 cc. of water and 50 g. of zinc dust was added. After refluxing for two hours, 70 cc. of concd. hydrochloric acid was added and the refluxing continued for four hours. At the conclusion of this time, the mixture was cooled, extracted with ether and the ether solution washed with sodium bicarbonate solution. After removal of the ether, 25 g. of a liquid boiling at 147–149° at 761 mm. corr. was obtained. On redistillation'the pure hydrocarbon, boiling at 148–149° corr. at 761 mm. resulted; $d_4^0 = 0.9331$; $d_4^{25} = 0.8136$.

Anal. Calcd. for C_9H_{16}: C, 87.00; H, 13.00. Found: C, 86.84; H, 13.14. Mol. *wt.* (Freezing point in benzene): calcd., 124. Found: 125.

This hydrocarbon was highly unsaturated, reducing bromine and permanganate instantaneously.

The boiling point of the hydrocarbon described by Kishner as 1,2-diethyl-cyclopentene-1 was 151–152° (751 mm.); $d_4^{20} = 0.8124$.

Summary

a-Methyl-, a-ethyl- and a-isopropyl-a-carbethoxy-cyclopentanones have been prepared by an improved method. From a-ethyl cyclopentanone the 1,2-diethyl- and the 1-propyl-2-ethyl-cyclopentanol-1 have been obtained. On conversion into the iodide and treatment with zinc and acetic acid, the unsaturated hydrocarbon was obtained rather than the desired dialkyl cyclopentane.

BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

THE DECOMPOSITION OF ORGANIC COMPOUNDS AT HIGH TEMPERATURES AND PRESSURES[1,2]

BY LEE R. HERNDON[3] AND E. EMMET REID

RECEIVED JULY 30, 1928 PUBLISHED NOVEMBER 6, 1928

Introduction

The purpose of this investigation was the determination of the effect of high temperatures upon organic compounds at constant volume.

Numerous experiments have been carried out on decomposition of organic compounds at high temperatures by various methods, such as passing the vapors through hot tubes in the presence of catalysts or by electrical discharge, but, for the most part, these have been carried out under atmospheric pressure. Sealed tubes and autoclaves have been used but these are not designed to withstand extremes of temperature and pressure. Very few experiments have been made at temperatures above 250" and at pressures greater than a few hundred atmospheres. It seemed desirable to study the decomposition of pure organic compounds when heated at constant volume and the consequent pressure at temperatures from 250–525°.[4]

Apparatus and Procedure

The apparatus used in these experiments was designed to withstand a pressure of 20,000 atmospheres at 400°, at which temperature the tensile strength of the chrom-vanadium5 steel used is at a maximum. The design was such that at the weakest place in the structure the wall was three-fourths of an inch in thickness. The bomb which was used was of the same design as that used by Morey[6] except that the chamber was made longer so as to contain 100 cc. A thermocouple well was bored down the center of the plunger to within one-half inch of the reaction chamber. The bomb was heated in an electric furnace which was controlled by means of an automatic regulator? to which the thermocouple was connected, and in series with three lamp-banks, two of which were connected to the regulator through relays. By this means it was possible to maintain any given temperature between 250 and 525°, within ±2° for any desired length of time.

The threads were dusted with graphite, which was used as a lubricant. The bomb was then sealed with a copper gasket and made tight by means of a long handled, double ratchet wrench. The heating was usually for two hours for the initial run, the

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[1] In memory of Ira Remsen.

[2] Presented at the Richmond meeting of the American Chemical Society, April, 1927.

[3] From the Ph.D. dissertation of Lee R. Herndon, June, 1928.

[4] This was made possible by the use of a type of bomb developed in the Geophysics Laboratory and brought to our attention by Dr. F. R. Bichowsky.

[5] Procured from the Midvale Steel Co., Philadelphia, Pa.

[6] Morey, THIS JOURNAL, 36, 215 (1914).

[7] Leeds and Northrup Co., Philadelphia, Pa.

time being lengthened if necessary to effect decomposition. At the desired time the bomb was removed from the furnace and allowed to cool spontaneously to room temperature. It was then set in the holding device, and the wrench applied very slowly until the gaseous products could be heard to escape, then the wrench was quickly removed and the bomb transferred to the water-bath and gas collecting apparatus. This was an inverted 14-liter bottle filled with water. Through the stopper passed a funnel and a tube to discharge the water displaced by the gas. After the gas had escaped the bomb was taken from the bath, dried, opened and the liquid products were removed by means of a pipet. If there were two layers, these were weighed separately. The gaseous products were measured and analyzed and the liquid products subjected to distillation and the products identified as far as possible.

The bombs withstood all pressures to which they were subjected except in one case. In one run with ethylene glycol at 400° the bomb burst. A slit about three inches long opened in the side. The furnace was wrecked but little other damage was done as there were no flying pieces of metal. The bursting was probably due to the thermal expansion of the liquid glycol due to the bomb being too nearly filled with the charge.

Results

Alcohols.—The aliphatic alcohols, methyl-, ethyl-, propyl-, isopropyl-, *n*-butyl-, isobutyl-, *sec.*-butyl-, *tert.*-butyl- and n-amyl-; the aromatic, benzyl- and phenylethyl; and the terpene, fenchyl alcohol have been decomposed by heating at temperatures above 400° for two hours. Temperatures were chosen such that decomposition was not quite complete in this time. All of the above mentioned alcohols yielded a great variety of products. There seem to be two simultaneous reactions: (1) dehydration and subsequent polymerization of the hydrocarbon residues, and (2) dehydrogenation followed by the splitting off of carbon monoxide and then polymerization. Three distinct types of compounds were derived from these decompositions: (1) gaseous, (2) water-insoluble portion, **(3)** water and water-soluble portion.

The gaseous products were analyzed in a number of cases, the results of which are given in the following table.

TABLE I

PERCENTAGE COMPOSITION OF THE GASEOUS PRODUCTS FROM ALCOHOLS

Alcohol	CO_2	CH_4	$CH_2{=}CH_2$	CO	C_2H_6	H_2
Methyl	8.1	41.8	0.8	3.1	..	39.4
Ethyl	10.2	31.8	8.0	7.6	36.6	..
n-Propyl	9.8	36.8	2.0	21.6	..	20.0
Isopropyl	8.6	..	18.4	2.8	51.2	12.6
Benzyl	14.2	4.2	0.6	64.6	..	11.0
Phenylethyl	10.4	5.8	..	44.6	..	33.0
Fenchyl	10.0	32.2	2.4	51.0	..	..

Methyl alcohol gave exceptional results in that no liquid hydrocarbon or insoluble portion was obtained, the products of decomposition being gaseous with the exception of water. Peytral[8] and Ipatiev[9] state that

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[8] Peytral, *Compt.* rend., 165, 703 (1917).

[9] Ipatiev, Ber., **34,** 3579 (1901); **35,** 1047 (1902).

the products are all gaseous, the decompositions taking place according to the following reactions

$$CH_3OH = H_2 + CH_2O \qquad (1)$$
$$CH_2O = CO + H_2 \qquad (2)$$

In the bomb the above reactions appear to be accompanied by hydrogenation. That reaction (2) takes place is proved by the presence of carbon monoxide in the gaseous product; however, the dioxide is present to a greater extent than the monoxide. This may be accounted for by the reaction:

$$2CO = CO_2 + C \qquad (3)$$

which Briner and Wroczynski[10] found to take place at 320–330° and 400 atmospheres.

Ethyl alcohol showed dehydrogenation, dehydration and polymerization of the hydrocarbon residue to compounds of wide boiling range, as shown in Table II, which also shows the density and bromine absorption for each cut.

TABLE II

FRACTIONAL DISTILLATION OF 591 G. OF UPPER LAYER PROM 30 RUNS OF 59 G. EACH OF ETHYL ALCOHOL AT 425° FOR TWO HOURS

Fraction	2'. °C.	G.	Density	Br abs , g. per cc.	Fraction	T, °C.	G.	Density	Br abs , g. per cc.
1	18–30	22	0.6252	0.1122	10	138–160	31	0.7751	0.2019
2	30– 40	24	.6380	.1047	11	160–166	38	,7936	,2188
3	40– 50	32	,6830	.1327	12	166–195	43	.8134	.1927
4	50– 63	107	.7034	.1421	13[a]	90–110	47	.8430	.1627
5	63– 80	22	.7120	,2468	14"	110–130	28	.8509	.1208
6	80– 98	32	.7252	.1701	15"	130–150	15	.8526	.1458
7	98–106	28	.7430	.2262	16"	150–170	15	.8591	.1645
8	106–119	28	.7552	.2337	17[a]	170-200	13	9243	.1533
9	119–138	51	.7647	,2075	18[a]	200-270	15	.9710	.0195

[a] At 15 mm.

Unsaturation was also evident in the gaseous product. This unsaturation cannot be entirely credited to the lack of hydrogen in the decomposition products because the gaseous portion from isopropyl alcohol was even more unsaturated than that from ethyl alcohol and still contained about 12% hydrogen.

Sec.-butyl alcohol was exceptional in so far as no gaseous product was obtained.

Tert.-butyl alcohol was almost completely decomposed when heated at 400° for two hours, yielding nearly the theoretical quantity of water, showing that the primary reaction is dehydration. This was the lowest temperature at which any of the alcohols underwent complete decomposition.

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[10] **Briner and Wroczynski,** *Compt.* **rend., 150,** 1324 (1910).

Benzyl alcohol yielded carbon monoxide as the chief gaseous product. The toluene formed must have resulted from hydrogenation, since both water and hydrogen were present in the final products of the decomposition.

Hydrocarbons.—Normal heptane, the only aliphatic hydrocarbon subjected to 400° for two hours, underwent slight decomposition into simpler products as well as some of more complex character. The simpler products were gaseous, while the most complex were of the character of lubricating oil. The mechanism given by Thorpe and Young[11] for butane is

$$CH_3CH_2CH_2CH_3 = CH_3CH_3 + CH_2{=}CH_2$$

but Pease[12] has shown it to be

$$CH_3CH_2CH_2CH_3 = CH_4 + CH_3CH{=}CH_2 \tag{1}$$

$$CH_3CH_2CH_2CH_3 = H_2 + CH_3CH_2CH{=}CH_2 \tag{2}$$

In the bomb the normal saturated hydrocarbon yields simpler saturated hydrocarbons together with unsaturated hydrocarbons, which under the influence of heat and pressure polymerize to give higher hydrocarbons. Each fraction contained some unsaturates, since each took up an appreciable quantity of bromine.

Benzene is quite stable at 400° and was only slightly decomposed when heated at 500" for two hours. More complete decomposition was effected by heating at 525" for forty-eight hours, but even then the decomposition was incomplete, 27% of the benzene being recovered. With the exception of the hydrogen the decomposition products were solids. Diphenyl, *m*-diphenyl- and *p*-diphenylbenzenes were formed in quantities sufficient for identification, while other products of higher boiling point did not yield readily to the action of solvents or the formation of derivatives.

Toluene decomposed almost completely when heated at 525° for ten hours, with the deposition of some carbon. Distillation of the resulting product indicates the formation of xylenes and a number of isomers with the empirical formula $C_{14}H_{14}$, which boil over the range of 278--300°.

Other aromatic hydrocarbons with side chains, such as ethylbenzene, *iso*propylbenzene, *tert.*-butylbenzene and unsymmetrical diphenylethane behave much as does toluene.

Acids.—Acetic acid at temperatures above 400° decomposes into gaseous products rather than yielding liquid products of varied boiling points, as is shown by the distillation range of the product.

Adipic acid at 450" for three hours breaks down completely into liquid and gaseous products with the deposition of carbon. The liquid portion was in two layers, the upper being a dark brown oil, while the lower layer was colorless and mostly water.

Benzoic acid heated at 400° for two hours yielded a thick, black sub-

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[11] *Thorpe and* **Young,** *Proc. Roy. Soc., 21, 184* (1873).

[12] Pease, THIS JOURNAL. 50, 1779 (1928).

stance which was chiefly undecomposed benzoic acid with a little carbon and some gas as decomposition products.

Citric acid decomposes at 400° into two liquid layers, a large quantity of gas and a little carbon. The upper layer was composed of hydrocarbons, while the lower layer contained acetone, acetic acid and water.

Stearic acid when heated at 400° for two hours gave a pale yellow, soft solid which appeared to be the unchanged acid.

Aldehydes.—Acetaldehyde at 335° for two hours gave two liquid layers of almost equal volume and two liters of gas. The upper layer gave a wide variety of products, as indicated by the boiling range of 55–360". The lower layer distilled over a narrow range, 79–100°, the major portion within the last 5°. The gaseous product contained carbon dioxide, carbon monoxide, unsaturated hydrocarbons and methane.

Benzaldehyde at 400° for two hours gives benzene as the principal product as well as other higher boiling products.

Chloroform.—Chloroform decomposed at 425° yielding chlorine, and possibly hydrogen chloride, with two liquid layers and a pale yellow solid which had the correct melting point for hexachloro-ethane. Work was discontinued on this product because of the corrosive effect of the products of decomposition on the bomb.

Ester.—Ethyl acetate above 400" for two hours decomposes into two liquid layers, a little gas and a small-amount of carbon. The upper layer, consisting mostly of hydrocarbons, had a very wide boiling range, indicating a large number of compounds. The lower layer was chiefly water with some acetic acid formed by hydrolysis and a soluble ferrous salt, possibly the acetate.

Ether.—Diethyl ether decomposes when heated at 400° for two hours yielding acetaldehyde, considerable gas and a liquid distilling over the range of 22–48°.

Glycols.—Ethylene glycol decomposes into two liquid layers and some gas when heated at temperatures considerably below 400°.

Diethylene glycol undergoes almost complete decomposition at 400° for two hours. The products of decomposition consist of some gas and two immiscible liquids. The liquids show a very marked change in character from the original. In addition to having distillation ranges lower than the boiling point of pure diethylene glycol, the lower layer is chiefly water, as is the case with the lower layers of the alcohols, while the upper layer is composed of hydrocarbons of a wide boiling range.

Acetone.—Acetone at 400' for two hours decomposes into two layers, the lower of which is chiefly water and the upper layer of an oily consistency.

Benzophenone.—Benzophenone appears to be quite stable at 400° for two hours.

Phenol.—Phenol is stable at 400° and decomposes only slightly when heated at 525° for two and one-half hours.

Quinol.—Quinol undergoes some decomposition at 400° in two hours. The product from one experiment was not of sufficient quantity to justify attempts at identification.

Sucrose.—Cane sugar gave a black, porous mass when heated at 425° for two hours.

Table III

Summary of Results

Cpd.	Temp., °C.	Time, hours	Charge g.	Product		Gas, liters	Dist. range, °C.	Cpds identified and remarks
				Upper	Lower			
Methyl alcohol	400	2	60	39	..	10	64–100	H_2O, CH_3OH, CO_2, CO, CH_2, H_2
	435	2	50	20	..	Much	.....	
	450	2	60	20	..	15	.....	
	475	2	60	48	..	Much	64– 99	
Ethyl alcohol	425	2	59	17f[a]	15	14.5	Upper, 18–270; lower, 30–102	CH_3COOH, CH_3CHO H_2O, CO, CO_2, CH_4, C_2H_4, C_2H_6
	460	2	59	9f	15	19		
	425[b]	2	59	19.7f	16.7	14.5		
Propyl alcohol	400	2	40	40	..	...	.....	One layer
	415	2	40	29	..	Little	27–115	....
	425	2	40	19f	7	Much	27–105	C_2H_5CHO, H_2O, CO_2, CO, Hz, C_2H_4, CH_4
	425	2	48	30f	7	Much	35–165	
	425	2	60	12f	7	11.5	.....	
*Iso*propyl alcohol	400	2	42	42	..		79– 82	....
	425	2	42	23	..	Little	57–85	....
	425	2	42	3f	29	...	.....	CH_3COCH_3, H_2O, CO_2, C_2H_4, CO, C_2H_6, Hz
	425	8	42	11f	15r	...	.....	
	435	8	42	7f	117		.....	
	465	.	52	16f	16	Much	56–100	
	435	2	60	26f	26	3	35–112	
Butyl alcohol	400	2	40.5	40	..	...	65–119	Colorless liquid, H_2O
	435	2	40.5	21f	4	Much	52–200	
Isobutyl alcohol	400	2	60	42	..	Little	40–112	....
	400	4	60	11f	1	Much	.....	....
	400	16	60	8f	3	Much	.....	....
	425	2	60	7f	2	Much	.....	....
	450	2	60	8f	2	Much	.....	....
	475	2	60	3f	2	18	.....	....
Sec.-butyl alcohol	400	2	41	41	..	None	23–102	C_2H_5OH
	425	2	41	38f	3		.....	....
Tert.-butyl alcohol	400	2	39	20f	11		26–200	....
	300	2	39	26	..		80– 98	f liquid
n-Amyl alcohol	425	2	60	35f	10	5	30–215	H_2O
	450	2	60	38f	5	Little	35–215	....
	450	16	15	7	3	18	.....	....
Benzyl alcohol	425	2	50	38	5	3	78–305	C_6H_6, $C_6H_5CH_3$, BzOH, CO_2, CO, C_2H_4, CH_4, H_2
	425	2	50	43	5	Little	83–100	

Table III *(Continued)*

Cpd.	Temp., °C.	me, rs	Charge	Product		Gas, liters	Dist. range. °C.	Cpds. identified and remarks
				Upper	Lower			
Phenylethyl alcohol	425	2	50	42	6	1.5	60–330	CH_3OH, $C_6H_5CH_3$, CO_2, CH_4, H_2, CO, H_2O
	425	2	50	**43**	6	Little		
Fenchyl alcohol	435	2	75	57.3	1	2.5	30–335	H_2O, CO_2, C_2H_4, CO, CH_4
Acetic acid	350	2	79	49		...	114–118	....
	412	2	79	41	..	3.7	110–118	
Adipic acid	450	3	60	3	15	Much		
Benzoic acid	400	2	15	12	..	Little		....
Citric acid	400	2	50	10	8	Much	.....	H_2O, CH_3COCH_3, CH_3COOH
	250	2	50	14	10	Much	.....	
Stearic acid	400	2	15	15	..	Little		Yellow solid
Acetaldehyde	425	2	60	8	12	Much	. . .	....
	325	2	60	20	17	2	55–360	CO_2, C_2H_4, CO, CH_4
Benzaldehyde	400	2	52	33		Much	81–297	C_6H_6 C_6H_5COOH
	400	2	52	36		Much	81–297	
n-Heptane	400	2	52	29		5	27–295	....
Benzene	400	2	66	55		0.5	68– 80	f liquid
	400	24	66	66			75– 80	f liquid
	450	24	66	50		...	70– 80	f liquid
	500	2	66	63		Little	69– 82	f liquid
	600	.	66	17			250–280	Solid
	500	18	66	60		5.5	70–310	Solid
	500	24	66	66			80–254	f liquid, diphenyl
	525	4	66	65			80–500	f liquid
	525	24	66	59		Little	80–260	Liq., solid diphenyl
	525	48	66	50		Much	80–500	H_2, $C_6H_5C_6H_5$, *m*-$C_6H_4(C_6H_5)_2$, *p*-$C_6H_4(C_6H_5)_2$
	525	48	66	55		Much	80–500	
	525	48	66	58		Much	80–500	
Toluene	400	2	43	43			108–110	....
	500	2	43	43			97–110	....
	525	10	57	54			100–300	C_6H_6
	525	48	57	35			.....	....
Ethylbenzene	400	2	44	43			130–138	....
	400	8	58	54			130–140	....
	450	2	58	51			125–145	....
	450	2	66	66			124–140	....
	450	10	66	66		Little	108–140	....
	450	24	58	27		Much	.....	Solid, 14 g.
	500	2	66	41			97–140	C_6H_6,
	500	2	66	66		Little	105–305	$C_6H_5CH_3$
	500	2	66	62		Little	105–305	
*Iso*propyl benzene	450	3	57	50	..	Little	140–200	
Tert.-butyl-benzene	450	2	59	51	..	Little	105–175	$C_6H_5CH_3$
Diphenyl-ethane	425	16	55	34	..	2		

TABLE III (*Concluded*)

Cpd.	Temp., °C.	Time, hours	Charge g.	Product Upper	Product Lower	*Gas.* liters	Dist. range, °C.	Cpds. identified and remarks
Chloroform	425	2	112	35	23	...	100–109	Cl_2, HCl, C_2Cl_6
Ethyl acetate	400	2	42	19	11	Little	39–178	CH_3COCH_3, CH_3COOH, H_2O, CH_3CHO
	425	2	42	18	9	Little	33–200	
Ether	400	2	36	18	.	Much	22–48	CH_3CHO
Glycol	400	2	64	15	19	13.6	68–101	....
	350	4	84	2	82	1.5	67–205	....
Diglycol	400	2	56	10	14	Much	50– 90	....
	400	2	56	10	24	5	65–101	C_2H_5OH, H_2O
	400	22	56	8	18	Much	.....	....
Acetone	400	2	26	26	..	...	56– 60	....
	400	2	39	30	5	Little	53–170	H_2O
Benzophenone	400	2	37	36	..	...	293–310	....
Phenol	400	2	50	*50*	..	....		....
	500	2.5	50	50	..	...	80–187	....
Quinol	400	2	44	38	..	Little	98–280	....
Sucrose	425	2	15	15	..	...	.....	....

[a] The figures for the third run with ethyl alcohol are the average of those obtained in 30 runs under the same conditions.

[b] f = fluorescent.

Summary

A study has been made of the decomposition of organic compounds at constant volume, constant temperature (between the limits of 300–525°), at consequent pressure and for periods of time ranging from two to forty-eight hours, the temperature and duration of heating depending upon the stability of the compound under investigation.

The following substances have been heated: methyl-, ethyl-, n-propyl-, isopropyl-, n-butyl-, isobutyl-, *sec.*-butyl-, *tert.*-butyl-, *n*-amyl, benzyl-, phenylethyl and fenchyl alcohols; acetic, adipic, benzoic, citric and stearic acids; acetaldehyde and benzaldehyde; n-heptane; benzene, toluene, ethylbenzene, isopropylbenzene, *tert.*-butylbenzene; unsymmetrical diphenylethane; chloroform; ethyl acetate; diethyl ether; ethylene and diethylene glycols; acetone and benzophenone; phenol; quinol; and sucrose.

The products of decomposition have been separated and identified as far as possible.

BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF ANTIOCH COLLEGE]

THE NOMENCLATURE OF PARENT RING SYSTEMS[1,2]

BY AUSTIN M. PATTERSON

RECEIVED JULY 30, 1928 PUBLISHED NOVEMBER 6, 1928

General Principles

1. *Any attempt to construct a strictly logical system of names for the large number of parent ring systems now known seems impractical, at least so far as common use is concerned.* Brief special or "trivial" names (Trivialnamen) for many systems have become well established and have proved their convenience, while systematic names tend to become long and to be complicated with numbers and letters in order to distinguish isomers.

J. J. Sudborough, J. *Indian Inst. Sci.*, *7*, 145–195 (1924); C. A., 19, 825–826, has developed a scheme of nomenclature for ring systems, He names each form by selecting a peripheral ring as a basis and indicating how it is bridged, which is possibly the simplest method that could be chosen. According to his plan the name for what has been called 9,10-diphenylenephenanthrene (a six-ring parent hydrocarbon) is "5B–1:1:22, 2:2:15, 3:3:8, 9:9:14, 16:16:21,-*cyclo*-hexacosa-$\Delta^{4:6\ 10:12:17:19:23:25}$-octene." T. S. Wheeler, Chem. *News*, **126**, 33–35, 49–50, 66–67, 113–115 (1923), proposes to proceed in *a* linear manner from one component ring to another, characterizing each on the way. His name for the compound just mentioned is "hexar-3,4-hexar′-2,3-hexar″-2,3-hexar; 4′,5′-hexar; 4″,5″-hexar." It is hard to imagine that such names as these could ever come into extended use. They might conceivably be employed in a telegraphic code or in some systematic form of indexing.

2. *On the other hand, it would not be wise to coin a special name for each parent compound known.* The number of such names would be large. Ingenuity would be taxed to find names that should aptly characterize each one. Such names make demands on the memory or require access to a reference book, and they throw little or no light on structural relations.

3. *Consequently, any practical system of naming parent ring compounds will be a compromise between brevity and logical system.* A parent compound that has an important family of derivatives or that has become prominent for any other reason should have a name of convenient length. On the other hand, it is an advantage to name ring systems so as to indicate

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[1] In memory of Ira Remsen.

[2] The substance of this article was communicated in manuscript form in March, 1926, to the other members of the Comité de Travail on Organic Nomenclature of the International Union of Pure and Applied Chemistry. It has now been revised for publication, with comments on an article since published by Prof. Robert Stelzner. The writer found, on visiting Hofmannhaus (Berlin) in 1925, that the workers there and those of *Chemical Abstracts* had arrived independently at some of the same ideas, especially as regards the naming of heterocyclic systems, while differing rather definitely on certain points. He takes this opportunity of expressing his appreciation of the cordial attitude and cooperation of Professor Stelzner, Professor Prager, Doctor Kuh and Doctor Stern.

their structure, either as to component atoms (as in "triazole") or as to component rings (as in "benzopyran"). "Triazole" happens to be both brief and systematic. It should be possible to name some compounds in more than one way; for example, it is useful to be able to say that camphane is, 1,7,7-trimethyl-norcamphane and that norcamphane is bicyclo[2.2.1]-heptane. If our names are to be both convenient and logical, there must be some flexibility. In what follows, only the possibilities for systematic naming will be discussed.

4. *Existing* names and usages *should* be conserved in so far as they can be adopted into a *fairly* consistent *general* plan. Nomenclature in use must be reckoned with. No matter what is substituted for it, it will persist for a certain time. The more such confusion can be avoided, the better. Really discredited names will slowly drop out.

5. In general, the *presence* of all the component rings of a ring system should be clearly indicated in its name. It is very easy to disguise the presence of rings by using a prefix denoting a multivalent radical. Thus, thiodiphenylamine suggests two separate benzene rings but actually is the name of a three-ring complex; benzoyleneguanidine contains a two-ring complex; while malonylurea, at first sight an aliphatic compound, is the derivative of a six-membered ring. Such names not only do not express clearly the nature of the ring system; they often prevent a compound from being indexed with other compounds of related structure and they often fail to provide sufficiently for naming derivatives. There are exceptions to the principle stated at the head of the paragraph. Names like malonylurea have their uses and should not be suppressed. Moreover, some compounds, as lactones and acid anhydrides, are more suitably named with reference to the compound from which they are formed than with reference to the cyclic system which they contain, Also, it may at times be desirable to use a multivalent radical prefix to name a bridge, as in 1,4-*imino*-benzene. Nevertheless, the general principle of naming compounds so as to recognize clearly all rings present, unless there is definite reason to the contrary, seems valid.

6. There should be a clear distinction between the *names* of ordinary substituting atoms or radicals and the names of *atoms* or rings used *in* forming the names of parent ring systems. This becomes immediately evident when one attempts to index substances under the names of their parent compounds. "Thio," for example, is used to denote the replacement of oxygen (or sometimes hydrogen) by sulfur; but it may also denote the replacement of methylene by sulfur in *a* ring (as in "thiodiazole"). Similarly, "oxy" may mean replacement of hydrogen by oxygen (or even by hydroxyl), and also the replacement of methylene by oxygen in a ring. In order to avoid confusion with the ordinary meanings of oxy-, thio-, azo-, etc., it is recommended that the forms oxa-, *thia-*, aza-, etc., be employed to indicate the presence of hetero atoms in a ring (the *a* being dropped before a vowel).[3]

Thus one would have thiadiazole, oxadiazole (which is more euphonious than oxdiazole), thiazine, oxazine. Combining forms to indicate the presence of rings in a complex are usually clear enough (for example, benzo-, naphtho-) and not liable to confusion with the names of corresponding radicals (as phenyl, phenylene, naphthyl).

7. *There is a useful analogy between the naming of individual compounds as derivatives of a parent compound and the naming of complex ring systems as derivatives of a less complex parent system.* For example, the names dichloro-ethane and dibenzocarbazole we analogous, even though in the one case there is replacement of hydrogen by chlorine, while in the other case two benzene rings are regarded as having been "fused" with the carbazole complex (a highly theoretical assumption). It is worth while to follow out this analogy (see especially p. **3081**).

8. *With regard to terminations, three general methods of naming parent ring systems are in vogue.* The first is illustrated by such names as ethylene oxide, tetramethylene, hexamethylenetetramine. It consists in juxtaposing the names of the radicals or atoms that make up the system without much regard to consequences, and must therefore be regarded as rather unsatisfactory, especially for naming derivatives. The second is based on analogy with aliphatic hydrocarbons. According to it, saturated carbocyclic systems form names ending in -ane, while unsaturation is indicated by -ene, -diene, etc., depending on the number of double bonds present; examples: cyclopropane, bicyclononene, spiroheptadiene. Such names are convenient and systematic and are much used for non-aromatic systems. The third method, which is used for the great majority of ring

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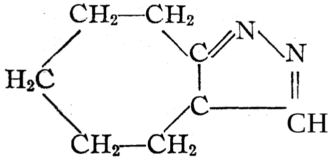
[3] As previously stated, the proposals in this article were made to the Comité de Travail on Organic Nomenclature in 1926. A similar scheme for the use of oxa-, thia-, aza-, etc., was published in the same year by Professor R. J. Stelzner (Literatur-Register der *organischen* Chemie, 5, ix–xv). The *a* endings had previously been used by Bouveault (Ber., 31, 3373 (1898); Beilstein's "Handbuch," 3rd ed., Vol. 4, p. 1 (1899)); Ingold (*J. Chem. Soc.*, 125, 87 (1924)), Sudborough (J. Indian *Inst. Sci.*, 7, 182 (1924)), and probably others.

Both Professor Stelzner and the writer would employ the principle for various classes of heterocyclic ring compounds (see the following pages). It might also be extended to open chains of mixed composition. For example, the compound $CH_3N{=}NNHCH_3$ could be called 2,3,4-triaza-2-pentene, semicarbazide would be 1,2,4-triazabutan-3-one, and $CH_3OCH_2OCH_3$ would be 2,4-dioxapentane. Such a nomenclature would provide much simpler names for certain polyethers, polysulfides, etc., than we have at present; this is mentioned merely to show its possibilities. The same idea has already been used to some extent for aliphatic silicon compounds (for example, siliconpremium, $C_8H_{20}Si$).

The use of such forms as thiona-(–SO–) and sulfona-(–SO_2–) in making ring names does not seem advisable. It would be better to use thia-(–S–) and treat the sulfoxides and sulfones as oxides of the fundamental form, systems, assigns to unsaturated hydrocarbons the ending -ene, no matter what the degree of unsaturation, and to heterocyclic compounds such endings as -ine, -ole and -an. This system has arisen largely in connection with aromatic and quasi-aromatic compounds, in which a stage of low saturation is looked on as the fundamental form, as naphthalene, pyrrole, furan. Increasing stages of saturation are usually represented by "hydro" or "hydride" names (as, dihydronaphthalene) but in some cases by special endings (as, pyrroline, pyrrolidine). Although the last two methods are to some extent contradictory,[4] a continuation of both seems inevitable.

Simple Carbocyclic Rings (Class A I)[5]

The Geneva names for monocyclic saturated hydrocarbons, namely cyclopropane, cyclobutane, etc., and also the corresponding names cyclopropene, cyclobutadiene, etc., have been well accepted. They are unquestionably superior to the older names such as trimethylene, and they also seem to be preferred to Zincke's names (R-pentene, etc.), which are seldom seen nowadays. The "cyclo" names are clear and systematic and they correlate cyclic with aliphatic compounds. Nevertheless, it should be pointed out that these names are unlike those of the majority of ring systems (see p. 3076). There is a chemical reason for this in the distinction between aromatic and non-aromatic properties. It would, however, conduce to uniformity of cyclic names and numberings if we had, for example, a basal name for cyclopentadiene and named cyclopentene and cyclopentane as the dihydro and tetrahydro compound, respectively. The "cyclo" names do not yield very convenient prefixes for use in naming complex systems. For instance, derivatives of the compound exist, and it has been called "cycloheptanopyrazole" by its discoverer. Less saturated stages would presumably be called "cycloheptenopyrazole," "cycloheptadienopyrazole," etc. Thus there is a multiplication of prefixes and parent forms, which does not occur with benzo-, naphtho, pyrrolo-, etc. In the *Chemical* ***Abstracts*** indexes the form of lowest saturation, that is, cycloheptatrienopyrazole, has been called "cycloheptapyrazole" and the more saturated forms are treated as hydro derivatives, but the name is not altogether satisfactory, as it might be taken to imply the combination of seven pyrazole rings into one grand cycle. There is therefore a certain lack due to the



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[4] For a discussion of one difficulty caused by their conflict, see Patterson, THIS JOURNAL, 47, 553–554 (1925).

[5] The classification is that adopted in "Proposed International Rules for Numbering Organic Ring Systems," THIS JOURNAL, 47, 543–561 (1925).

absence of brief names for cyclopropene, cyclobutadiene, cyclopentadiene, cycloheptatriene, etc.

Simple Heterocyclic Rings (Class A II)

About a dozen three-membered heterocyclic rings are known. Those that are named at all are given such titles as ethylene oxide, hydrazimethylene (see general principle 8, p. 3076); there is no systematic way of naming them. Almost the same is true of the four-membered rings, of which there are about two dozen. Some are called trimethylene oxide, trimethylene sulfide, etc.; others are called betaine, thetin and "phosphorbetain." Hale[6] has coined the name "urete" for a four-membered parent ring, $C_2H_2N_2$, and the Chemical *Abstracts* indexes, following this lead, have adopted *-ete* as an ending for other four-membered rings (azete, triazete).

For five-membered rings proposals made by Widman,[7] Bouveault[8] and others have found their way into use. The ending *-ol* or -ole appears in such names as pyrrole, imidazole and even dioxole (which is non-nitrogenous). It conflicts with the ending *-ol* for alcohols and phenols (hence the modified spelling -ole), but its use to denote a five-membered ring is well known. Perhaps the most easily understood names are those that prefix to this ending syllables denoting the kind and number of hetero atoms present, thus: diazole, triazole, thiodiazole (better, thiadiazole). The suffixes -oline and -olidine are in use for the hydrides of these rings (as pyrroline, pyrrolidine).

In the field of six-membered rings are found names corresponding to the above systematic names for five-membered rings, but with the suffix *-ine* or *-in* replacing -ole (or -ol), as: triazine, oxazine, thiodiazine, dioxin (the latter being non-nitrogenous). Thus the ending -ine (or -in), although regarded as properly the ending for bases, has a specific sense in which it indicates a six-membered ring. For rings of more than six members there is no system in use, beyond names like trimethylene tetrasulfide, diethylene tetrasulfide, trimethylene-ethylenediamine, etc. (see general principal 8, p. 3076). Crowther, McCombie and Reade[9] have used the name "dioxazseptane" for a seven-membered ring.

Such is the present state of affairs. Convenient special names like pyrrole, thiophene and pyridine are not likely to be displaced, but systematic names are needed for many simple heterocyclic systems. In what **way** can progress be made? Ingold[10] has proposed to form names according to the first method mentioned under general principle 8 (p. 3076), as trimethyleneimine, oxatrimethylene (trimethylene oxide), 1,3-dioxadi-

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[6] Hale, THIS JOURNAL, 41, 376 (1919).

[7] Widman, J. *prakt. Chem.*, [2] *38*, 189 (1888).

[8] See Beilstein's "Handbuch," 3d ed., Vol. 4, p. 1.

[9] Crowther, McCombie and Reade, J. *Chem. Soc.*, *105*, 933–947 (1914).

[10] Ingold, ibid., 125, 87-88 (1924).

imine. He deals with four-membered rings only, but the same principle could of course be extended. The objections to the plan are that the names are made up of names of radicals and atoms and therefore do not present the parent ring systems clearly as entities (see general principle 5, p. 3075), that hydrogenation or dehydrogenation changes the names rather profoundly, and that the names do not lend themselves well to indexing or to the formation of prefixes for naming more complicated forms. Stelzner[11] would use the combining forms oxa-, thia-, etc., referred to under general principle 6 (p. 3075), prefixing them to *the* name of *the carbocyclic form* of the same number of members and same saturation. Thus, ethylene oxide would be oxacyclopropane; pyrrole would be aza-5-cyclopentadiene-1,3. This plan has much to recommend it, being easy to understand and apply. It should at least prove useful in systematic works of reference. The disadvantages of the method are: *(a)* the names of bases are not given a characteristic ending, but terminate like those of the hydrocarbons. This might perhaps be obviated by arbitrarily adding the ending -ine. Thus, ethylenimine might be called, not azacyclopropane but azacyclopropanine. (b) Tautomeric compounds such as pyrrole, isopyrrole and pyrrolenine (which Stelzner calls, respectively, aza-5-, aza-1- and aza-2-cyclopentadiene-1,3) do not have the same number for the hetero atom. This could be remedied easily by assigning varying positions to the double bonds, and in the writer's opinion this would be preferable, as chemists are accustomed to regard the position of the hetero atom as fixed. Stelzner, however, does not favor this solution and it could not well be applied to complex systems like indole and pseudo-indole (belonging to Class B; see p. 3084). (c) The names tend to be rather long and do not yield convenient combining forms if these should be desired for naming complex systems.

An alternative method would be to improve and extend the existing practice of using characteristic *syllables* to indicate the *number* of members in the ring. In spite of objections that might be urged against it, this method furnishes many neat names and combining forms (as triazole, triazolo-, oxazine, oxazino-). With a precedent already set for et (four members, compare "tetra") and with *ol* (five members) and in (six members) already confirmed by usage, it would only be necessary to supply three syllables more to cover all but rare cases. These might be *ir* (from "*tri*," reversed) for three members, ep (from "*hepta*") for seven members, and oc (from "octa") for eight members. The series could be extended if desired by selecting on (from "nonus") for nine members, and *ec* (from "*deca*") for ten members. Some of these syllables are not acceptable as *endings* because of prior use (for example -ol for alcohols) but they may be used in the middle of a name without objection. Examples of the resulting names and combining forms are: oxirene, oxirane (ethylene oxide),

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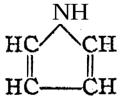
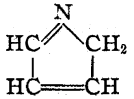
[11] Stelzner, "Literatur-Register der organischen Chemie," 5, ix–xv (1926).

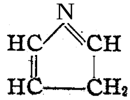
ox*iro*-, azetine, azeto-, oxetane (trimethylene oxide), oxeto-, tetrazepine, tetrazepo-, 1,2,4,6-tetrathi*ep*ane (trimethylene tetrasulfide), s-tetrazocanine (tetramethylene tetramine), 1,3,5-triaz*oc*anine (parent substance of acetonylbiuret). In the last two cases the ending -ine (characteristic of names of bases) has been attached to names that would otherwise have terminated in -ane. The wide use that such names have attained in the five- and six-membered series illustrates the fact that an extremely compact systematic name is often better than either a more extended systematic name or an arbitrarily coined special name.

Order of Hetero Elements.—In the "Rules for Numbering,"[12] the order of hetero elements is determined according to a descending order of groups in the periodic table and an ascending order of atomic numbers in each group. This results in the following order for commonly occurring hetero elements: O, S, Se, Te, N, P, As, Sb, Si, Sn, Pb, Hg. A majority of names in the literature conform to this order (cf. oxazine, thiodiazine), but not all (cf. thioxole). In the judgment of the writer it is better than an order based on valence, since the latter is a variable property. It is important that changes in valence, hydrogenation, etc., should not affect names and numberings profoundly.

Distinguishing Isomers.—Various methods are now employed to distinguish isomeric heterocyclic rings, among which may be mentioned: Arabic numerals (e. g., 1,2,4-oxdiazole), Roman letters (e. g., pyrro[ab]-diazole), Greek letters (e. g., γ-pyran), abbreviations denoting structure (e. g., as-triazine), prefixes (e. g., isothiazole), suffixes (e. g., pyrrol*enine*), and different special names (e. g., pyrazole and imidazole). In important cases the isomers should probably have different names; in the others Arabic numerals indicating the positions of the hetero atoms seem to be clearest, though sometimes a little cumbrous. The numerals are often made to indicate at the same time the position of methylene groups when this is necessary. It would be well, however, to reserve some prefix, preferably *iso*-, to indicate isomerism caused by change in position of hydrogen. For example, if the two isomers of pyrrole had not already established names they might be called, respectively, 2- and 3-isopyrrole


Pyrrole


2-Isopyrrole
(*Iso*pyrrole)


3-*Iso*pyrrole
(Pyrrolenine)

Complex Ortho-Fused Ring Systems (Class B)

Many systems of this class have well recognized special names, as naphthalene, phenanthrene, quinoline. Where such names do not exist it is

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[12] Patterson, This journal, 47, 545 (1925).

customary to build up names from the simpler systems which may be regarded as present in the complex system to be named, as benzo-pyran. As the Meyer-Jacobson "Lehrbuch"[13] points out, there is no generally observed system for doing this. Certain principles may, however, be laid down (some of these are corollaries of general principle 7, p. 3076):

(1) Other things being equal, the largest component having a simple name is to be taken as the parent form, to which the other rings or complexes are regarded as being attached. Thus we would naturally say "pyridocarbazole," not "carbazolopyridine."

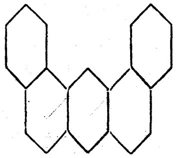
(2) A heterocyclic component is to be preferred to a carbocyclic as the parent form, even though smaller. Thus we say "naphtho-thiophene," not "thiophenonaphthalene."

(3) A nitrogenous component, if present, is preferred as the parent form, in order that the name of the system may have a termination indicating a base. Thus it is customary to say "furo-pyrrole" not "pyrrolofuran."

(4) No ring in the complex system should be expressed more than once in the name of the complex.[14]

Thus, "naphthacridine" most appropriately designates a five-ring system composed of a naphthalene complex and an acridine complex, united by ortho fusion. The name has been used (unwisely, as it seems to the writer) to designate a four-ring system in which a naphthalene complex and an acridine complex exist, to be sure, but having one benzene ring in common; in other words, there is overlapping and this benzene ring is expressed twice in the name. Meyer and Jacobson[14b] also disapprove of the overlapping method ("the Grabe-Skraup use of prefixes") and favor the non-overlapping plan (of Hantzsch and Widman).

(5) Like components should be treated alike if possible. Thus, for the system



the name "dibenzanthracene" would be chosen in preference to "naphthophenanthrene" (this is analogous to the choice of "diphenyhethane" in preference to "benzylbenzene)."

(6) Other things being equal, the parent form should be so chosen as to make the "substituents" as simple as possible. Like (5), it would lead to the name "dibenzanthracene" in preference to "naphthophenan-

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[13] Meyer and Jacobson, "Lehrbuch der organischen Chemie," 1920, Vol. 2, Part 3, p. 31.

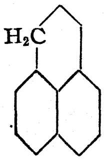
[14] (a) Cf. Patterson, **This Journal, 39, 1632** (1917); (b) Meyer and Jacobson, 1920, Vol. **2**, Part 3, pp. 31–32, 1105.

threne." This principle is questionable, since it might lead to longer names, for brevity is of great importance in naming ring systems.

(7) For each important "substituent" component there should be a recognized prefix. In general this would be formed from its name with use of o as final vowel; as, pyrrolo-, pyridino-, fluoreno-. Some well established contractions should be accepted, as anthra-, benzo-, naphtho-, but none that is ambiguous; thus, it would be better not to use pyrazo- at all but to employ the more exact pyrazolo- and pyrazino-. It should be noted that the prefix pheno- or phen- has been used to indicate *two* benzene rings (as in phenazine, phenoxazine) and also in other ways (as in phenanthrene, phenobarbital); the natural conclusion is that "benzo" should always be used when one wishes to denote the attachment of a single benzene ring by ring fusion.

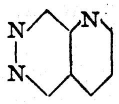
(8) In accordance with the aromatic nature of the compounds, the basal names of ring systems of this class are usually given to the least saturated form, stages of greater saturation being named as hydro derivatives or hydrides. In the writer's opinion it is well to adhere to this rule even when a non-aromatic ring is a component of such a system. For instance, it seems simpler to have one combining form "cyclopenta-" or "cyclopento-" for the five-membered carbon ring than to attempt to distinguish between cyclopentano-, cyclopenteno- and cyclopentadieno- when this ring is attached, say, to a quinoxaline complex (cf. "cycloheptano-pyrazole", p. 3077). The whole system can be reduced to lowest hydrogenation and hydro derivatives indicated.

(9) The true names of components should be used in forming the name of the complex system. This statement seems obvious yet it is frequently disregarded in practice. For example, the system



has been called *peri*-naphthindene, yet it does not contain the indene structure as a component; it is *peri*-benzonaphthalene.[15]

Again, the form



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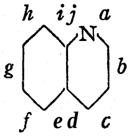
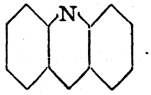
[15] Meyer and Jacobson and Stelzner and Kuh have sought to avoid naming "peri" systems in the same manner as ordinary ortho-fused systems because the two classes are not isomeric; e. g., *peri*-benzonaphthalene is $C_{13}H_{10}$, while the ordinary benzonaphthalenes (anthracene and phenanthrene) are $C_{14}H_{10}$, but the writer feels that any advantage gained by distinguishing the two classes by such prefixes as benzo- and benzi-, or benzo- and benzolo-, are at least offset by corresponding drawbacks.

is not a benzotriazine, even though it is an isomer of those systems; it is a pyridopyridazine.

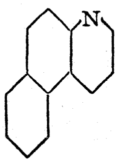
Distinguishing Isomers.—As in the case of simple heterocyclic rings, isomers in the complex ortho-fused systems are at present distinguished in a very opportunist way: by numbers, by Roman, italic or Greek letters, by prefixes (as iso-, pseudo-, lin-, ang-), by different special names, etc. Here again the more important isomers may well have names of their own (as anthracene and phenanthrene). For the other cases there should be some general system. Following out the analogy of general principle 7 (p. 3076), it would seem that such a system should be based on the numbering of the "parent" component[16] and that of the "substituent" components The "Rules for Numbering"[17] would furnish a standard for this purpose. The following plan is suggested: for the numbering of the "substituents" retain their Arabic numerals; for the numbering of the "parent" component start with the side 1,2 and letter the sides of the complex with Greek, or rather (since chemists seem to be less and less familiar with that language), small italic or Roman letters. Letter every side, even where there are no numbered positions, as fusion may occur on any side. Then use only such of these symbols as are needed to indicate where the fusion has occurred. Place them in the heart of the name, as Baeyer did in naming the "bicyclo" compounds, so as to avoid confusion with other symbols. A few examples will make the plan clear:



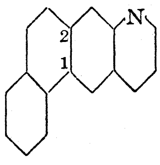
Quinoline



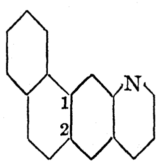
Benzo[*b*]quinoline (Acridine)



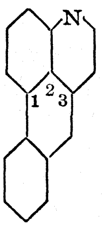
Benzo[*f*]quinoline



Naphtho[1,2-*g*]quinoline



Naphtho[2,1-*g*]quinoline



Naphtho[3,2,1-*d e*]quinoline

As all six positions on the benzene ring are equivalent, it is not necessary to introduce numbers in the benzoquinoline names. In the last three examples the order of the numbers (1,2 and 2,1, etc.) indicates whether

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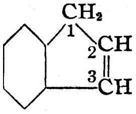
[16] Cf. Bally and Scholl, *Ber.*, **44**, 1662–1665 (1911).

[17] Patterson, THIS JOURNAL, 47, 543–561 (1925).

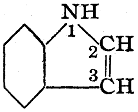
the numbering of the "substituent" (naphthalene) travels *with* or against that of the "parent" on the side where fusion occurs.[18]

This method of distinguishing isomers has been experimented with in the indexes to *Chemical* Abstracts and has been found satisfactory and of very general application. It applies to "peri" systems, in which case more than one letter is used (see the last example on p. 3083), and to the rare spiro systems of this class.

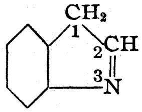
Use of the Aza-, Thia-, etc., Names.--For heterocyclic systems of this class, Stelzner proposes to use the same method as already described (p. 3079), that is, basing the name on the corresponding carbocyclic form and using prefixes to indicate the hetero atoms. The plan has the same advantages and disadvantages as outlined above (p. 3079), with two additional considerations. The first is, that it does not remove the necessity for coining names for the carbocyclic compounds, which must still be handled by some other method. The second and more serious consideration relates to the effect of the plan on complex ring systems differing only as to the position of hydrogen atoms. The remedy suggested on page 3079 cannot be applied here. Indole, for example, would be (if the "Rules for Numbering" are followed) aza-1-indene, while ordinary pseudo-indole (indolenine) would be aza-3-indene.



Indene



Aza-1-indene
(Indole)



Aza-3-indene
(Indolenine)

This causes the numberings of the two systems to become quite different, although they are desmotropes. Chemists would naturally much prefer that the nitrogen atom retain the number 1 in both cases.

Simple Bridged Systems (Class C I)

Carbocyclic Systems.—The method proposed by Baeyer[19] for naming and numbering the carbocyclic systems of this class has been adopted into general use. One very slight change could be made to advantage, namely, reversing the order of the figures in the middle of the name: e. g., bicyclo[0,1,3]hexane would become bicyclo[3,1,0]hexane. As Baeyer himself remarked, the order of these figures is not significant; but the decreasing order is in accord with Baeyer's numbering of the system and also is the appropriate one in Class C III (see p. 3086).

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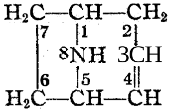
[18] The orientations here given are intended to show relationship to quinoline. Each ring system has, according to the "Rules for Numbering," an orientation and numbering of its own and the symbols in the heart of the name (in brackets) have nothing to do with this.

[19] Baeyer, Ber., 33, 37714775 (1900).

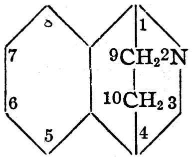
Heterocyclic Systems.—The "Rules for Numbering" extend the Baeyer method to heterocyclic systems, choosing as low numbers as possible for the hetero atoms. Such systems are named conveniently by using the prefixes "aza-," "oxa-," etc., in connection with the Baeyer names for the corresponding carbocyclic forms, as the difficulty about tautomers referred to under Class B (see p. 3084) does not arise. Thus, nortropidine



may be called aza-8-bicyclo[3,2,1]octene-3; or, if it seems desirable to have all such compounds appear together under "Bicyclo-" in an index, it may be called bicyclo[3,2,1]-az-8-octene-3. If the characteristic ending for the names of bases be added, the termination would be changed from "-octene-3" to "-octen-3-ine."

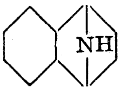
Complex Bridged Systems

Systems Related to Class B.—The "Rules for Numbering" have distinguished as "Class C II" a small class of parent compounds which may be regarded as formed by throwing a bridge or bridges across an ordinary ortho-fused system of Class B (naphthalene, anthracene, quinoline, etc.). These systems, when not too complex, may be suitably named by prefixing the name of the bridge to the name of the corresponding Class B form. Thus, the system



would be named ethyleno[1,4]isoquinoline. It is questionable whether the more complicated members of this class will ever need to be named as parent compounds.[20]

It should be remarked that the plan just proposed does not give to bases names ending in -ine if the nitrogen is in the bridge. For example the system



would be imino[1,4]naphthalene. On this account it might be better in such cases to indicate the bridge last and choose the name naphthalen-[1,4]imine.

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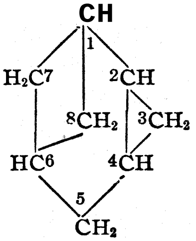
[20] See some of the formulas given under Class C II in This Journal, 47, 559 (1925).

Tricyclo and Tetracyclo Systems (Class C **III**)

These systems are numbered, in the "Rules for Numbering," by a simple extension of the Baeyer method. If these rules are adhered to, names similar to the Baeyer names for bicyclic systems can be given to them, with these differences: (1) the name must now begin "**tricyclo**" (or, rarely, "tetracyclo," etc.) and (2) the additional bridge or bridges must be designated as to number of members and position. This can most simply be done by inserting additional numbers in the middle of the name, with indices to show where the bridge ends are **attached**.[21] For example, the system

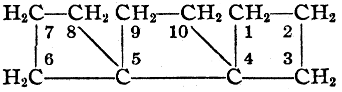


may be called **tricyclo**[4,1,1,$0^{2,4}$]**octane**, the zero denoting that the additional bridge contains no atoms and the "2,4" showing where it is attached. It will now be seen why the *decreasing* order of announcing these numbers was preferred on a previous page (3084).

Heterocyclic systems of this class would be named in exactly the same manner as the simple heterocyclic bridged systems (see p. 3085).

Simple **Spiro** Systems (Class D I)

Simple spiro systems containing one or more spiro atoms can be given names similar to those of the bridged systems. For example, the system



could be called **spiro**[3,0,3,2]**decane**, the figures denoting the numbers of members in the bridges between spiro atoms, in the order in which the "Rules for Numbering" number the system. The number of figures in the brackets is equal to twice the number of spiro atoms present. Perhaps it would be better to say bi- (or di-) **spiro**[3,0,3,2]**decane** in the above case and trispiro- when three spiro atoms are present, and thus make the names still more analogous to those of the Baeyer compounds.[22] An advantage of using simply spiro- in all cases is that these compounds will then all be found in one place in indexes (as may be seen in the indexes to *Chemical Abstracts*).

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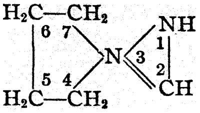
[21] Such indices were proposed by Buchner and Weigand, ***Ber.***, 46,2110–2113 (1913). They are here used in a slightly different and (the writer believes) clearer manner.

[22] See Radulescu, ***Ber.***, 44, 1023–1024 (1911).

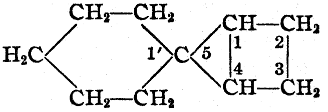
Hetero atoms may be indicated in the same way as recommended for bridged systems. Thus, the system



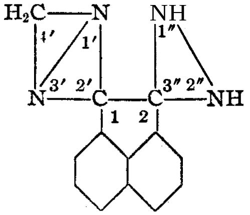
would be called spiro[2,4]diaza-1,3-heptene-2 (or -hepten-2-ine).

Complex Spiro Systems (Class D II)

These systems contain other unions in addition to the spiro unions and are numbered provisionally in the "Rules for Numbering." They may be given corresponding names by juxtaposing the names of the components after the prefix "spiro" and indicating which is the common atom. For example, the system



would be spiro-bicyclo(2,1,0)pentane[5,1′]cyclohexane, while the unusually complex system



would be spiro-acenaphthene[1,2′]bicyclo(1,1,0)diaza-1′,3′-butane[2,3″]-hydrazimethylene. If such a compound should prove of importance as a parent substance a special name should be coined for it, as has been done for fluoran.

Additional References

Beesley and Thorpe, J. *Chem. Soc.,* 117, 591–598 (1920); Béhal, *Bull. soc. chim.,* [4] 11, 264–275 (1912); Beilstein, "Handbuch," 3d ed., Vol. 4, pp. 1–2 (1899); Borsche, *Ann.,* 377, 71–78 (1910); Bredt, *Ann.,* 292, 123 (1896); Bredt and Savelsberg, *J. prakt. Chem.,* 97, 1–22 (1918); Grignard, *Chem.-Ztg.,* 34, 941 (1911); *Bull. soc. chim.,* [4] 11, 124 (1912); Richter, *Ber.,* 29, 586–608 (1896); Stelzner and Kuh, *Literatur-Register der organischen Chemie,* 3, 13–100 (1921).

Summary

Several general principles are formulated for the correct naming of parent ring systems. The individual classes of ring systems are then considered. The present state of their nomenclature is presented, the more promising methods for forming their names are discussed, and some new proposals are submitted.

Yellow Springs, Ohio

[CONTRIBUTION FROM THE LABORATORY OR ORGANIC CHEMISTRY, MASSACHUSETTS AGRICULTURAL COLLEGE]

THE PREPARATION OF COMPOUNDS OF THE TYPE OF MALACHITE GREEN AND OF PHENOLPHTHALEIN BY MEANS OF THE GRIGNARD REACTION[1]

BY JOSEPH S. CHAMBERLAIN AND MALCOLM F. DULL[2]

RECEIVED JULY 30, 1928 PUBLISHED NOVEMBER 6, 1928

Malachite Green Type

Baeyer and Villiger[3] used the Grignard reaction for preparing *p*-aminotriphenylcarbinol from paminobenzoic acid methyl ester and phenylmagnesium bromide and also from *p*-aminobenzophenone and the same Grignard reagent. At the same time they prepared numerous related compounds, including the dye Malachite Green, which resulted from the reaction between phenylmagnesium bromide and Michler's ketone, 4,4-tetramethyldiaminobenzophenone. Votocek and Matejka[4] prepared alkoxy derivatives of Malachite Green by the reaction between Michler's ketone and magnesium compounds of ring-halogenated phenol ethers and also from the esters of anisic acid by reaction with the Grignard reagent made from p-bromodimethylaniline. Gilman and Schulze[5] made use of the formation of colored products from Michler's ketone as a qualitative test for Grignard reagents.

Thus the preparation of Malachite Green itself by the Grignard reaction is well established, and also the formation of the Grignard reagent from p-bromodimethylaniline. However, the preparation of the latter seems to have been difficult and uncertain for Baeyer and Villiger[3] were unable to obtain it in their efforts to make methyl violet. Sachs and Ehrlich[6] successfully prepared the Grignard reagent from p-bromodimethylaniline by activating the magnesium with ethyl bromide and Baeyer[7] prepared Grignard reagents from o-, *m*- and p-iododimethylaniline by activating the magnesium with iodine. Hurd and Webb[8] prepared and used the Grignard reagent from *p*-bromodimethylaniline in making *p*-dimethylaminophenylmethylcarbinol. The formation of magnesium compounds with halogen derivatives of other tertiary amines was also studied by F. and L. Sachs.[9]

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[1] In memory of Ira Remsen.

[2] The results presented in this paper represent a part of the material contained in the thesis presented by Mr. Dull to the Graduate School of the Massachusetts Agricultural College, June, 1928, for the degree of Master of Science.

[3] Raeyer and Villiger, *Ber.*, 36,2794 (1903).

[4] Votocek and Matejka, *Ber.*, 46, 1755 (1913).

[5] Gilman and Schulze, THIS JOURNAL, 47, *2002* (1925).

[6] Sachs and Ehrlich, *Rer.*, 36, 4296 (1903).

[7] Baeyer, *Ber.*, 36, 2759 (1903).

[8] Hurd and Webb, THIS JOURNAL, 49,546 (1927).

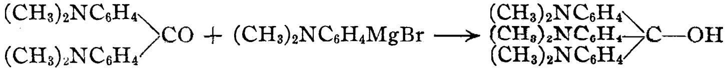
[9] Sachs and Sachs, *Ber.*, 37,3088 (1904).

The first part of the present investigation concerns the preparation of the Grignard reagent from p-bromodimethylaniline, by Sachs and Ehrlich's or Baeyer's method of activating the magnesium, and the reaction of this reagent with Michler's ketone, resulting in the formation of methyl violet, and also the preparation of the Grignard reagent from *p*-bromobenzoic acid and its reaction with Michler's ketone to the formation of chrome green.

Experimental

As a preliminary experiment Malachite Green was prepared in the same manner in which Baeyer and Villiger made it by the reaction of phenylmagnesium bromide on Michler's ketone. The carbinol was obtained in good yield, purified and analyzed. It was also converted into its salts. All of the results identified the product as Malachite Green, thus corroborating the work of Baeyer and Villiger.

Methyl Violet.—This compound, being the hexamethyltriaminotriphenylcarbinol, if possible of preparation by the Grignard reaction as attempted by Baeyer and Villiger, should result from Michler's ketone by reaction of the Grignard reagent obtained from *p*-bromodimethylaniline.



$$\begin{matrix}(CH_3)_2NC_6H_4\\(CH_3)_2NC_6H_4\end{matrix}\Big>CO + (CH_3)_2NC_6H_4MgBr \longrightarrow \begin{matrix}(CH_3)_2NC_6H_4\\(CH_3)_2NC_6H_4\\(CH_3)_2NC_6H_4\end{matrix}\Big>C—OH$$

Michler's ketone Grignard reagent Methyl violet (carbinol)

The p-bromodimethylaniline was prepared and identified, and from it the Grignard reagent was obtained by the following procedure, activating the magnesium by Sachs and Ehrlich's method.

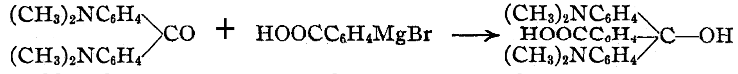
One and three-tenths grams of magnesium turnings was placed in a 150cc. flask and an ethereal solution of 8 g. of ethyl bromide added. The ether used in all cases was specially prepared for use in making Grignard reagents by drying over phosphorus pentoxide, and during reactions was protected from outside moisture by tubes of calcium chloride. The ethyl bromide used was specially purified also.

The flask containing the mixture of magnesium and ethyl bromide was then connected with a reflur condenser carrying a calcium chloride tube at the top. A crystal of iodine was now added to the contents of the flask. After the reaction had continued for three or four minutes, the bulk of the liquid was rapidly decanted and an ethereal solution of 12.5 g. of p-bromodimethylaniline added in its place. The new mixture was then warmed gently on the steam-bath and in a very short time a vigorous reaction began. When the magnesium had all dissolved the contents of the flask were cooled and 15 *g.* of Michler's ketone was added through the condenser tube. The flask was then again warmed for an hour. The ether layer in the flask became deep red in color and a gummy solid was deposited. After cooling, the ether layer was decanted and evaporated. A gummy, almost black mass separated which, in water, yielded an intense violet color. This product was hydrolyzed by boiling with water and after drying yielded 9.0 g. The ether-insoluble product that remained in the flask proved to be unchanged Michler's ketone and amounted to 7.0 g. **A** part of the product obtained from the ether solution was converted into the chloride salt, and also into the double salt of zinc chloride, yielding characteristic products with brilliant turkey bronze coloration. Its water solution gave a deep violet color. The original carbinol was then purified by recrystallization from alcohol and analyzed with the following results.

Anal. Calcd. for $C_{25}H_{31}N_3O$: C, 77.07; H, 8.03; N, 10.79; O, 4.11. Found: C, 77.06; H, 7.65; N, 10.36; O (by diff.) 4.93.

There seems to be no doubt, therefore, that a reactive Grignard reagent may be prepared from p-bromodimethylaniline and that with Michler's ketone it yields methyl violet.

Chrome Green.—This dye, being the p-carboxy derivative of Malachite Green, should result by the Grignard reaction from Michler's ketone and the Grignard reagent obtained from p-bromobenzoic acid.



$$\begin{matrix}(CH_3)_2NC_6H_4 \\ (CH_3)_2NC_6H_4\end{matrix}\!\!>CO + HOOCC_6H_4MgBr \longrightarrow \begin{matrix}(CH_3)_2NC_6H_4 \\ HOOCC_6H_4 \\ (CH_3)_2NC_6H_4\end{matrix}\!\!>C{-}OH$$

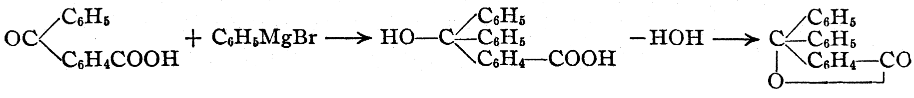
Michler's ketone Grignard reagent from p-bromo-benzoic acid Chrome green (carbinol)

The preparation of the Grignard reagent from p-bromobenzoic acid was unsatisfactory, though various methods of activating the magnesium were tried. It was found, however, that on the addition of Michler's ketone a noticeable sea-green color was produced. The ether solution contained enough of this color product to dye wool mordanted with potassium dichromate (a property of chrome green dye) a permanent sea-green color. It was not possible, however, to obtain a sufficient quantity of this compound to afford identification other than the qualitative one just mentioned.

Phenolphthalein Type

To study the Grignard reaction for the preparation of compounds of the type of phenolphthalein, it was decided to attempt the preparation of phthalophenone (diphenylphthalide) from o-benzoylbenzoic acid.

According to Beilstein [4th ed., Vol. VII, p. 828] the reaction of phenylmagnesium bromide upon esters of this ketone acid results in the formation of o-dibenzoylbenzene. This product is obtained by the reaction of one molecule of the Grignard reagent with the carboxyl carbonyl of the ester. If, however, the phenylmagnesium halide should react with the ketone carbonyl, then phthalophenone should result by the loss of water from the o-carboxytriphenylcarbinol, which would be the direct product of the Grignard reaction.



$$OC\!\!<\!\begin{matrix}C_6H_5 \\ C_6H_4COOH\end{matrix} + C_6H_5MgBr \longrightarrow HO{-}C\!\!<\!\begin{matrix}C_6H_5 \\ C_6H_5 \\ C_6H_4{-}COOH\end{matrix} \quad -HOH \longrightarrow C\!\!<\!\begin{matrix}C_6H_5 \\ C_6H_5 \\ C_6H_4{-}CO\end{matrix}\ (O\text{ bridging C and CO})$$

o-Benzoylbenzoic acid o-Carboxytriphenylcarbinol Phthalophenone

Ostersetzer[10] studied this reaction but was unable to obtain phthalophenone as "only an oily reaction product" resulted. He did, however, ob-

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[10] Ostersetzer, *Monatsh.*, 34, 795 (1913).

tain methylphenylphthalide, analogous to phthalophenone (diphenylphthalide) by using methylmagnesium iodide instead of phenylmagnesium iodide.

Experimental

A preliminary attempt to effect a reaction between *o*-benzoylbenzoic acid itself and one molecule of phenylmagnesium bromide resulted in failure, practically all of the acid being recovered unchanged. The direct product formed was unquestionably the magnesium salt or the magnesium halide double salt of the acid.

The procedure was then modified by using double molecular quantities of the Grignard reagent. Five and four-tenths grams of magnesium turnings was placed in a one-liter flask, to which was then added 200 cc. of dry ether and 40 g. of bromobenzene. The reaction was started in the usual manner. After it had ceased and the contents of the flask had cooled, an ethereal solution of 20 g. of o-benzoylbenzoic acid was added slowly and with constant shaking. The flask was connected with a reflux condenser and heated for about thirty-six hours. It was then cooled and the ether solution filtered off with suction. After being washed several times with dry ether, the residue was dried over sulfuric acid in a vacuum. When the last traces of ether had been removed, the solid product was treated with about 200 cc. of water containing about 20 cc. of sulfuric acid and kept cool under running water. A rather vigorous reaction took place with the formation of a solid mass of yellow, gummy material. This was treated four times with boiling water in order to remove any traces of unchanged benzoylbenzoic acid. After drying, it was extracted with petroleum ether to remove any bromobenzene. It was then recrystallized three times from hot alcohol.

The compound thus obtained was difficultly soluble in cold alcohol but easily in hot, from which it crystallized in leaflets melting at 115°. This is the melting point of phthalophenone while that of dibenzoylbenzene is 145". It was soluble in ether, benzene, acetone, concentrated sulfuric acid and hot alcoholic alkali, from which latter solution it was reprecipitated by diluting with water and acidifying. It was insoluble in water, petroleum ether, aqueous alkali and concentrated hydrochloric acid. After several careful tests no oxime could be obtained on treating the substance with hydroxylamine, thus indicating that it was not a ketone.

An analysis was made for carbon and hydrogen and the molecular weight was determined by the freezing-point method using benzene as the solvent. The results obtained are as follows.

Anal. Calcd. for $C_{20}H_{14}O_2$: C, 83.89; H, 4.93; O, 11.18; mol. wt., 286.2. Found: C, 83.99; H, 5.14; O (by diff.) 10.87; mol. wt., 277.5.

As dibenzoylbenzene and phthalophenone are isomers, the above molecular weight determination and analysis would apply equally well to either. The properties, however, as given above do not agree with those given for dibenzoylbenzene, but are those of phthalophenone. It seems reasonable to conclude, therefore, that the product obtained was phthalophenone.

Summary

Grignard reagents were prepared from *p*-bromodimethylaniline and (qualitatively) from p-bromobenzoic acid. These reagents yielded with Michler's ketone dyes of the Malachite Green type, namely, methyl violet and chrome green.

The Grignard reagent, phenylmagnesium bromide, reacts with *o*-benzoylbenzoic acid in the proportion of two molecules to one, with the formation of phthalophenone and not dibenzoylbenzene.

AMHERST, MASSACHUSETTS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

PSEUDO BASES AND THEIR SALTS IN THE ISOXAZOLE SERIES. SECOND PAPER[1]

BY E. P. KOHLER AND N. K. RICHTMYER

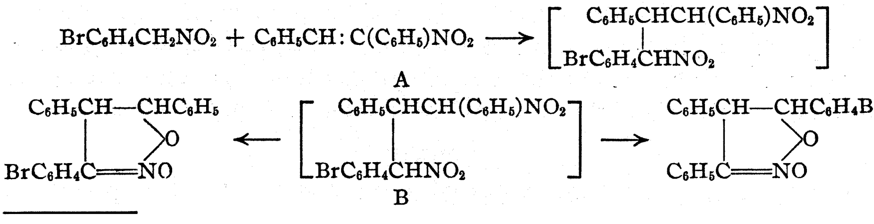
RECEIVED AUGUST 2, 1928 PUBLISHED NOVEMBER 6, 1928

In the first paper[2] it was shown that when the salts that are obtained by methylating triphenyl isoxazole are treated with bases they undergo a series of transformations which can be represented by the sequence

$$\text{Salt} \rightleftharpoons \text{base} \rightleftharpoons \text{pseudo base} \longrightarrow \text{anhydro compound}$$

Owing to the instability of the base and the pseudo base it was possible to isolate only the first and last members of this series, and it was impossible to establish the structure of the pseudo base, the anhydro compound and their derivatives because all of these substances contain three groups which are the same. We have now found that some of these difficulties can be avoided by alkylating with ethyl instead of with methyl sulfate and that most of the others can be overcome by substituting bromophenyl for one of the phenyl groups.

The change from methylation to ethylation presented no complications but the preparation of a substance which differs from triphenyl isoxazole only in having a substituent in one of the phenyl groups proved to be exceedingly troublesome. No isoxazoles of this type are known and no intermediates are available for making them by any of the methods employed in the preparation of triphenyl isoxazole. Since all methods which hold any promise of success are equally likely to give a mixture of isomers we decided to undertake the preparation of the p-bromo compounds by way of the isoxazoline oxides.[3] To this end we condensed p-bromophenyl nitromethane with nitrostilbene. It was to be expected that this condensation would give a mixture of two isoxazoline oxides



$$BrC_6H_4CH_2NO_2 + C_6H_5CH{:}C(C_6H_5)NO_2 \longrightarrow \left[\begin{matrix} C_6H_5CHCH(C_6H_5)NO_2 \\ | \\ BrC_6H_4CHNO_2 \end{matrix}\right]$$

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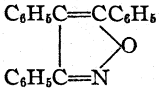
[1] In memory of Ira Remsen.

[2] Kohler and Blatt, THIS JOURNAL, 50, **1217 (1928).**

[3] Kohler and Barrett, *ibid.*, 46, 2105 **(1924).**

Instead of the two oxides expected we actually obtained three, because some of the nitrostilbene is hydrolyzed and the resulting phenylnitromethane leads to the formation of a small quantity of the unbrominated triphenyl isoxazoline oxide. The separation of this mixture is not feasible; the oxides crystallize indistinctly and since they decompose below the melting point, it is impossible to ascertain whether or not any method of crystallization really results in separation. The mixture of oxides was therefore boiled with alcoholic sodium methylate and thus transformed into a mixture of the corresponding isoxazoles: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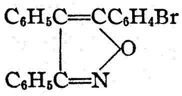
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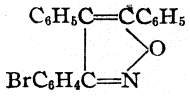
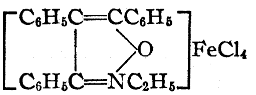

III

These isoxazoles crystallize fairly well, and they have definite melting points but apparently they are capable of forming mixed crystals in all proportions. The attempt to separate at this stage was, therefore, abandoned. The isoxazoles were ethylated and then transformed into a mixture of ferric chloride salts containing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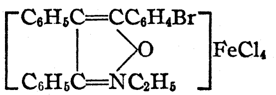
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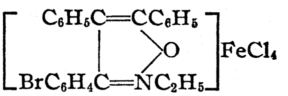
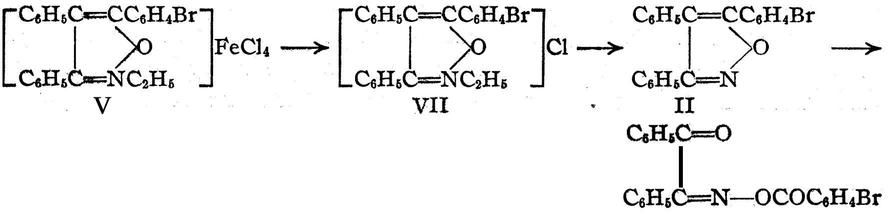

VI

By systematic fractional crystallization of this mixture it was possible to isolate one salt which crystallized well from a number of solvents, had a sharp melting point and appeared to be a pure substance. This contained bromine and therefore was either V or VI but inasmuch as the salts are not attacked by ozone it was necessary to convert it into the corresponding isoxazole in order to establish its structure. The isoxazole proved to be 3,4-diphenyl-5-*p*-bromophenyl isoxazole (II) because it formed an ozonide that on hydrolysis gave the p-bromobenzoate of *β*-benzilmonoxime.


V VII II VIII

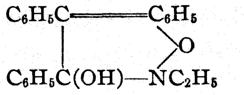
As a result of these operations we now had available for investigation the salt IV, which was easily obtained in a pure condition by ethylation of triphenyl isoxazole, and the salt V which was free from its isomer but—to judge from the analytical results—generally contained a small quantity of the unbrominated compound. We also had a supply of the salt VI which was sufficiently pure for most purposes but always contained appreciable quantities of the unbrominated compound and was not entirely free from its isomer.

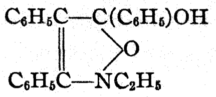
These salts are not attacked by ozone, either in water or in organic solvents—a property which serves to distinguish them as well as the corresponding salts with other acids from all the substances into which they can be transformed. They are readily oxidized by permanganate, both when suspended in water and when dissolved in acetone. Since the salt which has the bromophenyl group in the 5-position gives *p*-bromobenzil and benzoic acid, while that in which the same group occupies the 3-position is oxidized to benzil and *p*-bromobenzoic acid, this reaction with permanganate supplies a reliable means for determining the structure of salts of this type.

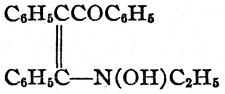
When any one of these salts is added to caustic alkalies in the presence of ether, ferric hydroxide is precipitated and all of the organic matter is immediately found in the ether. Under these conditions, therefore, the change from salt to pseudo base appears to be direct and instantaneous. But when a salt is treated with barely enough cold, saturated sodium bicarbonate to precipitate all of the iron, it yields a clear, colorless, strongly basic solution which contains nothing that can be extracted with ether. This strongly alkaline solution must contain the true base in equilibrium with its carbonates. At low temperatures such solutions remain clear for days but all ultimately become cloudy and deposit the pseudo base and all attempts to concentrate such solutions by evaporation or freezing invariably end in pseudo base. It is not possible, therefore, to isolate any substances corresponding to quaternary ammonium bases; increase in concentration of the hydroxyl ions more than compensates for the effect of lowering the temperature in decreasing the rate of formation of the pseudo bases.

While these pseudo bases are readily formed by the action of alkalies on the salts, they are not easily isolated. It was possible, however, to obtain in pure crystalline form those corresponding to salts IV and V. They are quite insoluble in water, readily soluble in organic solvents. Acids dissolve them slowly but even very dilute acids extract them rapidly and completely from their solutions in organic solvents. Like the pseudo bases derived from unsaturated cyclic amines, they readily form ethers which behave toward acids exactly like the bases themselves.

The pseudo bases and their ethers also behave alike toward oxidizing agents. Aqueous permanganate does not attack them but they are rapidly oxidized in acetone, and unlike the salts they are also easily ozonized. All methods of oxidation yield essentially the same products. Thus the pseudo base corresponding to the unbrominated salt IV invariably gives benzoic and acetic acids and benzil; but permanganate also forms variable quantities of acetaldehyde, while ozone gives some nitrogenous compound. The oxidation products, unfortunately, do not distinguish between all possible formulas of the substance. These are


IX

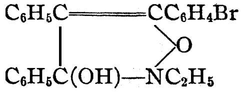

X

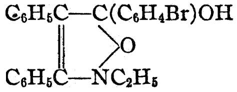


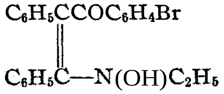
$$\begin{array}{l} C_6H_5CCOC_6H_5 \\ \quad \| \\ C_6H_5C{-}N(OH)C_2H_5 \end{array}$$

XI

Each of these formulas represents a substance which by a combination of oxidation and hydrolysis could give benzil and benzoic acid. In the case of the pseudo base from the brominated salt V the results are somewhat more helpful. Here the oxidation products are bromobenzil, benzoic and acetic acids, and the possible formulas


XII


XIII



$$\begin{array}{l} C_6H_5CCOC_6H_4Br \\ \quad \| \\ C_6H_5C{-}N(OH)C_2H_5 \end{array}$$

XIV

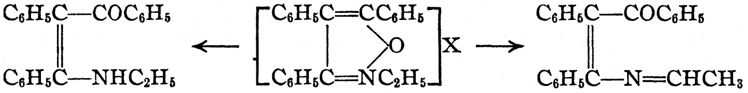
Since the first of these formulas cannot be reconciled with the formation of bromobenzil, this type of formula is definitely excluded for the pseudo bases of the triphenyl isoxazole series.

Between the remaining formulas it is probably impossible to distinguish by chemical methods. Indeed it is not at all improbable that they represent two phases of the same substance which can coexist in solution. Either formula is satisfactory for interpreting the reactions of the pseudo bases but in order to gain an insight into the mechanism by which these substances are formed it is desirable to secure some compound which is formed in a similar manner but has a group less mobile than hydroxyl or methoxyl. With this end in view we treated the chloride with a sulfinate and later with a sulfocyanide but in each case obtained only the corresponding salt. Soluble cyanides formed a cyanogen compound that is not a salt but this proved useless for our purpose because it behaved exactly like the pseudo base and its ether, the cyanogen group disappearing in every reaction.

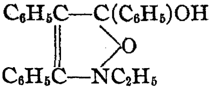
Since the experiments involving the interaction of soluble salts showed fairly conclusively that it would not be possible to secure the desired type of compound in this manner, it became necessary to resort to metallic derivatives. In a well-conceived series of investigations, Freund[4] showed that the salts of unsaturated cyclic ammonium bases differ much in their behavior toward organic magnesium compounds. Some react very readily; others not at all; but whenever a reaction does occur, the product is always a substance that is constituted like the corresponding pseudo base, the hydrocarbon residue occupying the position of the hydroxyl group.

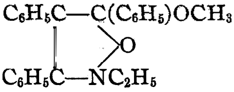
[4] Freund, *Ber.*, 37, 4666 (1904); Freund and Beck, *Ber.*, 37, 4673, 4679 (1904); Freund and Richard, *Ber.*, 42, 1101 (1909); Freund and Bode, *Ber.*, 42, *1746* (1908).

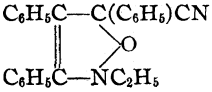
We found that our chloride reacts slowly with methyl magnesium iodide and that the ferric chloride double salt reacts very smoothly both with methyl magnesium iodide and with phenyl magnesium bromide. In each case, however, the reaction is quite different from that described by Freund: chlorine is removed, hydrogen is introduced, and the product is an open chained amine—XV. Still another type of reaction occurs between the chloride and sodium malonic ester in benzene, but here again the product (XVI) does not meet our needs because it is not constituted like the pseudo bases.


XV XVI

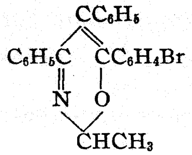
In the absence of definite proof it is necessary to base a choice between the two possible types of formulas for the pseudo bases and the substances constituted like them on circumstantial evidence. Even this is slight. The open chained amine XV, the analogous methyl, and isopropyl compounds, the corresponding unsubstituted amine as well as its more complicated substitution products are all yellow in color while the pseudo base, its ethers and the corresponding cyanogen compound are colorless. This invariable difference would hardly be expected if the difference in structure were not greater than that represented by the possible open chained formula of the pseudo base (XI) and the established formula of the amine (XV). Although this evidence is not conclusive—and could not be tested because we were unable to replace the remaining amino hydrogen in the yellow compounds with anything else—we nevertheless deem it sufficiently significant to make us prefer the cyclic formula for the colorless compounds. We shall therefore represent these substances with the formulas.


X

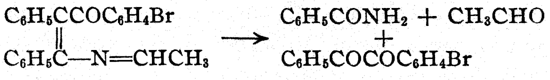

XVII


XVIII

All of these colorless compounds differ notably from the corresponding derivatives of pyridine and other similar unsaturated cyclic nitrogen compounds in stability. Above the melting point and in solutions containing traces of a base they lose water, alcohol or hydrocyanic acid and pass into an "anhydro compound." In the earlier paper the structure of these anhydro compounds was left in doubt. It has now been established with certainty by ozonizing the substance that is formed when the brominated pseudo base loses water. The ozonization products—p-bromobenzil, acetaldehyde and benzamide—definitely exclude the cyclic formula XIX and prove that the substance must be constituted like a Schiff base XX.



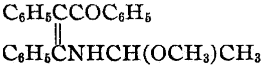
XIX



$$\begin{array}{l} C_6H_5CCOC_6H_4Br \\ \| \\ C_6H_5C{-}N{=}CHCH_3 \end{array} \longrightarrow \begin{array}{c} C_6H_5CONH_2 + CH_3CHO \\ + \\ C_6H_5COCOC_6H_4Br \end{array}$$

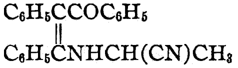
XX XXI

These anhydro compounds are, as would be expected, very actively unsaturated. They combine with alcohols to form alkoxyl compounds that are isomeric with the ethers of the pseudo bases, with hydrocyanic acid to form cyanogen compounds isomeric with those formed from the salts, and with Grignard reagents to form unsaturated secondary amines.



$$\begin{array}{l} C_6H_5CCOC_6H_5 \\ \| \\ C_6H_5CNHCH(OCH_3)CH_3 \end{array}$$

XXII



$$\begin{array}{l} C_6H_5CCOC_6H_5 \\ \| \\ C_6H_5CNHCH(CN)CH_3 \end{array}$$

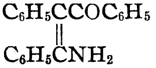
XXIII

$$\begin{array}{l} C_6H_5CCOC_6H_5 \\ \| \\ C_6H_5CNHCH(CH_3)_2 \end{array}$$

XXIV

These addition reactions are promoted by bases. Since the ethers and cyanides are sensitive even to traces of base, they show a marked tendency to undergo a rearrangement that ends in yellow amines which constitute the final products of the action of basic reagents on the salts. These amines are always due to secondary reactions but, inasmuch as the changes follow each other in rapid succession, they are easily mistaken for primary products. Thus only the colorless methyl ether (XVII) is formed when slightly less than the equivalent quantity of sodium methylate is added to the chloride in methyl alcohol, but when slightly more than one equivalent is added the sole product is the yellow amino compound XXV.

Another manner in which the active unsaturation of the anhydro compounds manifests itself is in the ease with which they are hydrolyzed. In the presence of traces of acid all of them rapidly pass into the corresponding amines



$$\begin{array}{l} C_6H_5CCOC_6H_5 \\ \| \\ C_6H_5CNH_2 \end{array}$$

XXV

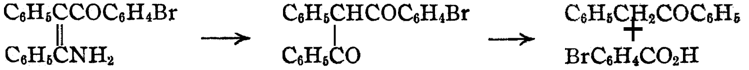
$$\begin{array}{l} C_6H_5CCOC_6H_4Br \\ \| \\ C_6H_5CNH_2 \end{array}$$

XXVI

$$\begin{array}{l} C_6H_5CCOC_6H_5 \\ \| \\ BrC_6H_4CNH_2 \end{array}$$

XXVII

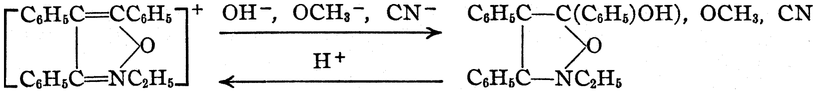
In the presence of more concentrated acid the process does not stop even here but gives first a β-diketone and finally a monoketone and an acid



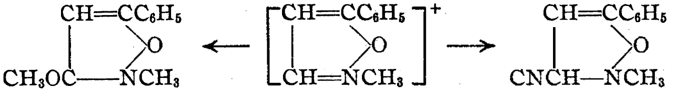
$$\begin{array}{l} C_6H_5CCOC_6H_4Br \\ \| \\ C_6H_5CNH_2 \end{array} \longrightarrow \begin{array}{l} C_6H_5CHCOC_6H_4Br \\ | \\ C_6H_5CO \end{array} \longrightarrow \begin{array}{c} C_6H_5CH_2COC_6H_5 \\ + \\ BrC_6H_4CO_2H \end{array}$$

A survey of these transformations explains the precautions that are necessary for securing the pseudo bases of the isoxazole series. If the ether that is used is not entirely free from alcohol, the base becomes contaminated with its ethyl ether or the corresponding isomeric amino compound. These prevent it from crystallizing promptly. As it tarries in the solution it begins to lose water and form the anhydro compound. If the ethereal solution is carefully protected this may ultimately crystallize, but the solution generally catches a trace of acid from the air, turns yellow and finally ends by depositing an equivalent quantity of the amine, which is stable under these conditions and crystallizes well.

It is difficult to compare our results with those of earlier investigators who have studied other isoxazoles because since no pseudo bases have heretofore been isolated, it is frequently impossible to distinguish between primary and secondary products. In the triphenyl isoxazole series the first step is probably a direct union of ions to form the undissociated pseudo bases, their ethers or cyanides and the process can easily be reversed.



The same process seems to occur in the case of the salts formed from 3-methyl isoxazole,[5] and 3-phenyl isoxazole,[5] for, although owing to the difference in the number of substituents, the final products obtained from these substances are quite different from ours they appear to be formed from the same type of pseudo base. The salts from 5-methyl isoxazole[6] and from 5-phenyl isoxazole,[7] however, must form a different pseudo base, because such final products as $CH_3COCH_2C(CN){=}NCH_3$, $C_6H_5COCH_2C(OCH_3){=}NCH_3$ and $C_6H_5COCH_2C(CN){=}NCH_3$ can come only from substances that are formed by adding the negative ion in the 3-position



The factors that determine the mode of addition of these ions, therefore, appear to be the same as those which determine the mode of addition in reactions that are not usually supposed to involve ions.

Experimental Part

I. Results Obtained with Triphenyl Isoxazole. A. Cyclic Compounds

Three classes of cyclic compounds were investigated: salts, the pseudo base, and substances which are formed by metathetical reactions of the salts but are constituted like the pseudo base. The distinction between these metathetical products and the salts which are isomeric with them was, in all cases, based on the behavior toward ozone. The salts are not attacked by ozone, while all these other cyclic compounds are readily ozonized.

Ethylation, the Ferric Chloride Double Salt, IV.—Ethyl sulfate was added to triphenyl isoxazole by heating a mixture containing 100 g. of the former and 25 g. of the latter at 120° for five hours. In order to decompose the excess of reagent and

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[5] Mumm, "Dissertation," Kiel, 1902.

[6] Claisen, *Ber.*, 42, 67 (1909); Mumm and Bergell, *Ber.*, 45, 3040 (1912).

[7] Mumm and Munchmeyer, *Ber.*, 43, 3355 (1910).

convert the addition product into a simple salt, the solution was digested on a steam-bath for an hour with 50 cc. of concd. hydrochloric acid diluted with an equal volume of water. The resulting clear solution was cooled, thoroughly extracted with ether and then treated with excess of 1:1 aqueous ferric chloride. This precipitated a pale yellow salt which was washed—first with 1:1 concd. hydrochloric acid and then with ether—and dried to constant weight on a steam-bath; yield 42.0 g. instead of 44.1 g. calculated.

Although the salt was practically pure, it was recrystallized from ethyl bromide, from which it separates in pale yellow plates melting at 165–167°.

Anal. Calcd. for $C_{23}H_{20}ONCl_4Fe$: C, 52.7; H, 3.8; Fe, 10.7. Found: C, 51.9; H, 3.7; Fe, 10.9.

The salt is very soluble in acetone, moderately soluble in ethyl bromide and in glacial acetic acid, sparingly soluble in water and alcohol, insoluble in ether.

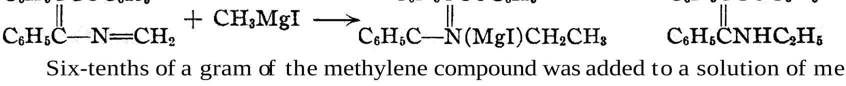
Oxidation.—A current of ozone was passed for six hours through solutions of 2 g. of the salt in water and in ethyl bromide but in each case all of the salt was recovered. A solution of potassium permanganate was then added gradually and in excess to one gram of the salt which was partially dissolved and partially suspended in 50 cc. of water. Each addition of reagent produced a violet colored precipitate—the permanganate—which rapidly turned brown and the odor of acetaldehyde soon became perceptible. On completion of the oxidation the mixture was decolorized with bisulfite and extracted with ether. From the ethereal solution sodium carbonate extracted 0.2 g. of benzoic acid and a trace of acetic acid. The solution was then dried and evaporated. It left 0.31 g. of benzil.

Reaction with Grignard Reagents.—Two g. of the salt was added to a solution of methyl magnesium iodide made from 1 g. of magnesium. The salt reacted at once and the solution became black. It was immediately poured into cracked ice, the ethereal layer separated and the mixed hydroxides extracted with ether until they were free from organic material. The combined ethereal solutions on drying and evaporation deposited a single substance which crystallized in yellow prisms and melted at 118–119°.

Anal. Calcd. for $C_{28}H_{21}ON$: C, 84.4; H, 6.4. Pound: C, 84.5; H, 6.5.

The composition of the product corresponds to that of a substance which has hydrogen in place of the $FeCl_4$ group and the color indicated that it was an open chained compound. It was therefore hydrolyzed. This was accomplished by dissolving 1 g. in 10 cc. of boiling methyl alcohol, adding a few drops of concd. hydrochloric acid to the solution, then diluting it with hot water to incipient cloudiness and setting it aside until it became colorless. The colorless crystalline compound which separated was collected on a filter and identified as phenyl dibenzoyl methane by comparison with a sample on hand. The filtrate was thoroughly extracted with ether and then evaporated to dryness. It left a colorless, hygroscopic hydrochloride that crystallized in needles and melted at 78–79°, the melting point of ethylamine hydrochloride.

Synthesis.—In an earlier paper,[2] it was shown that organic magnesium compounds combine with anhydro compounds to form the magnesium derivatives of unsaturated secondary amines. If, as seemed probable from its hydrolysis products, our yellow compound is a secondary amine of this type, then it should be possible to synthesize it from the anhydro compound described in the earlier paper



$$\begin{array}{l} C_6H_5CCOC_6H_5 \\ \quad \| \\ C_6H_5C{-}N{=}CH_2 \end{array} + CH_3MgI \longrightarrow \begin{array}{l} C_6H_5CCOC_6H_5 \\ \quad \| \\ C_6H_5C{-}N(MgI)CH_2CH_3 \end{array} \quad \begin{array}{l} C_6H_5CCOC_6H_5 \\ \quad \| \\ C_6H_5CNHC_2H_5 \end{array} \qquad XV$$

Six-tenths of a gram of the methylene compound was added to a solution of methyl magnesium iodide containing 0.5 g. of magnesium. The mixture was stirred for fifteen minutes and then decomposed with ice. The ethereal layer gave a product which crystallized in yellow prisms, melted at 117–119° and caused no depression of the melting point of the product from the salt.

Ethyl-1,2-diphenyl-2-benzoyl-vinylamine, XV, is formed with equal ease by the action of methyl magnesium iodide and phenyl magnesium bromide on the ferric chloride double salt. The chloride does not react with phenyl magnesium bromide and it reacts only very slowly with methyl magnesium iodide but it forms the same product as the more soluble ferric chloride double salt.

The Pseudo Base, 2-Ethyl-3,4,5-triphenyl-5-hydroxy Isoxazoline, X.—The pseudo base was obtained in various ways of which the most convenient was as follows. To a solution of 8 g. of sodium hydroxide in 40 cc. of water were added in succession 25 cc. of alcohol-free ether, 50 g. of ice and 8 g. of finely ground ferric chloride double salt. The mixture was shaken for ten minutes, after which the ethereal layer was removed and the aqueous layer extracted a few more times with ether. All ethereal solutions were then combined, dried with sodium sulfate and concentrated under diminished pressure. The result was an oil which solidified when diluted with petroleum ether and rubbed. The yield was 4.5 g. of pseudo base and a residue of base mixed with a small quantity of anhydro compound.

Anal. Calcd. for $C_{23}H_{21}O_2N$: C, 80.5; H, 6.1. Found: C, 80.6; H, 6.4.

The substance is readily soluble in all organic solvents except low-boiling petroleum ether; it is insoluble in water. Unless solid is available for inoculation, it tends to separate from solution as an oil and when this is allowed to remain in contact with the solution it slowly loses water. It is most readily purified by dissolving it in benzene and diluting this solution with petroleum ether. It then crystallizes in colorless prisms. When heated rapidly in a capillary tube it melts with effervescence at about 120".

Oxidation.—The pseudo base does not reduce cold aqueous permanganate. In acetone the permanganate is reduced, slowly at first, then as rapidly as added; the products are the same as those obtained from the salts. A current of ozonized oxygen was passed for two hours through a cold concentrated solution of 2 g. of the pseudo base. It precipitated a pasty ozonide which was decomposed with water. The resulting oily emulsion, on distillation with steam, yielded 0.5 g. of benzoic acid and 1.1 g. of benzil, and it left a small quantity of a red nitrogenous residue.

Salt Formation.—By shaking an ethereal solution of the pseudo base with an inadequate amount of an acid it is possible to get an aqueous solution of the corresponding salt. From such a solution of the chloride, ferric chloride regenerates the double compound, while potassium chlorate precipitates a moderately soluble salt, potassium bromide, and bromine a very sparingly soluble perbromide and potassium permanganate a violet colored permanganate. At low temperatures and in the presence of acid the permanganate persists for a time but ultimately it turns brown and passes into benzil, acetaldehyde, ammonia and potassium benzoate. Its formation accounts for the fact that the salts are oxidized by permanganate while they are not attacked by ozone or chromic acid.

Metallic Derivatives.—Although the pseudo base is insoluble in aqueous alkalies, it is capable of forming easily hydrolyzable metallic derivatives. Thus when a solution of a salt is added to cold concd. sodium hydroxide it first imparts a yellow color to the solution and then, as the quantity is increased, produces an oily yellow precipitate. The color of both oil and solution fades on dilution with water and when the suspension is shaken with ether the oil disappears and both the ethereal and the water layers become colorless. The ether contains only pseudo base, the water only inorganic compounds.

Slightly less than the calculated quantity of powdered sodium was added to a solution of *2* g. of the pseudo base in absolute ether. Hydrogen was evolved and the sodium slowly changed to a lemon yellow, crystalline powder. This was thoroughly washed with ether, dried and analyzed.

Anal. Calcd. for $C_{23}H_{20}O_2NNa$: Na, **6.3.** Found: Na, **6.2, 6.4.**

Reaction **with** Methyl Magnesium Iodide.—A quantitative determination showed that one mole of the pseudo base reacts with **3** moles of methyl magnesium iodide and liberates **2** moles of gas. In accordance with this it was found that the product of the reaction is the same as that formed from the anhydro compound.

The Methyl Ether, **2-Ethyl-3,4,5-triphenyl-5-methoxy** Isoxazoline, **XVII.**—The ethers are easily made by dissolving the pseudo base in alcohols but it is more convenient to prepare them directly from the ferric chloride double salt. Thus the methyl ether was obtained by exactly the same procedure that was employed for making the pseudo base, except that methyl alcohol was substituted for most of the water. Much of the ether crystallized during the operation. This was redissolved by repeated extraction with ether. In order to prevent premature crystallization, a little acetone was added to the ethereal solution, which was then distilled to a small volume. The product was purified by recrystallization from acetone and methyl alcohol; yield 17 g. instead of a possible **18.4** g. from **27** g. of the double salt.

Anal. Calcd. for $C_{24}H_{23}O_2N$: C, **80.7;** H, **6.4.** Found: C, **80.7;** H, **6.5.**

The methyl ether crystallizes in small prisms and melts at 100°. It is readily soluble in acetone, moderately soluble in methyl alcohol and in ether. As would be expected, the ether is more stable than the pseudo base but above 150° it effervesces freely as it loses methyl alcohol and passes into the anhydro compound. It is oxidized by permanganate under the same conditions and in the same manner as the pseudo base and it also gives the same products when it is ozonized. Concentrated aqueous sodium hydroxide does not attack the ether but methyl alcoholic solutions that contain the merest trace of base soon become yellow and ultimately all of the ether is changed into the same yellow methoxyl compound that is formed by adding methyl alcohol to the anhydro compound. Since the ether behaves toward acids exactly like the pseudo base, is stable and is easily made and purified, it constitutes the most convenient intermediate for the preparation of soluble salts.

The Cyanide, **2-Ethyl-3,4,5-triphenyl-5-cyano Isoxazoline, XVIII.**—Dry hydrogen chloride was passed into a cooled solution of **5** g. of the methyl ether in absolute ethyl ether until the precipitation of the crystalline chloride was complete. The chloride was collected on a filter, washed with dry ether and dissolved in water. The slightly acid solution was neutralized and then treated with a solution of **3** g. of sodium cyanide in **10** cc. of water. The resulting paste was extracted with ether, the ethereal solution dried with sodium sulfate, concentrated under diminished pressure and diluted with low-boiling petroleum ether. It deposited the cyanogen compound in colorless prisms which after recrystallization melted at 89°; yield, **4.1** g.

Anal. Calcd. for $C_{24}H_{20}ON_2$: C, **81.8;** H, **5.7.** Found: C, **81.5;** H, **5.9.**

The cyanogen compound behaves toward permanganate, ozone and acids exactly like the methyl ether. At the melting point it loses hydrocyanic acid with effervescence and passes into the anhydro compound. It is exceedingly soluble in organic solvents. The ethereal solution soon smells of hydrocyanic acid and if it is allowed to stand for some time in a closed vessel the cyanide gradually changes into an isomeric compound.

B. The Open Chained Compounds

'She anhydro compound and the substances that are obtained from it by addition or hydrolysis constitute a class of compounds with properties entirely different from those of the cyclic compounds. All of the latter are readily converted into each other and all are also easily transformed into the anhydro compound, but neither the anhydro compound itself nor any of its derivatives or addition products can be changed into one of the cyclic compounds. The distinction between the two classes, therefore, presents no difficulties.

The Anhydro Compound, Ethylidene-α,β-diphenyl-β-benzoyl-vinylamine, $C_6H_5COC(C_6H_5)=C(C_6H_5)N=CHCH_3$.—The anhydro compound is formed from the pseudo base by loss of water, from the methyl ether by loss of alcohol and from the cyanogen compound by loss of hydrocyanic acid. Owing to the ease with which it is hydrolyzed, it is difficult to get a pure product by any procedure. In order to avoid this hydrolysis as far as possible it is important to decompose these substances at the lowest possible temperature, to remove the volatile product as rapidly as possible and to crystallize the residue without undue contact with the air of the laboratory.

Thus 4 g. of the pseudo base was heated at 120° under 3 mm. pressure for ten minutes, at the end of which time effervescence ceased. The residue was dissolved in the minimum quantity of alcohol-free ether, the solution immediately diluted with an equal volume of petroleum ether and cooled in a freezing mixture. It deposited 3.2 g. of yellow needles melting at 105°. After several recrystallizations the melting point rose to 110° but the substance was still quite yellow. Rapid solution in methyl alcohol followed by immediate chilling in a freezing mixture finally gave needles which were almost colorless and melted at 112°.

Anal. Calcd. for $C_{23}H_{19}ON$: C, 84.7; H, 5.8. Found: C, 84.9; H, 5.9.

The anhydro compound is readily soluble in all organic solvents except low-boiling petroleum ether. Although it combines with alcohol it can be recrystallized from methyl alcohol provided that this is entirely free from bases. It reduces permanganate and it is readily ozonized.

α-Methoxyethyl-α,β-diphenyl-β-benzoyl-vinylamine, $C_6H_5COC(C_6H_5)=C(C_6H_5)NHCH(OCH_3)CH_3$.—When the anhydro compound is dissolved in boiling methyl alcohol which contains a trace of base, the solution almost immediately turns yellow and in a comparatively short time a pale yellow addition product begins to crystallize. The same substance is formed with equal rapidity by similar treatment of the cyanogen compound (XVIII) and, more slowly, also from the methyl ether (XVII). It was purified by recrystallization from methyl alcohol, from which it separates in yellow plates melting at 140°. Above the melting point it loses methyl alcohol and reverts to the anhydro compound.

Anal. Calcd. for $C_{24}H_{23}O_2N$: C, 80.7; H, 6.4. Found: C, 80.6; H, 6.5.

α-Cyano-ethyl-α,β-diphenyl-β-benzoyl-vinylamine, $C_6H_5COC(C_6H_5)=C(C_6H_5)NHCH(CN)CH_3$.—When a saturated ethereal solution of the cyanogen compound XVIII was kept in a stoppered flask at the ordinary temperature, it slowly deposited a more sparingly soluble substance which separated in large, very pale yellow prisms which melt at 130°. Like the methoxyl compound it decomposes above the melting point and reverts to the anhydro compound and like it, also, it is easily ozonized and hydrolyzed. With concentrated hydrochloric acid, the products of hydrolysis are phenyl dibenzoyl methane and alanine hydrochloride.

Anal. Calcd. for $C_{24}H_{20}ON_2$: C, 81.8; H, 5.7. Found: C, 82.0; H, 5.7.

Addition of Methyl Magnesium Iodide, *Iso*propyl-α,β-diphenyl-β-benzoyl-vinylamine, XXIV.—The anhydro compound obtained by heating 2.2 g. of the methyl ether to 150° under diminished pressure was added to a solution of methyl magnesium iodide containing one g. of magnesium. The solution became hot and deposited a colorless, crystalline magnesium derivative. This was separated by decanting the supernatant liquid, washed with ether and stirred into cracked ice and ether. The ethereal layer and washings yielded 1.7 g. of a yellow solid which was purified by recrystallization from ether and from methyl alcohol.

Anal. Calcd. for $C_{24}H_{23}ON$: C, 84.5; H, 6.7. Found: C, 84.9; H, 7.3.

The amine is readily soluble in all organic solvents except petroleum ether. It crystallizes in yellow needles and melts at 115°. Its structure was established by hydrolysis. For this purpose a small quantity of concd. hydrochloric acid was added to a solution of 1 g. of the substance in boiling methyl alcohol. The solution was diluted with an equal volume of hot water; then set aside until it was colorless. It deposited phenyl dibenzoyl methane. The filtrate from the diketone was thoroughly extracted with ether and then evaporated to dryness. It left a hydrochloride which after one recrystallization from dry methyl alcohol and anhydrous ether melted at 152–153°. This hydrochloride when treated first with sodium nitrate and then with an alkaline solution of iodine gave iodoform. It is therefore the hydrochloride of *iso*-propylamine.

Hydrolysis of the Anhydro Compound, **α,β-Diphenyl-β-benzoyl-vinylamine, XXV.**—The pure solid anhydro compound is not altered by air but when it is not quite pure or when its solutions are not securely protected against contamination by acids, it is hydrolyzed to the corresponding amine. In petroleum ether this hydrolysis is very slow. It occurs most rapidly when solutions in moist ether are exposed to the air of the laboratory. The product separates as a bright yellow solid. This was purified by recrystallization from acetone and methyl alcohol.

Anal. Calcd. for $C_{21}H_{17}ON$: C, 84.3; H, 5.7. Found: C, 84.2; H, 5.9.

The amine is sparingly soluble in methyl alcohol, moderately soluble in ether and very readily soluble in acetone. It crystallizes in needles and melts at 162°. Its structure was established by ozonization and by hydrolysis.

Ozonization.—A current of ozone was passed for several hours through a solution of the amine in carbon tetrachloride. The ozonide was decomposed with ice, the solvent pumped off and the residue dissolved in ether. After the removal of a small quantity of benzoic acid with sodium carbonate the ethereal solution was dried and allowed to evaporate slowly. It deposited first a white solid which was purified by sublimation and identified as benzamide, and then pale yellow prisms, identified as benzil.

Hydrolysis.—When the anhydro compound is triturated with cold concd. aqueous hydrochloric acid the hydrolysis stops at the amine. In alcohol both the anhydro compound and the amine undergo further hydrolysis. Thus when a drop of concd. hydrochloric acid was added to a solution of 0.6 g. of the amine in methyl alcohol, the color gradually faded and the solution deposited an almost equal quantity of a colorless solid which was identified as phenyl dibenzoyl methane. A similar solution was boiled. It became colorless in a few minutes but gave, in addition to the diketone, methyl benzoate and desoxybenzoin.

Isomeric **Amine.**—In one experiment in which a considerable quantity of crude methylene anhydro compound[8] which had been kept in a vial for several years was recrystallized from ether without protection against the acid in the air, a more sparingly soluble yellow compound made its appearance. This separated from ether in small prisms and melted at 208°.

Anal. Calcd. for $C_{21}H_{17}ON$: C, 84.3; H, 5.7. Found: C, 84.7; H, 5.8.

This new product is isomeric with the amine melting at 162°. It is hydrolyzed

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[8] Ref. 2, p. 1224

under the same conditions as the lower melting substance and also gives the same products—phenyl dibenzoyl methane and ammonium chloride. It is therefore difficult to comprehend how it can be anything except a geometrical isomer of the lower melting compound. There is, however, one grave objection to this interpretation. When the lower melting amine is treated with standardized methyl magnesium iodide, it consumes two moles of reagent, liberates two moles of gas, and is recovered when the magnesium derivative is decomposed. The higher melting amine likewise dissolves in the reagent but it consumes only one mole of it and it liberates only one mole of gas. It also is recovered when the resulting magnesium compound is decomposed.

Synthesis.—In order to secure more of this isomer we hydrolyzed both the methylene and the ethylidene anhydro compounds in different solvents and under varying conditions. All these attempts ended in the lower melting amine. We therefore turned to synthesis. Amines of this type have been obtained by Claisen,[9] who found that some isoxazoles react with phenyl magnesium bromide to form compounds to which he assigned this structure. We added triphenyl isoxazole to a solution of phenyl magnesium bromide containing 5 equivalents of the reagent. The isoxazole is sparingly soluble and the reaction was extremely slow. After boiling for sixty-four hours the mixture was decomposed in the usual manner. It gave, besides unchanged isoxazole, only the amine melting at 162°.

Although methyl magnesium iodide seldom acts as a reducing agent, we found that it reacts with triphenyl isoxazole much more rapidly than phenyl magnesium bromide. The sole product in this case also was the lower melting amine. This amine was also the only product obtained in an entirely different method of synthesis which started with the nitrile of benzoyl-phenyl-acetic acid: $C_6H_5CH(COC_6H_5)CN \longrightarrow C_6H_5CH(COC_6H_5)C(C_6H_5){=}NMgBr \longrightarrow C_6H_5C(COC_6H_5){=}C(C_6H_5)NH_2$.

II. Experiments with Diphenyl p-Bromophenyl Isoxazoles

As outlined in the introduction, the first step in the preparation of the brominated isoxazoles was the condensation of nitrostilbene and *p*-bromophenyl nitromethane. In the earlier experiments this condensation was conducted in such a manner as to give the best yield of isoxazoline oxides. When it became evident that the separation of the oxides is not feasible, the conditions were changed in order to secure the isoxazoles instead of the oxides. The procedure then was as follows.

A solution of one g. of sodium in 75 cc. of methyl alcohol was added in the course of a few minutes to a boiling solution of 9.0 g. of nitrostilbene and 8.6 g. of bromophenyl nitromethane in the same solvent. After boiling for about five minutes, during which it became filled with a mass of solid oxide, it was treated with sodium methylate from 8 g. of sodium dissolved in 125 cc. of methyl alcohol and boiled for three to four hours. It was then cooled and filtered. The yield of crude washed and dried product melting at 168–171° was 105 g. from 90 g. of nitrostilbene. Recrystallization from ether raised the melting point to 172–173° where it became constant, but ozonization showed that the recrystallized product was a mixture.

Ethylation.—The mixture of isoxazoles was ethylated by exactly the same procedure that had been employed with the unbrominated compound and thus converted into a mixture of ferric chloride double salts This was subjected to fractional recrystallization from ethyl bromide. The least soluble component separated from cold solutions in greenish yellow needles, and from boiling solutions in brown plates or

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[9] Claisen, Ber., 59, 150 (1926).

tables. Both forms melt at 172–174° and the yellow slowly passes into the brown form if it is allowed to remain in contact with the mother liquor. From 22 g. of the mixed isoxazoles was obtained 34 g. of crude, washed and dried ferric chloride double salts: of this approximately 50% was later isolated in the form of the salt V.

Anal. Calcd. for $C_{23}H_{19}ONBrCl_4Fe$: C, 45.8: H, 3.2; Cl, 23.5 Found: C, 45.7; H, 3.1; Cl, 24.2.

3,4-Diphenyl-5-bromophenyl Isoxazole, II.—In order to locate the bromophenyl group it was necessary to convert the double salt into the isoxazole. To this end an ethereal solution of the corresponding pseudo base was prepared by shaking 8 g. of the powdered double salt with a mixture of 50 cc. of 20% sodium hydroxide, 50 g. of ice and 100 cc. of ether. This etherral solution was repeatedly extracted with small quantities of concd. hydrochloric acid which had been diluted with an equal volume of water until the ether left no residue when evaporated. The combined acid extracts when chilled in a freezing mixture and freed from ether by evaporation in a draught deposited a hydrated chloride in colorless needles. The chloride was collected on a glass filter and partially dried by suction, then transferred to a flask and heated in a rapid current of air. As the temperature rose the chloride melted, lost first water then ethyl chloride, resolidified and finally melted again at about 170°. The product was recrystallized from acetone and methyl alcohol.

Anal. Calcd. for $C_{21}H_{14}ONBr$: C, 67.0; H, 3.7 Found: C, 67.4; H, 3.9.

The isoxazole is readily soluble in acetone, moderately soluble in ether, sparingly soluble in methyl alcohol. It crystallizes in needles and melts at 172–173°, almost exactly the melting point of the mixture of the two isomeric isoxazoles. In open vessels it sublimes freely at its melting point.

Ozonization.—The isoxazole was ozonized in ethyl bromide in the usual manner, the solvent removed under diminished pressure and the pasty residue shaken with ice water for two hours, during which most of it solidified. Solid and oil were then dissolved in ether. From the ethereal solution sodium carbonate extracted only a trace of *p*-bromobenzoic acid. The dried ethereal solution on evaporation deposited small colorless prisms that melted at 145–146°.

Anal. Calcd. for $C_{21}H_{14}O_3NBr$: C, 61.8; H, 3.1. Found: C, 61.6; H, 3.7.

β-Benzilmonoxime-*p*-bromobenzoate, VIII.—The ozonization product was readily hydrolyzed both with acids and with bases. Acids gave mainly benzil, hydroxylamine and *p*-bromobenzoic acid, while sodium methylate formed mainly benzonitrile and methyl *p*-bromobenzoate. In order to determine whether, as is usual in the case of phenylated isoxazoles, ozonization results in a derivative of β-benzil monoxime, the substance was synthesized by shaking 1.7 g. of β-benzil monoxime with 2.3 g. of *p*-bromobenzoyl chloride in 20 cc. of pyridine for two hours. The product melted at 145–146° and a mixture of the two substances melted at the same temperature.

The Pseudo Base, **2-Ethyl-3,4-diphenyl-5-bromophenyl-5-hydroxy** Isoxazoline, XIII.—From the ferric chloride double salt the brominated pseudo base was obtained by the method previously employed for getting its unbrominated analog. It crystallized in colorless prisms and melted with effervescence at about 105°.

Anal. Calcd. for $C_{23}H_{20}O_2NBr$: C, 65.4; H, 4.7. Found: C, 66.0; H, 4.7.

Ozonization.—Two grams of the pseudo base was ozonized in ethyl bromide for two hours. After removing the solvent the pasty residue was boiled with water for a short time, then cooled and dissolved in ether. From the etherral solution sodium carbonate extracted benzoic acid and a very small quantity of *p*-bromobenzoic acid which, like the analysis, indicated that the base was contaminated with a small quantity of the unbrominated compound. The ethereal solution on evaporation deposited pale yellow needles. After repeated recrystallization from petroleum ether containing a few drops of ether these melted at 89–90°.

Anal. Calcd. for $C_{14}H_9O_2Br$: C, 58.1; H, 3.1. Found: C, 58.9; H, 3.4.

p-Bromobenzil, **XXI**, is readily soluble in all organic solvents. It has a pronounced tendency to separate from solution as an oil and consequently is extremely difficult to purify. The analyses show that our sample was contaminated with benzil. Our melting point, therefore, is doubtless a little too low but the fact that the substance readily formed a quinoxaline derivative and was oxidized to equivalent quantities of benzoic and *p*-bromobenzoic acids by alkaline hydrogen peroxide leaves no doubt as to its character.

The **Anhydro** Compound, **Ethylidene-α,β-diphenyl-β-bromobenzoyl-vinylamine, XX.**—The anhydro compound was made like its bromine-free analog. It crystallizes from ether and from methyl alcohol in very pale yellow needles and melts at 102°.

Anal. Calcd. for $C_{23}H_{18}ONBr$: C, 68.3; H, 4.5 Found: C, 68.7; H, 4.7.

Ozonization.—The substance was ozonized in ethyl bromide The products, isolated in the same manner as those from the bromine free compound, were *p*-bromobenzil and benzamide

Hydrolysis. **α,β-Diphenyl-β-bromobenzoyl-vinylamine, XXVI.** Like its bromine-free analog, the anhydro compound is hydrolyzed with the utmost ease to acetaldehyde and a yellow, unsaturated amine. The amine was purified by recrystallization from acetone and methyl alcohol. It is readily soluble in acetone, moderately soluble in ether, sparingly soluble in methyl alcohol. It crystallizes in deep yellow needles and melts at 172°.

Anal. Calcd. for $C_{21}H_{16}ONBr$: C, 66.7; H, 4 2 Found: C, 67.4; H, 4.7.

Summary

This paper contains a description of the isolation of two pseudo bases in the triphenyl isoxazole series, an account of their properties, an opinion as to their structure, and a discussion of the mechanism by which such pseudo bases are formed from their salts.

CAMBRIDGE 38, MASSACHUSETTS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA]

PARA-CYMENE STUDIES. XI. PARA-CYMYL-2-CARBITHIOIC ACID

BY ALVIN S. WHEELER AND CHARLES L. THOMAS[1]

RECEIVED MAY 31, 1928 PUBLISHED NOVEMBER 6, 1928

Fleischer[2] was the first to make a dithio add, the dithio-benzoic acid Two years later Engelhardt, Latschinoff and Malyscheff[3] obtained its lead salt by the action. of benzoyl chloride on lead sulfide. Klinger[4]

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[1] This paper is an abstract from a Bachelor's Thesis presented to the Faculty of the University of North Carolina in June, 1928.

[2] Fleischer, *Ann*, **140,** 241 (1866)

[3] Engelhardt, Latschinoff and Malyscheff, *Z Chem*, **1868,** 353; *Jahresb. über der Fortschritte der Chemie*, **1868,** 595

[4] Klinger *Ber*, **15,** H62 (1882)

treated benzal chloride with potassium sulfhydrate. In 1902 Houben and Kesselkaul[5] announced the formation of the acid by the action of carbon disulfide on phenylmagnesium bromide. In 1906 Houben[6] described a series of arylcarbithioic acids.

In this paper is described the preparation of *p*-cymyl-2-carbithioic acid by the action of carbon disulfide on *p*-cymyl-2-magnesium bromide. From this acid various salts and esters were prepared.

The name given to the dithio acid follows the suggestion of Houben. The expression "dithiocarboxylic acid" indicates oxygen as well as sulfur and as there is no oxygen present such a designation should be avoided. The name given is made up of car (carbon), bi (two) and thio (sulfur) and seems to us to be a perfectly good and logical name.

Experimental Part

The Grignard Reagent.—2-Bromo-p-cymene was made by brominating cymene according to the method of Bogert and Tuttle.[7] The portion boiling at 103–105° at 5 mm. was used. Thirty *g.* of clean, dry magnesium turnings was washed with dry ether and covered with 500 cc. of dry ether. Several small crystals of iodine were allowed to dissolve at the bottom. In order to keep the iodine in contact with the magnesium the solution was not stirred while 250 cc. of bromocymene in 25cc. portions was added. The product was a grayish-black, somewhat sirupy liquid. It was decanted from the small residue of magnesium and used in this condition

***p*-Cymyl-2-carbithioic Acid, $C_6H_3CH_3C_3H_7CSSH$.**—The Grignard reagent (the whole amount prepared above) was cooled by a freezing mixture to −10° and then 180 cc. of carbon disulfide was added dropwise and slowly enough to keep the temperature at −10°. This operation took three hours. Air was almost entirely excluded. After stirring had been continued for another hour, the stirring assembly was removed, the flask stoppered and the mixture kept cold by the freezing mixture for twelve hours. The reaction mixture was then poured upon a kilo of ice and hydrochloric acid was added until the liquid was acid to Congo Red. A reddish-orange ether layer separated out on top. This was removed with a separatory funnel. The aqueous layer was extracted three times with 200cc. portions of ether. The ether extracts were then combined and extracted with 150cc. portions of 5% sodium hydroxide solution until the alkali solution assumed only a slight yellow color or none at all. This gives a solution of the sodium salt of the carbithioic acid with some excess of alkali. This solution is used for making other salts. It does not keep well, decomposing in two to three days.

The free acid is obtained by covering the alkaline solution with ether and adding hydrochloric acid until acid to Congo Red. The free acid is then extracted with ether It is a viscous red oil when its ether solution is evaporated in a vacuum. It does not solidify at −15°. It decomposes when an attempt is made to distil it at 2 mm. long before there is any evidence of boiling. The decomposition product is a thick brown oil of disagreeable odor. When the ether solution is allowed to evaporate in the air, a reddish-orange, gummy mass of slightly disagreeable odor remains. In ether solution the acid ranges from purple-red in concentrated solutions to orange in dilute solutions. The acid is fairly stable in ether solution. only slight decomposition being noticed

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[5] Houben and Kesselkaul, *Ber.* 35, 3696 (1902)

[6] Houben, *Ber.* 39, 3219 1906)

[7] Bogert and Tuttle, This Journal, 38, 1349 (1916)

after five months. The sodium, potassium, barium, strontium and calcium salts are soluble in water. The zinc salt is insoluble.

Zinc **Salt** of Cymylcarbithioic Acid, $(C_6H_3CH_3C_3H_7CSS)_2Zn$.—A solution of **6** *g*. of zinc chloride, 100 cc. of water and 15 cc. of glacial acetic acid was made. To this solution was added the freshly prepared solution of the sodium salt of the carbithioic acid, which contained some excess of sodium hydroxide, until no further precipitation took place. The precipitate was filtered off, dried and dissolved in absolute alcohol. The solution was boiled with animal charcoal and filtered The cooled solution was poured into water, whereupon the zinc salt precipitated. It is an amorphous powder of yellow ochre color, soluble in alcohol, benzene, carbon tetrachloride and acetone but does not crystallize from any of them. It melts at 92°.

Anal. Calcd. for $C_{22}H_{26}S_4Zn$: S, 26.50; C, 54.7; **H,** ***5.38;*** Zn, **13.62.** Found: S, 26.39; C, 56.0; H, **5.43;** Zn, 13.66.

Complex Salts

A number of salts were prepared in which the metal is half saturated with acetic acid and half with cymylcarbithioic acid. A metallic salt in dilute acetic acid solution is added to an aqueous solution of the sodium salt of the carbithioic acid. The precipitate is filtered and washed with a little alcohol to remove traces of resin. These salts dissolve in a number of organic solvents as alcohol, benzene, carbon tetrachloride and acetone, but they do not crystallize from them. The lead salt is brown and melts at 65°. The silver salt is a beautiful orange but it turns black in fifteen minutes. These were not analyzed.

TABLE I

TYPE FORMULA $C_6H_3CH_3C_3H_7CSS\text{-}M\text{-}OCOCH_3$

Salt used	Color	Form	M. p., °C.
Zinc chloride	Yellow	Amorphous	196 decomp.
Copper sulfate	Red-yellow	Amorphous	75 decomp.
Mercuric chloride	Yellow	Amorphous	>300
Cadmium acetate	Yellow	Amorphous	125 decomp.

	Analyses							
	Carbon		Hydrogen		Sulfur		Metal	
Formula	Calcd.	Obs.	Calcd.	Obs.	Calcd.	Obs.	Calcd.	Obs.
$C_{13}H_{16}O_2S_2Zn$	46.8	47.1	4.81	4.86	19.22	18.95	...	...
$C_{13}H_{16}O_2S_2Cu$	47.2	46.9	**4.83**	4.89	1 .	19.56	19.62	19.84
$C_{13}H_{16}O_2S_2Hg$	33.3	33.1%	3.31	3.40	13.04	14.03	...	...
$C_{13}H_{16}O_2S_2Cd$	41.0	40.9	4.61	**4.63**	16.79	**1 . 0**	...	...

Methyl Ester of Cymylcarbithioic Acid, $C_6H_3CH_3C_3H_7CSSCH_3$ The ester is prepared by treating the aqueous solution of the sodium salt with dimethyl sulfate until a thick brown oil collects on the surface and a further addition causes no brown color in the aqueous layer. The sulfate is added slowly with stirring The oil is separated, washed with dilute sodium hydroxide, then with water, dried over calcium chloride and distilled in vacuum. It is a sirupy liquid boiling at 167–168° and 8 mm. When pure it is not very disagreeable in odor. In dilute form it smells like a freshly cut turnip. It is quite stable When exposed to the air for three days no change was noticed and it did not change in color in a sealed tube in the sunlight for a week

Anal. Calcd **for** $C_{12}H_{16}S_2$ S, 28.57; C, 64.3 H, 7.148 Found S, 28.77; C, 64.1; H, 7.13.

Ethyl Ester. Liquid boiling at 141–2° and 3 mm.

Anal. Calcd. for $C_{13}H_{18}S_2$: S, 26.97; , 65.5; H, 7.57. Found: S, 26.88; C, 65.1; H, 7.53.

Action of Phenylhydrazine.—An unexpected reaction took place between phenylhydrazine and the carbithioic acid. Small, white plates were obtained, melting sharply at 112°. The substance was insoluble in most organic solvents and evolved hydrogen sulfide when heated with any such solvent. It contains 6.79% N and 16.18% S.

Acid Chloride.—The action of phosphorus pentachloride on the carbithioic acid gave a liquid boiling at 141° and 8 mm. Though its odor was somewhat sharp it gave no typical reaction with ammonia or aniline so doubt remains as to its nature.

Summary

1. *p*-Cymyl-2-carbithioic acid is obtained by the action of carbon disulfide on cymyl-2-magnesium bromide.

2. Its zinc salt was prepared.

. Complex salts of metals with acetic acid and carbithioic acid were obtained. Zinc, copper, mercury and cadmium gave such salts.

4. The methyl and ethyl esters of carbithioic acid were prepared.

5. Reactions (undetermined) took place between the carbithioic acid and phenylhydrazine, also phosphorus pentachloride.

CHAPEL HILL, NORTH CAROLINA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE COLLEGE OF LIBERAL ARTS OF NORTHWESTERN UNIVERSITY]

UNSYMMETRICAL ARSENO COMPOUNDS DERIVED FROM PARA-ARSONOPHENYLAMINO-ETHANOL AND PARA-ARSONOPHENYLGLYCINE-AMIDE[1]

BY CHARLES SHATTUCK PALMER AND ERNEST B. KESTER[2]

RECEIVED JUNE 6, 1928 PUBLISHED NOVEMBER 6, 1928

During recent years there has been considerable interest in the attempts to apply *p*-arsonophenylglycine-amide in the form of its monosodium salt, "tryparsamide" (I), to the treatment of diseases of protozoal origin. Especial success has attended its introduction into the treatment of trypanosomiasis,[3] and it has also shown promise in paresis.[4] To a lesser

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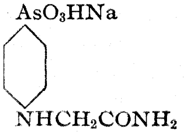
[1] An abstract of Part I of a thesis submitted to the Graduate School of Northwestern University by Ernest B. Kester in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

Research Fellow under grant from the Public Health Institute of Chicago.

[3] Jacobs and Heidelberger, THIS JOURNAL, **41**, 1587 (1919); Brown and Pearce, *J. Exptl. Med.*, **30**, 417–496 (1919); Pearce, *ibid.*, **34**, supplement 1 (1921); Chesterman, *Trans. Roy. Soc. Trop. Med. Hyg.*, **16**, 394 (1923); Smillie, *J. Am. V. M. A.*, September, 1923; Pearce, *J. Pharmacol.*, **25**, 199 (1925).

[4] Lorenz, Loevenhart, Bleekwenn and Hodges, *J. Am. Med. Assn.*, **80**, 1497 (1923); Moore, Robinson and Keidel, *ibid.*, **82**, 528 (1924); Lorenz, Loevenhart and Reitz, *Am. J. Med. Sci.*, **148**, 157 (1924); Lorenz, Loevenhart and Reese, *Z. Neur. Psych.*, **98**, 763 (1925); Loevenhart and Stratman-Thomas, *J. Pharmacol.*, **29**, 69 (1926).

extent the sodium salt (II) of *p*-arsonophenylamino-ethanol[5] has been under investigation. In the usual course of chemo-therapeutic study, when an arsonic acid, $RAsO_3H_2$, has been shown to be valuable, it is reduced to the corresponding arseno compound, RAs=AsR, in order that the effect of both pentavalent and trivalent arsenic may be determined in combination with the same K group. The arseno compound (III) from *p*-arsonophenylamino-ethanol has been made,[6] but it is soluble only in strongly acid solutions and is therefore useless for therapeutic purposes. No arseno compound derived from tryparsamide has been described, but this substance likewise could contain no substitutions which would make possible its dissolving to form a neutral aqueous solution.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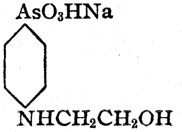
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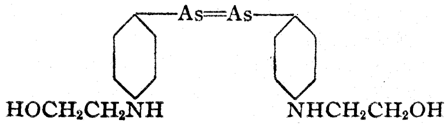
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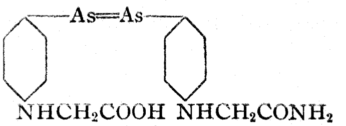
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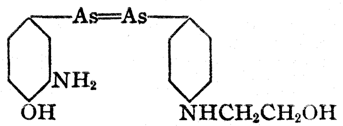
(V)

In order to obtain water-soluble arseno compounds with phenylglycine-amide and phenylamino-ethanol nuclei, it was decided to prepare unsymmetrical arseno compounds (IV, V) in which one arsenic is attached to either of the above-mentioned groups and the other to a benzene ring containing solubilizing substituents, for example,—$NHCH_2OSOH$, —OH, —$NHCH_2COOH$ and —OCH_2COOH.

Four general methods for preparing unsymmetrical arseno compounds are available. *A*. The action of a primary arsine on a primary arsine oxide or halide[7]

$$RAsH_2 + R'AsCl_2 \longrightarrow 2HCl + RAs{=}AsR'$$
$$RAsH_2 + R'AsO \longrightarrow RAs{=}AsR' + H_2O$$

B. Rearrangement of two symmetrical arseno compounds when warmed in solution to give the unsymmetrical derivative[8]

$$RAs{=}AsR + R'As{=}AsR' \longrightarrow 2RAs{=}AsR'$$

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[5] Hamilton, THIS JOURNAL, 45, 2751 (1923); Rodewald and Adams, ibid., 45, 3102 (1923); Raiziss, Severac and Moetsch, *Transactions of Section on Pharmacology and Therapeutics of the American Medical Association, 1* (1925); Loevenhart and Stratman-Thomas, *J. Pharmacol.*, 29, 69 (1926).

[6] Hamilton, THIS JOURNAL. 45, 2751 (1923).

[7] Kahn, *Chem.-Ztg.*, 36, 1099 (1912); *Z. angew. Chem., 25*, 1995 *(1912);* German Patent, 254,187; American Patent 1,033,904; Steinkopf, Schmidt and Smie, Bur, 59, 1468 (1926).

[8] Karrer, *Ber.*, 49, 1649 (1916); German Patent, 293,040; Hart and Payne, J *Am. Pharm. Assoc., 12,* 699 (1923).

C. Simultaneous reduction of two different arsonic acids, arsine oxides or arsine halides or of an arsine oxide with an arsonic acid, etc.[9]

$$RAsO_3H_2 + R'AsO_3H_2 + 8H \longrightarrow RAs{=}AsR' + 6H_2O$$
$$RAsO + R'AsCl_2 + 4H \longrightarrow RAs{=}AsR' + H_2O + 2HCl$$

D. Substitution in only one of the two groups attached to arsenic in a symmetrical arseno compound[10]

$$RAs{=}AsR \longrightarrow RAs{=}AsR'$$

Of the above methods, C was selected for use since it offered a means for preparing unsymmetrical arseno compounds from the readily procurable arsonic acids.

The uniform procedure was the reduction of equimolar solutions of *p*-arsonophenylamino-ethanol or *p*-arsonophenylglycine-amide with some other arsonic acid by means of a reagent specific for the arseno group. Sodium hydrosulfite was not used since it frequently contaminates the reduced product with sulfur-containing impurities. Hypophosphorous acid or stannous chloride are free from this objection and will act at the low temperatures necessary in preparing arseno compounds of complex structure because of their instability. Those derived from *p*-arsonophenylglycine-amide and p-arsonophenylamino-ethanol are particularly sensitive. For example, 4-amino-4'-β-hydroxyethylamino-arsenobenzene (VI), arsenic content, 33.24%, is prepared readily at 5–10°. If, however, the reduction of arsanilic acid and parsonophenylamino-ethanol is carried out at 55–60°, the product contains 61% of arsenic, while at 100° a substance containing 78% of arsenic is formed. As a result, all of the arseno compounds described below (which were derived from *p*-arsonophenylglycine-amide or parsonophenyl-amino-ethanol) had to be made below room temperature.

When *p*-arsonophenylglycine-amide and *p*-arsonophenylglycine were reduced simultaneously with hypophosphorous acid, it was not found possible to obtain the unsymmetrical arseno compound. Instead, a product resulted which from an arsenic analysis seemed to be tetra-arsenobenzene-4-glycine-4'-glycine-amide. Stannous chloride, on the other hand, produced the pure arseno compound, arsenobenzene-4-glycine-4'-glycine-amide (IV).

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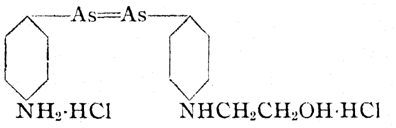
[9] Bertheim, *Chem. Ztg.*, **38**, 756 (1914); Faragher, *J. Chem. Soc.*, **117**, 866 (1920); King. *J. Chem. Soc.*, **119**, 1107 (1921); Christiansen, This Journal, **43**, 2202 (1921); Hart and Payne, *J. Am. Pharm. Assoc.*, **12**, 688, 762 (1923); German Patents, 251,104, 253,226; American Patent, 1,017,657; Steinkopf, Schmidt and Smie, *Ber.*, **59**, 1468 (1926).

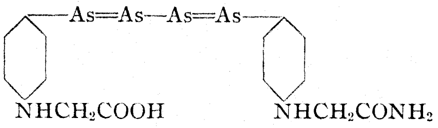
[10] German Patents, 245,766, 249,726, 250,745, 260,235, 263,460, 264,014, 271,893; American Patents, 1,024,993, 1,048,002, 1,053,300 (reissue 13,848); Binz, *Z. angew. Chem.*, **33**, 256 (1920); **36**, 551 (1923); Binz and Bauer, *Z. angew. Chem.*, **34**, 261 (1921); Voegtlin, Dyer and Thompson, *Am. J. Syphilis*, **6**, 526 (1922); Hart and Payne *J. Am. Pharm. Assoc.*, **12**, 688 (1923).

The mechanism of the formation of unsymmetrical arseno compounds is undoubtedly, first, reduction of each arsonic acid to its arseno derivative and, second, rearrangement of the two arseno compounds to the unsymmetrical according to method B above. Thus *p*-arsonophenylamino-ethanol can be reduced with a large excess of hypophosphorous acid in hydrochloric acid to give a solution of *p*-arsenophenylamino-ethanol (III). Within a short time after adding an equimolecular proportion of *p*-arsonophenoxyacetic acid, and an additional quantity of the reducing agent, the unsymmetrical derivative, 4-hydroxyethylamino-arsenobenzene-4′-oxyacetic acid (VIII) begins to precipitate.

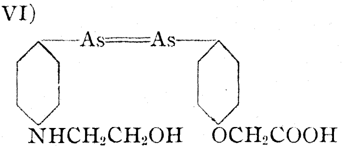
It is not to be inferred, however, that the successive or even simultaneous reduction of two arsonic acids leads invariably to the formation of the unsymmetrical arseno compound. One case, in particular, was encountered in which the two symmetricals predominated in the reaction product, regardless of experimental conditions, namely, in the reduction of phenyl arsonic acid with 3-amino-4-hydroxyphenylarsonic acid.



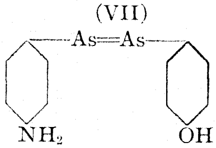
(VI)



(VII)



(VIII)



(IX)

The unsymmetrical compounds described in the experimental part show variety in the choice of conditions and reducing agents. In the earlier experiments where hypophosphorous acid was employed, no catalyst was used. Later work, however, showed that the time element could be shortened from a period of several days to a few minutes by the introduction of a small amount of potassium iodide; but with or without catalyst, in all reductions involving tryparsamide or etharsanol, the temperature needed to be kept under 15°.

The proof that each unsymmetrical arseno compound derived from *p*-arsonophenylglycine-amide or *p*-arsonophenylamino-ethanol and another arsonic acid containing a solubilizing group of an acidic nature, is not a mixture of two symmetrical products, rests on the observation that they are wholly soluble in aqueous alkalies. If any symmetrical arseno compound from p-arsonophenylamino-ethanol or *p*-arsonophenylglycine-amide were present it would remain as a residue insoluble in alkali. Moreover, the products behave as single definite compounds when derivatives such as hydrochlorides or methylenesulfoxylic acids are prepared. In one case, the methylenesulfoxylic acid of the unsymmetrical was produced directly by treatment of the two arsonic acids with formaldehydesulfoxylic acid.

The pharmacological study of several of the compounds described is being carried out by Dr. A. S. Loevenhart at the University of Wisconsin, but is not yet complete.

The toxicity of arseno compounds is a function not alone of the molecular configuration but also of the method of preparation. Contact with air usually increases toxicity, probably because arsine oxides are formed. Hence, in preparing specimens for biological testing, filtrations were performed in carbon dioxide atmosphere. It was found, too, that toxicity could be reduced in the case of compounds having a phenolic function by dissolving in dilute sodium hydroxide and precipitating with carbon dioxide. By this treatment arsine oxides that may have been in the reaction product because of incomplete reduction were left in solution as the sodium salt. After filtering, the base could then be converted to the hydrochloride.

Experimental

Derivatives of p-Arsonophenylamino-ethanol

(1) 4-Amino-4'-p-hydroxyethylamino-arsenobenzene Dihydrochloride **(VI)**.—A solution of a fiftieth mole each of *p*-arsonophenylamino-ethanol and arsanilic acid in 30 cc. of water and 10 cc. of 12 *N* hydrochloric acid was prepared. This was treated with one-half mole of 50% hypophosphorous acid and kept at a temperature below 15° for three days. No precipitate appeared but the clear solution became light yellow in color. Precipitation was brought about by stirring into 100 cc. of cold, 6 *N* hydrochloric acid. The product was granular in character and could be filtered easily in the open air without discoloration due to oxidation. It was washed repeatedly with dilute hydrochloric acid and then triturated in a mortar with 30 cc. of methanol to which had been added 5 cc. of hydrochloric acid (d., 1.19). After filtering again, washing with ether left the compound almost dry; yield, 7 g. or 78%.

This compound does not dissolve in water of itself but merely turns red and gumlike. If, however, a small quantity of hydrochloric acid be added, solution proceeds quickly.

Anal. Subs., 0.1803, 0.1375: 35.35, 26.47 cc. of iodine soln. (1 cc. = 0.001703 g. of As). Calcd. for $C_{14}H_{18}ON_2Cl_2As_2$: As, 33.24. Found: As, 33.39, 32.78. Subs., 0.2231, 0.3721: AgCl, 0.1357, 0.2333. Calcd. for $C_{14}H_{18}ON_2Cl_2As_2$: Cl, 15.72. Found: 15 05, 15.51.

(2) 4-Amino-4'-β-hydroxyethylamino-arsenobenzene-N-methylenesulfoxylic Acid.—Five grams of the preceding compound was dissolved in 50 cc. of water to which had been added 3 cc. of hydrochloric acid (d., 1.19), and a solution of 2.5 g. of sodium formaldehydesulfoxylate in 25 cc of water added. In a few minutes a yellow precipitate began to form. Precipitation was complete in an hour at room temperature. The product was filtered in carbon dioxide and after it had been thoroughly washed with water was dried by washing with methanol and ether. The drying was completed in a vacuum desiccator over sulfuric acid for a period of eighteen hours. The yield was quantitative.

Anal. Subs., 0.1444, 0.1467: 23.80, 24.52 cc. of iodine soln. (1 cc. = 0.001965 g. of As). Calcd. for $C_{15}H_{18}O_3N_2SAs_2$: As, 32.86. Found: As, 32.29, 32.84. Subs., 0.2649, 0.2386: $BaSO_4$, 0.1301, 0.1205. Calcd. for $C_{15}H_{18}O_3N_2SAs_2$: S, 7.03. Found: S, 6.76, 6.94.

(3) **4-Hydroxy-4′-β-hydroxyethylamino-arsenobenzene Hydrochloride.**—The reduction of fiftieth moles of *p*-arsonophenol and *p*-arsonophenylamino-ethanol was carried out in a manner identical with (1). In this case the arseno compound precipitated as formed. Before filtering, 20 cc. of 12 N hydrochloric acid was added and the filtration then performed in a current of carbon dioxide. The product was washed repeatedly with dilute hydrochloric acid and finally with methanol acidified slightly with hydrochloric acid. It was dried in a vacuum over sulfuric acid and caustic soda and amounted to 5 g. of the hydrochloride or 60% of the theoretical. Smaller additional amounts were obtained by allowing the mother liquors to stand in the cold.

This compound is readily soluble in dilute caustic soda, somewhat soluble in methyl alcohol and acetone but only sparingly in dilute hydrochloric acid. Water turns it red and gum-like. An alkaline solution of it heated to boiling speedily clouds and on continued boiling forms a filterable precipitate. This may be the symmetrical *p*-arsenophenylamino-ethanol

Anal. Subs., 0.1200, 0.1843: 24.75, 37.95 cc. of iodine soln. (1 cc. = 0.001758 g. of As). Calcd. for $C_{14}H_{16}O_2NClAs_2$: As, 36.07. Found: As, 36.26, 36.20.

(4) The free base of this compound was prepared by dissolving the hydrochloride in dilute caustic soda and precipitating with carbon dioxide. The precipitate was fairly easily filtered and could be washed rapidly with warm water. It was found to be somewhat soluble in methanol.

Anal. Subs., 0.1410, 0.1067: 28.75, 21.65 cc. iodine soln. (1 cc. = 0.001940 g. of As). Calcd. for $C_{14}H_{15}O_2NAs_2$: As, 39.54. Found: As, 39.56, 39.36. Subs. 1.2678: 7.01 cc. of 0.500 N HCl. Calcd. for $C_{14}H_{15}O_2NAs_2$: N, 3.70. Found: N, 3.87.

(5) **3-Amino-4-hydroxy-4′-β-hydroxyethylamino-arsenobenzene Dihydrochloride (Free Base, V).**—Following the procedure as described under (1), fiftieth moles of 3-amino-4-hydroxyphenylarsonic acid and p-arsonophenylamino-ethanol were reduced to the unsymmetrical arseno compound. Precipitation, however, did not come about spontaneously and it was necessary to stir the reaction mixture into 100 cc. of 12 *N* hydrochloric acid in order to bring it about. The product was purified by dissolving in 66 cc. of water and pouring into an equal volume of 12 *N* hydrochloric acid. After repeating this treatment, the product was filtered, washed with dilute hydrochloric acid, then with a mixture of 50 parts each of methanol and ether and dried in a vacuum over sulfuric acid and caustic soda; yield, 5 g. or 53%. The compound was readily soluble in water or dilute alkali.

Anal. Subs., 0.1964, 0.1188: 37.90, 22.90 cc. of iodine soln. (1 cc. = 0.001671 g. of As). Calcd. for $C_{14}H_{18}O_2N_2Cl_2As_2$: As, 32.10. Found: As, 32.25, 32.21. Subs., 0.1998, 0.2405: AgCl, 0.1214, 0.1477. Calcd. for $C_{14}H_{18}O_2N_2Cl_2As_2$: Cl, 15.18. Found: Cl, 15.03, 15.19.

(6) **3-Amino-4-hydroxy-4′-β-hydroxyethylamino-arsenobenzene-N-methylene-sulfoxylic Acid.**—The procedure for preparing this compound was identical with that of (2). The yield, also, was quantitative.

Anal. Subs., 0.1146, 0.1334: 23.65, 27.35 cc. of iodine soln. (1 cc. = 0.001526 g. of As). Calcd. for $C_{15}H_{18}O_4N_2SAs_2$: As, 31.75. Found: As, 31.49, 31.28. Subs., 0.2130, 0.2178: $BaSO_4$, 0.1057, 0.1115. Calcd. for $C_{15}H_{18}O_4N_2SAs_2$: S, 6.79. Found: S, 6.82, 7.03.

(7) **4-β-Hydroxyethylamino-arsenobenzene-4′-N-glycine Dihydrochloride.**—A solution was prepared of one-hundredth moles each of *p*-arsonophenylamino-ethanol

and *p*-arsonophenylglycine in 20 cc. of hydrochloric acid (d., 1.19) and 30 cc. of water. After cooling to 15°, one-quarter mole of 50% hypophosphorous acid was added and the solution cooled as before. While stirring rapidly, a solution of one gram of potassium iodide in 10 cc. of water was added dropwise. During this process the color of the solution changed first to deep red and back again to a very light yellow. Finally, a heavy yellow precipitate appeared that was filtered and washed with very dilute hydrochloric acid. The product did not darken on exposure to air; yield, 4 g. or 78% of the theoretical. The product was wholly soluble in sodium bicarbonate.

Anal. Subs., 0.1870, 0.1038: 28.15, 15.74 cc. of iodine soln. (1 cc. = 0.001910 g. of As). Calcd. for $C_{16}H_{20}O_3N_2Cl_2As_2$: As, 29.45. Found: As, 28.75, 28.96.

This compound was also prepared by means of stannous chloride.

(8) The free base of this compound was prepared by dissolving 4 g. of the dihydrochloride in 30 cc. of water to which had been added sufficient sodium hydroxide to form the sodium salt. The solution was then stirred into a solution of 10 cc. of acetic acid in 50 cc. of water. The precipitate so formed was decidedly gelatinous and difficult to filter, but the product was rendered practically free from inorganic salts by repeated triturations with warm water, and finally was dried in a vacuum over sulfuric acid.

Anal. Subs., 0.1070, 0.1242: 19.55, 22.65 cc. of iodine soln. (1 cc. = 0.001910 g. of As). Calcd. for $C_{16}H_{18}O_3N_2As_2$: As, 34.37. Found: As, 34.90, 34.83.

(9) **4-β-Hydroxyethylamino-arsenobenzene-4'-oxyacetic Acid (VIII).**—A fiftieth mole of *p*-arsonophenylamino-ethanol was dissolved in a mixture of 10 cc. of hydrochloric acid (d., 1.19) and 30 cc. of water and treated with one-quarter mole of 50% hypophosphorous acid. It was allowed to remain on ice for eighteen hours, after which time the solution had a light yellow color.

A second solution was then made of a fiftieth mole of *p*-arsonophenoxyacetic acid in 25 cc. of hydrochloric acid (d., 1.19) and 10 cc. of water, added to the above, and then a second quarter mole of hypophosphorous acid. The solution, now containing *p*-arsenophenylamino-ethanol and the unreduced *p*-arsonophenoxyacetic acid, was allowed to remain on ice for five days, during which time a yellow precipitate formed. The filtered product was washed repeatedly with warm water, methanol and ether to an almost dry yellow powder; yield, 8 g. or 92% of the theoretical. A sample was found to be completely soluble in sodium bicarbonate solution.

Anal. Subs., 0.1072, 0.2020: 18.85, 35.60 cc. of iodine soln. (1 cc. = 0.001965 g. of As). Calcd. for $C_{16}H_{17}O_4NAs_2$: As, 34.30. Found: As, 34.55, 34.63.

The independent reduction of the *p*-arsonophenylamino-ethanol to the corresponding arseno derivative before the reduction of the *p*-arsonophenoxyacetic acid shows that, as the latter was reduced, there was a rearrangement of the two arseno compounds to give a product composed entirely of the unsymmetrical. The mother liquors in the filtrate were colorless and showed no trace of any *p*-arsenophenylamino-ethanol left in solution.

Derivatives of p-Arsonophenylglycine-amide

(10) **4-Amino-arsenobenzene-4'-N-glycine-amide Dihydrochloride.**—A solution was prepared of one-hundredth moles each of *p*-arsonophenylglycine-amide and arsanilic acid in 30 cc. of hydrochloric acid (d., 1.19) and 10 cc. of water. Twenty grams of crystalline stannous chloride was then dissolved in it portionwise, after which a solution of one gram of potassium iodide in 5 cc. of water was added. A heavy, light yellow precipitate instantly formed. It was readily filtered and washed with dilute hydrochloric acid, after which trituration in a mortar with dilute hydrochloric acid removed

occluded tin salts On filtering again, the cake was washed with dilute hydrochloric acid and methanol and dried in a vacuum over sulfuric acid; yield, 4 g. or 86%. This compound is not appreciably soluble in water and difficultly soluble in warm dilute hydrochloric acid. The latter seems to promote decomposition.

Anal Subs., 0 1043, 0 1244: 17 15, 20.00 cc. of iodine soln. (1 cc. = 0.001940 g. of As) Calcd. for $C_{14}H_{17}ON_3Cl_2As_2$: As, 32 31. Found: As, 31.90, 32.12. Subs., 0 2707, 0 25-10 AgCl, 0.1684, 0.1543. Calcd. for $C_{14}H_{17}ON_3Cl_2As_2$: Cl, 15.28. Found: As, 15 06, 14 97.

(11) **4-Amino-arsenobenzene-4′-glycine-amide-N-dimethylenesulfoxylic Acid.**—Owing to the difficulty encountered in obtaining a solution of the preceding compound, the methylenesulfoxylic acid derivative was produced by reduction of the two arsonic acids with sodium formaldehydesulfoxylate. The subsequent analysis showed that part at least of the product contained only one methylenesulfoxylic acid group.

To a solution of fiftieth moles each of arsanilic acid and *p*-arsonophenylglycine-amide in 30 cc of water and 20 cc. of hydrochloric acid (d., 1.19) was added one-tenth mole of sodium formaldehydesulfoxylate in 50 cc. of water. A yellow precipitate began to form immediately and precipitation continued over a period of several days The product was filtered and washed with cold water, methanol and ether to a dry powder It was then placed in a vacuum desiccator over sulfuric acid; total yield, 2 g. or 18% of the calculated quantity.

Anal. Subs, 0 1072, 0 1042: 17 85, 17 15 cc of iodine soln. (1 cc. = 0.001742 g. of As). Calcd for $C_{16}H_{19}O_5N_3S_2As_2$ As, 27.39. Found: As, 29.01, 28 67. Subs.. 0 2127, 0.1905 $BaSO_4$, 0 1734, 0 1583 Calcd for $C_{16}H_{19}O_5N_3S_2As_2$: S, 11.72. Found: S, 11.20, 11 42.

(12) 4-Hydroxyarsenobenzene-4'-N'-glycine-amide Hydrochloride.—This compound was prepared in a manner similar to (1) from *p*-arsonophenylglycine-amide and p-arsonophenol except that the solvent in this case was a mixture of 30 cc. of water and 25 cc of hydrochloric acid (d., 1 19). The unsymmetrical arseno compound precipitated during reduction and after filtering was washed well with dilute hydrochloric acid, alcohol and ether to an almost dry state. After drying over sulfuric acid in a vacuum desiccator, the product weighed 6 g.. representing a yield of 67%. The analysis seemed to indicate a monohydrate. To confirm this, the free base was prepared.

Anal. Subs., 0.1060, 0.1300: 18.80, 23.15 cc. of iodine soln. (1 cc. = 0.001898 g. of As). Calcd. for $C_{14}H_{15}O_2N_2ClAs_2\cdot H_2O$: As, 33.57. Found: As, 33.98, 33.80. Subs., 0.2409, 0.2225: AgCl, 0 0749, 0.0695. Calcd. for $C_{14}H_{15}O_2N_2ClAs_2\cdot H_2O$: Cl, 7.94. Found: Cl, 7.69, 7.73.

(13) The free base was prepared in a manner similar to (4).

Anal. Subs., 0.1629, 0.1621: 33.75, 33.70 cc. of iodine soln. (1 cc. = 0.001826 g. of As). Calcd. for $C_{14}H_{14}O_2N_2As_2$: As, 38.24. Found: As, 37.83, 37.96. Subs., 0.2254, 0.1891: CO_2, 0.3498, 0.2926; H_2O, 0.0730, 0.0618. Calcd. for $C_{14}H_{14}O_2N_2As_2$: C, 42.87; H, 3.60. Found: C, 42.34, 42.21; H, 3.62, 3.66. Subs., 1.4763: 73.8 cc. of 0.100 N HCl. Calcd. for $C_{14}H_{14}O_2N_2As_2$: N, 7.14. Found: N, 7.00.

(14) 3-Amino-4-hydroxyarsenobenzene-4'-glycine-amide Dihydrochloride.—The reduction was carried out as in the preparation of (7), using hundredth moles of p-arsonophenylglycitie-amide and 3-amino-4-hydroxyphenylarsonic acid in 35 cc. of hydrochloric acid (d., 1.19), 20 cc. of water and one-quarter mole of 50% hypophosphorous acid. When the crude product was fiitered, purification was brought about by dissolving in 50 cc. of water containing enough sodium hydroxide to form the sodium salt and precipitating by stirring into 100 cc. of 6 *N* hydrochloric acid. The filtered product was washed with dilute hydrochloric acid and finally with absolute methanol containing 16% of hydrogen chloride. Drying was completed in a vacuum desiccator; yield, 3.5 g. or 73%. This compound is soluble in water and dilute caustic soda.

Anal. Subs., 0.1015, 0.1493: 16.42, 24.23 cc. of iodine soln. (1 cc. = 0.001940 g. of As). Calcd. for $C_{14}H_{17}O_2N_3Cl_2As_2$: As, 31.23. Found: As, 31.38, 31 48.

(15) The free base of the preceding compound was obtained after the manner of (4) and (13) except that in this case one *g.* of sodium sulfate was dissolved in the solution prior to passing in carbon dioxide, in order to obtain particles of larger size. The filtered product was washed repeatedly with warm water and dried in a vacuum desiccator over sulfuric acid.

Anal. Subs., 0.0959, 0.1079: 18.50, 20.80 cc. of iodine soln. (1 cc. = 0.001910 g. of As). Calcd. for $C_{14}H_{15}O_2N_3As_2$: As, 36.82. Found: As, 36.85, 36.82.

(16) **3-Amino-4-hydroxyarsenobenzene-4′-glycine-amide-N-methylenesulfoxylic** Acid.—The procedure for preparing this derivative of (14) from its parent compound was identical with that of (2) and (6).

Anal. Subs., 0.1380, 0.1878: 22.55, 30.80 cc. of iodine soln. (1 cc. = 0.001910 g. of As). Calcd. for $C_{15}H_{17}O_4N_3SAs_2$: As, 30.90. Found: As, 31.21, 31.32. Subs., 0.4790, 0.2530: $BaSO_4$, 0.2072, 0 1080. Calcd. for $C_{15}H_{17}O_4N_3As_2$: S, 6 61. Found: S, 5.94, 5.86.

(17) **Arsenobenzene-4-N-glycine-4′-N′-glycine-amide** Dihydrochloride (Free Base, IV).—To a mixture of 60 cc. of hydrochloric acid (d., 1.19) and 20 cc. of water was added fiftieth moles of *p*-arsonophenylglycine and *p*-arsonophenylglycine-amide. After warming to dissolve the solid matter and chilling again in an ice-bath, 40 g. of stannous chloride was put in portionwise. The mixture was shaken well until no stannous chloride remained undissolved, following which 2 g. of potassium iodide in a few cc. of water was added. A heavy yellow gum immediately separated. The supernatant liquor was decanted and the gum thoroughly worked with several portions of 6 *N* hydrochloric acid, and finally with oxygen-free water until it had assumed the form of a bright yellow powder. The filtered product was washed with very dilute hydrochloric acid. It was then dissolved in 200 cc. of water containing sufficient caustic soda to make the sodium salt and reprecipitated as a bright yellow, granular powder by stirring into 200 cc. of 6 *N* hydrochloric acid. The product so obtained was washed repeatedly with very dilute hydrochloric acid and dried over sulfuric acid in a vacuum; yield, 5 g. or 48%. It was entirely soluble in sodium bicarbonate solution, and also somewhat soluble in methanol.

Anal. Subs., 0.1251, 0.1806: 18.35, 26.65 cc. of iodine soln. (1 cc. = 0.001965 *g.* of As). Calcd. for $C_{16}H_{19}O_3N_3Cl_2As_2$: As, 28.72. Found: As, 28.82, 29.00. Subs., 0.2943, 0.2475: AgCl, 0.1628, 0.1356. Calcd. for $C_{16}H_{19}O_3N_3Cl_2As_2$: Cl, 13 58. Found: Cl, 13.68, 13.55.

(18) **Tetra-arsenobenzene-4-N-glycine-4′-N′-glycine-amide** Dihydrochloride (Free Base, VII) is formed as follows. A solution of fiftieth moles of *p*-arsonophenylglycine and *p*-arsonophenylglycine-amide was prepared in 25 cc. of hydrochloric acid (d., 1.19) and 30 cc. of water. It was treated with 53 cc. of 50% hypophosphorous acid and allowed to remain at room temperature for several days. There was a gradual color change of the solution from water white to deep red, at which stage precipitation began and yielded 4 g. of product, or 30% of the calculated. It was filtered, washed with dilute hydrochloric acid, methanol and ether and dried in a vacuum over phosphorus pentoxide.

Anal. Subs., 0.2438, 0.1462: 67.00, 40.30 cc of iodine soln. (1 cc. = 0.001664 *g.* of As). Calcd. for $C_{16}H_{19}O_3N_3Cl_2As_4$: As, 44.62. Found: As, 45.73, 45 87.

(19) Arsenobenzene-4-glycine-amide-4'-oxyacetic acid.—Fiftieth moles of *p*-arsonophenylglycine-amide and *p*-arsonophenoxyacetic acid dissolved in **35** cc. of hydrochloric acid (d., **1.19)** and **20** cc. of water were reduced with one-half mole of hypophosphorous acid without catalyst as in (12). After four or five days below **15"** the reaction mixture was warmed to 40° to dissolve any crystals of unreduced *p*-arsonophenoxyacetic acid, the arseno compound immediately filtered and washed repeatedly with water, methanol and ether; yield, 6 g or 67% of the calculated The compound was entirely soluble in alkaline solutions.

Anal. Subs., **0.1087, 0.1058: 18.80, 18.20** cc. of iodine soln. (1 cc. = **0.001965** g. of As). Calcd. for $C_{16}H_{16}O_4N_2As_2$: As, **33.30.** Found: As, **33.99, 33.87.**

Other Unsymmetrical Arseno Compounds

(20) 4-Hydroxyarsenobenzene-4'-glycine Hydrochloride.—The reduction of fiftieth moles of *p*-arsonophenylglycine and *p*-arsonophenol in **30** cc. of water and 25 cc. of hydrochloric acid (d., 1.19) was carried out as in **(19).** It was necessary to keep this solution on ice for five or six days before reduction was complete. The precipitated product was then filtered off, washed with dilute hydrochloric acid and a mixture of fifty parts of methanol and fifty parts of ether, and dried in a vacuum desiccator; yield, 5 g. or 56% Analysis showed it to be a monohydrate (cf 4-hydroxyarsenobenzene-4'-glycine-amide hydrochloride)

Anal. Subs, **0.1079, 0.1891: 18.48, 32.65** cc. of iodine soln. (1 cc. = **0.001965** g. of As). Calcd for $C_{14}H_{13}O_3NClAs_2 \cdot H_2O$: As, 33.57. Found. As, **33.67.** 33.92. Subs., 0.1995, **0.2623**: AgCl, **0.0619, 0.0809.** Calcd for $C_{14}H_{13}O_3NClAs_2 \cdot H_2O$: Cl, 7.94. Found: Cl, 7.68, **7.63.**

(21) 3-Amino-4-hydroxyarsenobenzene-4'-oxyacetic **Acid.**—Fiftieth moles of *p*-arsonophenoxyacetic acid and 3-amino-4-hydroxyphenylarsonic acid were dissolved in an acid mixture similar to **(20)** and reduced with one-half mole of hypaphosphorous acid at a temperature below 15° After eighteen hours, a light yellow precipitate had developed consisting of **3.5** g. of product. Before filtering, the mixture was warmed to 50° to dissolve any unreduced *p*-arsonophenoxyacetic acid The product **was** washed repeatedly with water and ethanol and dried in a vacuum. Warming the mother liquors at 100° for thirty minutes gave an additional crop of **2**.5 g. that **was** entirely free from decomposition products; total yield, 73%.

Anal. Subs., **0.1084, 0.1457: 20.00, 26.95** cc. of iodine soln. (1 cc. = **0.001965** g. of As). Calcd. for $C_{14}H_{13}O_4NAs_2$: As **36.65.** Found. As, **36.25, 36.35.**

(22) 3,4'-Diamino-4-hydroxyarsenobenzene Dihydrochloride.[11]—This compound was prepared like several of those already described but with the use of pyridine to prevent too rapid precipitation. The reaction mixture was made up from fiftieth moles of arsanilic acid and 3-amino-4-hydroxyphenylarsonic acid, **30** cc of water, 40 cc. of pyridine, **10** cc. of hydrochloric acid (d., 1.19) and **53** cc of hypophosphorous acid. The mixture was warmed on a water-bath at 100° for one-half hour and acquired a light reddish tint At this point it was poured into 100 cc. of hydrochloric acid, which caused the reaction product to precipitate. This was redissolved in **100** cc. of water acidified with a few cc of strong hydrochloric acid and reprecipitated by stirring into 100 cc. of 6 *N* hydrochloric acid The compound was filtered and washed with dilute hydrochloric acid, acetone and ether, yield, 5.6 g **or** 65%

Anal. Subs, **0.2270, 0.2287. 46.00, 17.23** cc of iodine soln. **(1** cc. = 0.001742 g. of As). Calcd for $C_{12}H_{14}ON_2Cl_2As_2$: **As,** 35.**44.** Found. **As. 35.30. 35.97.**

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[11] German Patent, **251,104,**

(23) **4-Amino-4′-hydroxyarsenobenzene Hydrochloride**[12] **(IX).**—To a solution of fiftieth moles of arsanilic acid and *p*-arsonophenol in 30 cc. of hydrochloric acid (d., 1.19) and 10 cc. of water, was added 20 g. of stannous chloride. After shaking until the latter was dissolved, 1 g. of potassium iodide in 5 cc. of water was stirred in and immediately a reddish-yellow precipitate formed. Filtration was performed with some difficulty because the solid matter was very finely divided, and it was finally washed with water, methanol and ether. Five g. of product or 67% of the calculated quantity was obtained. It was found to be completely soluble in caustic soda solution.

Anal. Subs., 0.1106, 0.1683: 32.30, 33.85 cc. of iodine soln. (1 cc. = 0.01905 g. of As). Calcd. for $C_{12}H_{12}ONClAs_2$: As, 40.35. Found: As, 39.61, 39.52.

(24) **3-Amino-4-hydroxyarsenobenzene Hydrochloride.**[13]—Repeated attempts to prepare this compound by simultaneous reduction of 3-amino-4-hydroxyarsenobenzene with phenylarsonic acid resulted in every case in mixtures of the two symmetrical arseno compounds, from which arsenobenzene and 3,3′-diamino-4,4′-dihydroxyarsenobenzene dihydrochloride (arsphenamine) were both isolated and identified.

Summary

1. A series of alkali-soluble unsymmetrical arseno compounds has been prepared by simultaneous reduction of equimolecular proportions of p-arsonophenylglycine-amide and an arsonic acid containing a solubilizing group, or in which solubilizing groups can be easily substituted.

2. A similar series from *p*-arsonophenylamino-ethanol has been prepared.

3. One unsymmetrical tetra-arseno compound, tetra-arsenobenzene-4-glycine-4′-glycine-amide dihydrochloride has been described.

4. Several unsymmetrical arseno compounds containing neither glycine-amide nor amino-ethanol groupings have been prepared in an effort to shed light on the mechanism by which unsymmetrical arseno compounds are formed.

EVANSTON, ILLINOIS

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[12] Kahn, *Chem.-Ztg.*, 36, 1099 (1912); Hart and Payne, *J. Am. Pharm. Assoc.*, 12, 688 (1923); German Patents, 254,187, 251,571, 352,226; American Patent, 1,033,904.

[13] German Patents, 251,104 and 254,187

[COMMUNICATION FROM THE DEPARTMENT OF INDUSTRIAL AND CELLULOSE CHEMISTRY, McGILL UNIVERSITY]

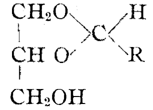
STUDIES ON THE REACTIONS RELATING TO CARBOHYDRATES AND POLYSACCHARIDES. XVII. STRUCTURE OF THE ISOMERIC METHYLIDENE GLYCEROLS

BY HAROLD HIBBERT AND NEAL M. CARTER[1]

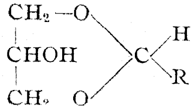
RECEIVED SEPTEMBER 13, 1928 PUBLISHED NOVEMBER 6, 1928

The work described in this paper is an outcome of attempts to investigate the structure and relative proportions of the isomeric cyclic acetals A and B formed when an aldehyde (RCHO) condenses with glycerol

(A)

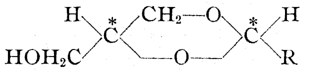


(B)

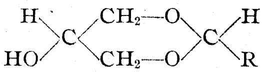


An examination of these two formulas shows that in a five-membered ring of Type I (corresponding to A), due to the presence of two asymmetric

(I)



(II)



carbon atoms(*), the product should be capable of existing in two geometrically isomeric *racemic* forms, while in Type II (corresponding to B), two geometrical isomers are theoretically possible, optical activity being excluded due to pseudo-symmetry.

The complications thus introduced by this considerable number of possible isomeric cyclic acetals make such investigations a matter of considerable difficulty and uncertainty and most probably account for the anomalous results sometimes obtained in the process of purification[3] and the gradual change taking place on standing in the melting points of crystalline derivatives of cyclic acetals.[3]

The view that only the five-membered type of cyclic acetal is formed in such condensations has, unfortunately, been accepted by various investigators. Thus in the recent paper by Yoder[4] dealing with the condensation of chloral and glycerol, the assumption is made that only the five-membered acetal is formed. An investigation by the present authors of this same reaction is in progress and will presumably yield evidence of the simultaneous formation of both the five- and six-membered acetals. In the condensation

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[1] Research Fellow, McGill University, Montreal. This work was carried out under the auspices of the coöperative research organization embracing the Canadian Pulp and Paper Association, the Pulp and Paper Division of the Forest Products Laboratory of Canada and the Department of Industrial and Cellulose Chemistry, McGill University. The authors wish to express their thanks for the support accorded them.

[2] Hill, Whelen and Hibbert, THIS JOURNAL, 50, 2237 (1928).

[3] Irvine, Macdonald and Soutar, J. Chem. Soc., 107, 344 (1915).

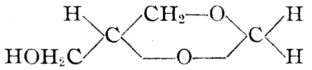
[4] Yoder, THIS JOURNAL, 45, 475 (1923).

of chloral with glucose the number of theoretically possible isomers (structural, geometrical, optical) capable of existence, is much greater, hence the confusion arising out of the various investigations[5] dealing with this reaction.

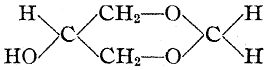
A solution not only of this but also of other problems in carbohydrate and polysaccharide chemistry, will doubtless be found in the further application of the principles enumerated in the series of investigations carried out by Hibhcrt and co-workers during the last eight years in this field, embracing, as they do, a recognition of the important role played by the somewhat neglected, but invaluable and indispensable "Partition Principle" of Arthur Michael[6] as well as of the deductions derivable from a consideration of the nature of the structural, geometrical and optical isomerism involved.[7]

The complications referred to above can be avoided if the study is confined to those acetals (or ketals) where such *geometrical* isomerism is impossible, as, for example, in the case of the isomeric methylidene glycerols,[8] III and IV.

(III)



(IV)



In Type III only one asymmetric carbon atom is present, so that the product should yield a single optically resolvable racemic form, while Type IV is not capable of existing in more than one, non-optically active, modification. The number of possible isomers is thus limited to one representative of each ring system, the five-membered acetal, however, being capable of active resolution.

In view of the relative stability of methylidene glycerol toward hydrolysis,[9] as compared with other acetals[10] and ketals,[11] this cyclic acetal was chosen as the simplest type conforming to the above requirements.

[5] Heffter, Ber., 22, 10.50 (1889); Hanriot and Richet, *Compt. rend.*, **116,** 63 (1892). 117, 734 (1893); 122, 1127 (1896); **Bull.** *sor. chim.*, *[3]*9,947 (1893); [3] 11, 37, 258, 303 (1894); Hanriot, *Ann chim phys*, 18,466 (1909); Hanriot and Kling, *Compt* **rend.**, 152,1398, 1596 (1911); 156, 1380 (1913); Meunier, *Ann. chim. phys.*, [6] 22,413 (1906); Petit and Polonowski, Bull *soc. chim*, [3] 11, 125 (1894); Pictet and Reichel, *Helv Chim. Acta*, **6,** 621 (1923).

[6] Michael, ***Ber.***, 39, 2138, 2143, 2149, 2153, 2157, 2569, 278.5, 2789 (1906); 40, 140 (1907); *J. prakt. Chem.*, ***60,* *339,* *341,*** 437 (1899).

[7] Researches dealing with many of these points are in active progress and the bearing of **such** in connection with the structure of cellulose, starch, etc., is to be reported on in the near future.--H. H.

[8] The name "methylidene glycerol" is employed to denote its relationship (as the lowest member) to a series of cyclic acetals, for example, ethylidene, propylidene, isopropylidene, etc , glycerols.

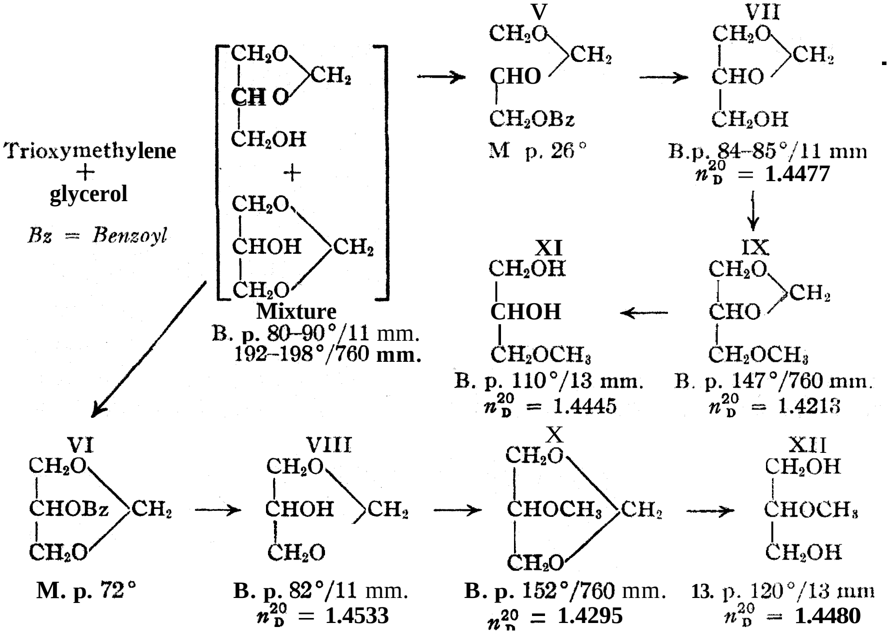
[9] ***Nef, Ann.***, 335,215 (1904)

[10] Hibbert and Timm, THIS JOURNAL, 46, 1289 (1924)

[11] Fischer and Pfähler, *Ber.*, 53, 1606 (1920).

Methylidene glycerol has long been known[12] and the existence of two isomeric benzoates was shown by Schulz and Tollens,[13] who, however, left open the question of their structure. Its properties were further studied by Nef,[9] and Peacock[14] obtained a partial optical resolution of his product which led him to assign to it the structure corresponding to I.

A careful study by the authors of the product formed in the reaction between formaldehyde (trioxymethylene) and glycerol has shown this to consist of the two isomeric cyclic acetals III and IV, which have been separated and identified by the method outlined in the following scheme.



This sharp separation into two isomeric series was rendered possible by the successful isolation of the two pure isomeric benzoates V and VI (as indicated in the experimental part) from which it was then possible to prepare, for the first time, the pure acetals **VII** and **VIII** and the methyl ethers **IX** and X.

These ethers yielded the corresponding α- and β-glycerol methyl ethers on hydrolysis, the identification of the β-derivative being definitely settled by comparison with the pure glycerol β-methyl ether recently isolated in this Laboratory.[15]

Among other attempts to obtain a separation of the isomeric acetals

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[12] Harnitzky and Menschutkin, Ann., 136, 126 (1865).

[13] Schulz and Tollens, *Ann.*, 289, 30, 33 (1896).

[14] Peacock, J. *Chem. Soc.*, 107, 815 (1915).

[15] Will, Whelen and Hibbert, THIS JOURNAL. 50, 2238 (1928).

from the original reaction mixture by means of crystalline derivatives, the *p*-nitrobenzoates were prepared, These crystallize much less readily than the corresponding benzoates and were more difficult to separate. The five membered derivative melted at 135° and its six-membered isomer at 185°.

The Interconversion of 1,2- and 1,1′-Methylidene Glycerols

The mixture of acetals obtained in the original condensation product can only be partially separated into its component isomers by fractional distillation at atmospheric pressure and it was in this connection that the observation was first made of a change in the higher boiling fraction (197–198") on standing for several months into approximately that of the lower (192–193°). It was found later that the unseparated mixture of acetals, on treating with a few bubbles of dry hydrogen chloride gas and allowing to stand for some hours at 100°, always gave, on benzoylation, a greater yield of the benzoate of the 1,1′-acetal than the untreated mixture. On the other hand, after the pure acetals had finally been isolated, treatment of each for thirty minutes at 100" with approximately 0.01% by weight of dry hydrogen chloride showed a large percentage conversion of VII into VIII, as indicated by change in refractive index, while VIII evidenced little, if any, change into VII. In view of this transformation from a 5- to a 6-membered ring under the catalytic influence of small amounts of acid, it was necessary to show that a similar conversion does not take place during the alkaline hydrolysis of the benzoates and the methylation of resulting acetals, also carried out in *alkaline* solution. This was accomplished by first hydrolyzing separate samples of V and VI and then re-benzoylating only after the acetals had first been given an opportunity of undergoing interconversion by heating in presence of alkali. In each case the original benzoate was obtained exclusively, showing that no tendency toward such change exists under these conditions. All subsequent operations with the free acetals were therefore performed in the presence of a small piece of solid potassium carbonate to ensure alkalinity.

Due to the sensitivity toward acid media and the close similarity in chemical properties of the two liquid isomeric acetals, it is difficult to determine, other than qualitatively, the ratio of the two isomers present in the original reaction product. The evidence, however, points to a preponderance of the 5-membered ring in the ratio of approximately 3 to 2.[16]

Experimental Part

Preparation of the Mixture of Isomeric Acetals.—As a result of many preliminary experiments on the preparation of the methylidene acetals,

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[16] The problem of finding an aldehyde capable of giving crystalline isomeric cyclic acetals has been solved by the use of pnitrobenzaldeliyde and it has been found possible to isolate the theoretical number of isomers in the case of *p*-nitrobenzylidene glycerol derivatives. This work is to appear in the near future.

using the original method of Schulz and Tollens,[13] and also employing several of the catalysts mentioned by Adams and Adkins[17] as being advantageous in acetal formation, the best yields were eventually obtained by the following original method.

An equimolecular mixture of 75 g. of pure glycerol and 26 g. of trioxymethylene was acidified with 2 cc. of concentrated hydrochloric acid, the whole well shaken in a stoppered flask, and then kept at 100° for one and one-half hours with frequent shaking. The resultant clear solution, while still hot but without further heating, was placed under reduced pressure (12 mm.) and the vacuum maintained until no further evolution of water was observed. This removal of water with consequent displacement of the equilibrium: trioxymethylene + glycerol acetal + water, was found materially to improve the yield of acetal. The residual liquid was allowed to stand for another twelve hours at 100° and then distilled under reduced pressure in the presence of the hydrochloric acid. The first drops of acetal commenced to distil at about 90° (10 mm.) and the temperature was then gradually raised until the distillate began to appear viscous, by which time most of the acetal had distilled over. Redistillation from a boiling water-bath yielded 50 g. (63%) of the pure mixed acetals boiling between 80–90° (11 mm.) $n_D^{20} = 1.4497$, the latter value indicating a mixture of approximately 60% of the 1,2- and 40% of the 1,1′-methylidene glycerol.

Conversion of Mixed Acetals into Benzoates.—The mixed acetals may be benzoylated directly, but since for the purpose of this investigation as large a yield as possible of the benzoate (VI) of the 6-membered acetal was desired, advantage was taken of the action of dry hydrogen chloride in bringing about a large conversion of the 1,2- into the 1,1′-acetal. Fifty g. of the isomeric mixed acetals as obtained by direct distillation, b. p. 80–90° (11 mm.), was treated with 0.01% by weight of dry hydrogen chloride and allowed to stand for half an hour at 100°, then cooled and added to 40 g. of pure, dry pyridine. The theoretical quantity (68 g.) of benzoyl chloride was slowly run in from a dropping funnel, with constant shaking, at such a rate that the temperature of the exothermic reaction was kept below 60°. The product was allowed to stand at 20° for forty-eight hours to complete the reaction, dissolved in slightly more than the minimum quantity of ether necessary for solution, washed successively with considerable water, then with very dilute sulfuric acid and finally with dilute sodium bicarbonate solution prior to being dried over fused calcium chloride. After removal of the ether under reduced pressure and cooling, the mixed isomeric benzoates were left as a more or less oily white crystalline paste; yield practically quantitative (95 g.).

Separation of the 1,2-Methylidene Glycerol 1′-Benzoate (V) from the Isomeric 1,1′-Methylidene Glycerol 2-Benzoate (VI).—The above semi-crystalline mass was dissolved in four times its volume of warm ether and cooled to room temperature (18°), when it deposited a network of fine, prismatic needles. These were filtered off by suction but not washed, since they are relatively quite soluble in the solvent at ordinary temperatures. By further cooling the filtrate to 0° a second crop could be filtered off at this temperature. Finally, sufficient solvent was evaporated from the remainder to cause the solution practically to solidify when cooled to −20° with stirring; the cold paste was transferred to a small, previously cooled Büchner funnel and suction applied while the whole was slowly allowed to warm to room temperature. The remaining thin layer of unmelted crystals was added to the two previous crops and the whole allowed to lose any adsorbed ether by standing at a temperature below 15°. Recrystallization from hot ligroin (b. p. 80–90°) gave pure 1,1′-methylidene glycerol 2-

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[17] Adams and Adkins, THIS JOURNAL, 47, 1361 (1925).

benzoate (VI) in the form of long (1–2 cm) colorless prismatic needles, m. p. 72°, corresponding to the product obtained by Schulz and Tollens.[13] The crystals are very soluble in benzene, and other solvents at 30° and are deposited readily from ether and alcohol as the temperature falls toward 0°; they are insoluble in water and cold ligroin. The yield in the most favorable experiment was approximately 50% of the mixed benzoates.

Anal. Subs., 0.1952: CO_2, 0.4536; H_2O, 0.0988. Calcd. for $C_{11}H_{12}O_4$: C, **63.4; H, 5.81.** Found: C, 63.3; H, 5.66%.

The ethereal solution of the remaining isomeric benzoate (V) contained residual traces of pyridine, which was removed by distillation and the residue then fractionated under reduced pressure.

The main product boiled at 172 175° (15 mm.) and undoubtedly was the "oily benzoate" analyzed by Schulz and Tollens; yield, 45% of total mixed benzoates. On long standing at 0° or by solution in methyl alcohol and cooling to −20°, large, colorless, tabular prisms of 1,2-methylidene glycerol 1'-benzoate (V) melting at 26° and possessing the same solubility relations in organic solvents as the first isomer were eventually obtained, though only with considerable difficulty.

Anal. Subs.. 0.2047: CO_2, 0.4741; H_2O, 0 1061 Calcd. for $C_{11}H_{12}O_4$: C, **63.4;** H, 5.81. Found: C, 63.2; H, 5.52. *Mol. wt* Subs., 0.4117; ethylene bromide, 40 07; ΔT, 0.566°. Mol. wt., calcd : 208 1. Found: 213.

Alkaline Hydrolysis of **1,2-Methylidene** Glycerol 1'-Benzoate (V) to **1,2-Methylidene** Glycerol **(VII).—Forty** g. of V was added to 110 g. of a 20% potassium hydroxide solution and continuously shaken at 75° for ten to fifteen minutes until the oil resulting from the melting of the crystals had dissolved completely to a clear solution. After cooling the solution, the excess of potassium hydroxide was converted into carbonate by passing in carbon dioxide and the solution completely saturated by adding anhydrous potassium carbonate. The resulting liquid acetal (together with some sodium benzoate thrown out of solution) was extracted by repeated shaking with ether and decantation, the sodium benzoate filtered off and the ether solution dried over solid potassium carbonate. After removal of the ether, distillation under reduced pressure in the presence of a small amount of solid potassium carbonate yielded 15 g (75%) of crude product. On redistillation pure 1,2-methylidene glycerol (VII) was obtained; b. p. 84–85° (11 mm.); 104° (28 mm.); 195° (760 mm.); n_D^{20} = 1.4477 d_4^{20} = 1.2113.

Anal. Subs., 0.2061: CO_2, 0.3414; H_2O, 0.1435 Calcd. for $C_4H_8O_3$: C, 46.12; H, 7.75. Found: C, 46.20; H, 7.79. *Mol. wt* Subs., 0.1049, 0.4312: ethylene bromide, 40.77, 40.77; ΔT, 0.250, 0.954°. Mol. wt., 122, 131.

These values indicate some association due to the free hydroxyl group, extrapolation to zero concentration giving a mol. wt. of 107 (theoretical, 104).

The substance is a slightly viscous, colorless, hygroscopic liquid, soluble in all proportions in ether, alcohol, water and warm benzene. When freshly distilled a very slight odor is noticeable which later disappears. Even on prolonged exposure no odor of formaldehyde is developed, hydrolysis only occurring on boiling with dilute acids (hydrochloric acid, etc.). This behavior is in marked contrast to most glycerin acetals.

When the acetal is mixed with 0.01% by weight of dry hydrogen chloride and heated to 100° for twenty minutes, the refractive index (which is practically unchanged immediately after addition of catalyst) rises from 1.4477 to 1.4540 (20°), thus indicating a large conversion to the 1,1'-isomer (VIII) described below.

Alkaline Hydrolysis of **1,1'**-Methylidene Glycerol **2-Benzoate** (VI) to **1,1'-Methylidene** Glycerol **(VIII).—Forty** grams of VI hydrolyzed in the same manner as the above corresponding isomer yielded 12 g. (60%) of 1,1'-methylidene glycerol (VIII). Careful distillation of the resulting product gave a slightly viscous. colorless, hygroscopic liquid; b. p. 82° (11 mm.); 100° (28 mm); 191° (760 mm.); n_D^{20} = 1.4533; d_4^{20} = 1.2266

Anal. Subs, 0.2037: CO_2, 0.3432; H_2O, 0.1416 Calcd. for $C_4H_8O_3$: C, 46.12; H, 7.75. Found: C, 45.95; H, 7.77. *Mol.* wt. Subs., 0.2009, 0.4074, 0.5116; ethylene bromide, 40.44, 40.44, 40.44; Δ*T*, 0.498°, 0.936°, 1.114°. Mol wt., 118, 127, 134. By extrapolation to zero concentration as before, mol. wt. = 107 (theoretical, 104.1).

In odor, solubility in solvents and resistance toward hydrolysis, it closely resembles the 1,2-isomer (VII). On similar treatment with hydrogen chloride, the refractive index, instead of falling as would be expected from a partial conversion into the isomer (VII), gradually rose over a period of twenty-four hours to 1.4583 at 20°, accompanied by discoloration and increase in viscosity, the latter phenomena indicating some more deep-seated change.

Methylation of **1,2-Methylidene** Glycerol (VII).—Ten grams of acetal (VII) was dissolved in 43 g. (3 moles) of methyl iodide and the usual methylation procedure followed by slowly adding 35 g. of dry silver oxide during a period of three hours, the mixture being refluxed and well stirred throughout the addition. After extracting with ether and drying over calcium chloride, fractionation of the resulting liquid yielded 8.5 g. (80%) of crude 1,2-methylidene glycerol 1'-methyl ether (IX), b. p. 145–150° (760 mm.). To remove unchanged acetal, glycerol, etc., this was heated with a globule of metallic sodium for a few minutes at 80°, the product filtered and the filtered liquid re-stilled. The pure methyl ether was then obtained as a colorless, mobile liquid possessing a pleasant, ethereal. odor, soluble in all proportions in ether, alcohol, benzene and water; b. p. 147° (760 mm.); n_D^{20} = 1.4213; d_4^{20} = 1.0788.

Anal. Subs., 0.1988: CO_2, 0.3651; H_2O, 0.1497. Calcd. for $C_5H_{10}O_3$: C, 50.8; H, 8.66. Found: C, 50.1; H, 8.43. *Mol.* wt. Subs., 0.3107; ethylene bromide, 40.50; Δ*T*, 0.741°. Mol. wt., 122 (theoretical, 118.1).

Methylation of **1,1'-Methylidene** Glycerol (VIII).—Ten grams of the acetal was methylated by means of dimethyl sulfate and caustic potash according to the method of Haworth[18] and the resulting methyl ether (X) separated from the reaction mixture by continuous ether extraction over a period of eight hours. Distillation of the extract yielded 6 g. (55%) of crude 1,1'-methylidene glycerol 2-methyl ether, b. p. 150–160° (760 mm).

Purification with metallic sodium as above and redistillation gave a pure product, b. p. 152° (760 mm.); n_D^{20} = 1.4295, and possessing the same appearance, odor and solubilities as the corresponding isomer (IX).

Anal. Subs., 0.2019: CO_2, 0.3731; H_2O, 0.1521. Calcd. for $C_5H_{10}O_3$: C, 50.80; H, 8.56. Found: C, 50.61; H, 8.43. *Mol. wt.* Subs., 0.2115; ethylene bromide, 43.11; Δ*T*, 0.508°. Mol. wt., 114 (theoretical, 118.1).

Acid Hydrolysis of **1,2-Methylidene** Glycerol 1'-Methyl Ether (IX).—Seven grams of the ether was dissolved in an equal volume of water and 6 drops of concentrated hydrochloric acid added. On refluxing for ten minutes at the boiling point, liberation of formaldehyde commenced and after further refluxing for thirty minutes it was allowed to simmer for two to three hours in a small open Erlenmeyer flask until the evolution ceased. Water was added from time to time to replace that lost by evaporation. The hot solution was then neutralized by adding solid lead carbonate, cooled, filtered and subjected to vacuum distillation. The sole product (b. p. 110° at 13 mm.) was readily recognized as glycerol α-methyl ether by its boiling point and refractive index, n_D^{20} = 1.4445;[3] yield, 3 g. (50%).

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[18] Haworth, *J. Chem. Soc.*, 107, 8 (1915).

Acid Hydrolysis of **1,1′-Methylidene** Glycerol 2-Methyl Ether (X.) Five grams of this ether was hydrolyzed by the same method and yielded 2 g. (45%) of pure glycerol β methyl ether;[15] b. p. 120° (13 mm.); $n_D^{20} = 1.4480$.

The identity was further confirmed by conversion of the product into 1,1′-*p*-nitrobenzylidene glycerol 2-methyl ether and isolation of the two crystalline isomers, m. p. 42 and 47°, respectively.[19]

Summary

1. The possibility of both optical and geometrical isomerism in the structurally isomeric cyclic acetals of glycerol is pointed out.

2. Advantage is taken of the absence of geometrical isomerism in the methylidene glycerols in order to isolate and determine the structure of the two isomers formed by partition of formaldehyde between the 1,2- and 1,1′-hydroxyl groups of glycerol during cyclic acetal formation.

8. The isolation and identification of the two isomeric methylidene glycerols and of certain of their derivatives are described.

4. The interconversion of the ring systems of the two isomeric acetals has been investigated.

MONTREAL, CANADA

NEW BOOKS

A Textbook of Inorganic Chemistry. Volume VI, Part I. Nitrogen. By EDMUND B. R. PRIDEAUX, M.A., B.Sc. (N. Z.), D.Sc. (Lond.), F.I.C., and HERBERT LAMBOURNE, M.A. (Cantab.), M.Sc. (Lond.), F.I.C. J. B. Lippincott Company. Philadelphia, 1928. xxviii + 242 pp. 25 figs. 15.5 X 23 cm.

This volume deals solely with nitrogen, and in view of the present importance and extensive literature on the subject, naturally presents a problem to the authors as to what they shall include in the 231 pages of text allotted to them.

The fourteen chapters include an introductory chapter on the nitrogen atom, the properties of nitrogen, one on ammonia, hydroxylamine, nitrogen and the halogens, oxy-halogen derivatives, hydrides and their derivatives, hyponitrous acid, the oxides of nitrogen, nitrous acid, nitric acid, nitrogen and sulfur and one on the fixation of nitrogen. Some space might have been saved in the chapter on ammonia by a more judicious selection of graphs. For textbook purposes a satisfactory discussion of the synthetic production of ammonia is presented, including a brief reference to the technical features of the process.

The authors' prefatory intention to avoid "undue detail in physical constants and in the minutiae of chemical processes" has been somewhat overlooked by the later inclusion of such data as the tables of the solubility of nitrogen in water, and in sea water, and the listing of five different equations for the specific heat of ammonia at constant pressure. This

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[19] A full account of this work has been submitted for publication in THIS JOURNAL

oversight, however, is not a serious one and merely attests to the zeal of the authors in making their book "a starting point for research."

The chapter on the fixation of nitrogen, in 26 pages, includes a discussion of the arc process, with a brief historical account of the early developments, and gives the reader some idea of the details of construction of the various furnaces. The section on Synthetic Ammonia includes a discussion of the "Haber" process with a brief discussion of the method of gas preparation and purification. The Claude, Casale and Fauser processes are briefly dealt with, as is also the commercial oxidation of ammonia. Brief mention is made of the Serpek, or aluminum nitride process, the Bucher cyanide process and the cyanamide process. A survey of the nitrogen fixation problem completes the chapter and the book.

As a whole the book is a valuable compilation of information on the chemistry and technology of nitrogen and should be of service to the student and research worker in this field.

H. J. KRASE

Physical Chemistry and Biophysics for Students of Biology and Medicine. By MATTHEW STEEL, Ph.D., Professor of Biological Chemistry, the Long Island College Hospital, Brooklyn, New York. John Wiley and Sons, Inc., New York, 1928. x + 372 pp. 38 figs. 15 × 23.5 cm. Price, $4.00.

Chapters 1 to 4 are entitled, respectively, General Introduction; Nature and Structure of Matter; General Properties of Matter; Energy Transformations in Living Matter. Chapters 3 to 12 contain the usual treatment of elementary physical chemistry. Such recent developments as the theory of Debye and Hückel and Cohn's studies of the physical chemistry of the proteins are unmentioned. Chapter 13, the last, is entitled "Dynamical Physical Chemistry of the Cell."

This book is fairly satisfactory in scope but the treatment of several subjects lacks precision. Thus on p. 106 we learn that when "a mixture is chemically and physically homogeneous, and no abrupt change in its properties results from a change in the proportions of the compounds of the mixture, it is a one-phase system and is termed a solution." However, this appears to be a definition not of solution but of "true solution," for glucose and water form "a homogeneous, one-phase system composed of two different substances, uniformly mixed with each other. Such a system is called a true solution, to distinguish it from heterogeneous mixtures, such as colloidal solutions." This ambiguity is accentuated on p. 108 where smoke in air is given as an illustration of solutions of solids in gases.

"Water as a Solvent" is the title of a paragraph on p. 120. Water has great "power of solution." "All kinds of substances dissolve in it. . . . . The urine, for instance, may have as many as a hundred substances dissolved in it. Among these are. . . adinine, allantoine,. . . tyrocine, . . .;

salts of sodium, . . . iron, carbonic acid, nitrogen, argon;. . . blood form elements and pigments, pus, . . . arsenic, mercury,. . . urorosin, urocromogen. . ." In this one paragraph, in addition to typographical errors, the words *power, substance* and *element* are used in the popular sense and an error of logic is made in illustrating the solvent "power" of water by the solvent "power" of urine.

This lack of precision may also be illustrated by inconsistency in nomenclature. Thus we have on p. 121 "ions of water," and on the same page, "OH-ions of the substrate are substituted for H-ions"; on p. 173, "quantity of H^+ ions and $OH-$ ions"; on p. 189, "$HCl \rightleftarrows H^+ + Cl'$" and "the H+-ion content"; on p. 232, "$Ct' - An' + H'OH' \rightleftarrows H' - An' + Ct' - OH'$", and on page 362, "the (H^+) and (OH^-) concentrations."

Although errors and inconsistencies appear to be rather numerous, it may be said that the plan and scope of the book should make it useful to students of biology who have little time to devote to chemistry and physics.

D. B. DILL

Holzchemie. (The Chemistry of Wood.) BY DR. ERIK HÄGGLUND, Professor of Wood Chemistry at the Academy of Åbo. Akademische Verlagsgesellschaft m. b. H., Markgrafenstrasse 4, Leipzig C 1, Germany, 1928. viii + 275 pp. 33 figs 16 × 23.5 cm. Price, unbound, M 18; bound, M 20

The name of Hagglund needs no introduction to students of wood chemistry. In the Foreword of his present book he calls attention to the lack of publications in the line of wood chemistry. He acknowledges recent American publications, but justifies his own book on the ground that he has drawn for material on a great number of German and Scandinavian investigators, and thus he gives his work a more widespread appeal.

This small but rather comprehensive text is divided into eleven chapters, commencing with a very interesting one on The Texture of Wood. This chapter is illustrated by photographs and diagrams on sections of various types of woody plant structures. The next chapter deals rather briefly with The Physical Attributes of Wood. It is in this chapter that the tremendous amount of work connected with gathering material for the text begins to become apparent. There are in the entire text somewhat over 175 tables and curves representing data either accumulated by the author or taken from other literature in support of one of his contentions.

The third and most elaborate chapter deals with The Constituents of Wood and their Chemical Properties. Therein are studied in some detail the usual. list of wood constituents. The formulas of lignin due to Klason and to Schrauth are presented. Subsequent chapters deal variously with the reactions of wood with acids, sulfites and alkali. The two last chapters treat of The Behavior of Wood Accompanying Storage

(Stratification) and Certain Opposing Reagents, and with The Decomposition of Woods in Nature.

Throughout the text are innumerable references to the literature, much of which is American. There is at the end of the book an eleven-page Author Index to the rich list of references, which, for one interested in this subject, is worth the price of the book, for the author has spared no labor in gathering these references.

As a whole, the text is a fine review of the subject, not adding much that is startlingly new, but organizing and tabulating that which had already been written in such a way as to eliminate much of the usual "dead timber."

R. LYMAN HEINDEL, JK.

Synthese der organischen Arzneimittel. (Synthesis of Organic Medicinals.) By PROFESSOR DR. ERNST WASER, Zürich. Ferdinand Enke, Stuttgart, Germany, 1928. xi + 227 pp. 16.5 X 25.5 cm. Price unbound, M 16; bound, M 18.

This book is an advanced text on the synthetic methods for preparing organic medicinals and is planned by the author as an aid to students in chemistry as well as to those in medicine and pharmaceutical chemistry who desire to become acquainted with this field. The discussion is limited essentially to the methods of preparation. The physical properties of the various drugs are described very briefly and the general physiological action of each is given in a table, classified in one of fourteen different groups, such as drugs exciting the central nervous system, drugs for local anesthesia, etc.

The discussion of the various compounds is under six headings.

(1) Aliphatic Compounds
    (*a*) Hydrocarbons and Halogen Compounds
    (b) Ouy-compounds (Alcohols, Ether and their Halogen Compounds and Esters)
    (*c*) 0x0-compounds (Aldehydes and their Halogen Compounds)
    (*d*) Sulfones
    (r) Carboxylic Acids and their Derivatives (Esters, Amides, Urethans, etc.)
    (*f*) Amino Alcohols and their Derivatives
    (*g*) Amino Acids and their Derivatives

(2) Aromatic Compounds
    (*a*) Phenols and Derivatives
    (b) Carboxylic Acids and Derivatives
    (*c*) Amines and Aminophenols
    (*d*) Aminobenzoic Acids and Derivatives

(3.7) Mixed Aliphatic–Aromatic Compounds
    (*a*) Halocaine Group
    (*b*) Novocaine Group
    (*c*) Tyramine Group

- (4) Alicyclic Compounds
- (5) Heterocyclic Compounds
  - (*a*) **5-Membered Heterocyclic Systems, such as Indole Derivatives, Pyrazole Derivatives, etc**
  - (*b*) **6-Membered Heterocyclic Systems, Such as Pyridine, Quinoline, Ecgonine Derivatives, etc**
- (6) Dyes
  - (*a*) Azo Colors
  - (*b*) **Phthaleins**
  - (*c*) **Acridine** Colors
  - (*d*) **Thiazine** Colors

References from which the information is obtained about the preparation of the drugs are included. Over 250 drugs are listed with their trade names.

The book is copiously supplied with structural formulas which are a great aid to the reader and make it possible to obtain proper information without too much study. All of the methods of preparation or references to all of them for each of the individual drugs are not in every case included; in fact now and again omission of a very important method has been noted. The author has made no attempt to indicate which of the methods described is of the greatest commercial value and frequently more detail is given about a less important method than about a more important one. As a consequence, the student must not be misled into believing that the information which is given is more than of general help in the development of a manufacturing process for any drug.

To the reviewer it seems a pity that the author could not have added to his rather extensive list of drugs a few of the more important ones which have been developed, manufactured and widely distributed in the United States, such as mercurochrome-220, hexylresorcinol and butyn. These are certainly of far more commercial value than a large proportion of those described which find only a very limited use and distribution. It should be mentioned also that the author has omitted a discussion of the therapeutic compounds of arsenic, antimony and mercury.

At the end of the book are appended five useful tables which indicate by means of structural formulas all of the various methods of preparation for novocaine, tyramine, hordenine, suprarenine and hydrastinine.

It is unfortunate that a chapter on the comparative medicinal value of the individual substances in any one class could not have been given but it is clearly recognized how difficult it is to procure this information.

If an occasional statement is overlooked such as that ethylene chlorohydrin is made from ethylene glycol, much valuable chemistry is involved in the book and is presented in a very condensed and readable form. The student, therefore, milt benefit by the study of this book from the purely synthetic organic chemical standpoint at the same time that he is acquiring a knowledge of synthetic drugs.

The book is one which any chemist interested in synthetic drugs should surely have at his disposal.

ROGER ADAMS

The Chemistry of Leather Manufacture. By **JOHN ARTHUR WILSON**, Chief Chemist, A. F. Gallun and Sons Co. (Tanners), Milwaukee, Wisconsin. Volume I, second edition. American Chemical Society Monograph Series. The Chemical Catalog Company, Inc., 419 Fourth Avenue, New York, 1928. 495 pp. 105 figs. 95 plates. 15.5 X 23.5 cm. Price, 610.00

The first English edition of this book appeared early in 1923. Its outstanding merit was instantly recognized as shown by the publication of translations in three foreign languages, the German in 1923, French in 1926 and Russian in 1027. Since the publication of the first edition, scientific knowledge of the fundamentals pertaining to the many materials used and the leathers produced by tanneries has grown enormously, the author himself being one of the most prolific contributors. As a result of the increase in exact information, together with "many and varied suggestions for increasing the scientific value and general usefulness of the book," the author has found it necessary to increase the size of the book to two volumes, each greater in size than the original book.

Volume I consists of 14 chapters including Histology and Chemical Constituents of Skin, Measurements of Acidity and Alkalinity, Physical Chemistry of Proteins, Microörganisms and Enzymes, the Preservation, Disinfection, Soaking, Fleshing, Unhairing, Bating and Pickling of Skins and the practical aspect of Vegetable Tanning Materials as well as their chemistry and evaluation.

The author has acquitted himself well in a difficult task, producing a work so fundamentally chemical that it possesses broad scientific value as well as being the authoritative reference and textbook for the leather and tanning industry.

ARTHUR W. THOMAS

The Journal of the American Chemical Society

VOL. 50 DECEMBER, 1928 No. 12

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 206]

A NEW EQUATION OF STATE FOR FLUIDS.
II. APPLICATION TO HELIUM, NEON, ARGON, HYDROGEN, NITROGEN, OXYGEN, AIR AND METHANE

BY JAMES A. BEATTIE AND OSCAR C. BRIDGEMAN[1]

RECEIVED MARCH 29, 1928 PUBLISHED DECEMBER 10, 1928

In the preceding paper,[2] the authors proposed an algebraic equation of state whose constants are easily and uniquely determinable from pressure–volume–temperature data, and which can readily be used for evaluating the usual thermodynamic relations. This equation of state is

$$p = \frac{RT\,(1-\epsilon)}{V^2}\,[V+B] - \frac{A}{V^2} \qquad \begin{aligned} A &= A_0\,(1-a/V) \\ B &= B_0\,(1-b/V) \\ \epsilon &= c/VT^3 \end{aligned} \qquad (1)$$

in which R is the gas constant and A_0, a, B_0, b and c are parameters which depend upon the kind of substance under consideration. It was shown that the data on gaseous ethyl ether and carbon dioxide were represented very satisfactorily by an equation of this form. A physical basis for this equation and the details of the method for the evaluation of the constants from the compressibility measurements will shortly be presented elsewhere.

In the present paper are given the results of the application of Equation 1 to the p–V–T data on eight gases extending over the temperature range from −252 to +400°, and to pressures of about 100 to 200 atmospheres. The region of high pressures (1000 atmospheres or over) will be treated later. The data used for the present comparisons have resulted from the investigations of Kamerlingh Onnes and his associates,[3] and of Holborn, Otto and Schultze[4] on helium, neon, argon, hydrogen, nitrogen, oxygen and air; of Bartlett[5] and Verschoyle[6] on hydrogen and

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[1] National Research Fellow in Chemistry.

[2] Beattie and Bridgeman, THIS JOURNAL, 49, 1665 (1927).

[3] *Communications of the Physical Laboratory of Leiden.*

[4] The data are summarized in Z. *Physik*, **33**, 1 (1925); 38, 359 (1926).

[5] Bartlett, THIS JOURNAL, 49, 687, 1955 (1927).

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

nitrogen; of Witkowski on hydrogen[7] and air;[8] of Smith and Taylor[9] on nitrogen; of Koch[10] and Amagat[11] on air; and of Keyes and Burks[12] on methane.

Within the density range studied, all of the measurements of the above observers were used for the determination of the values of the equation of state constants, and also in the comparisons given in Table II, with the following exceptions: helium, the isotherms below −252° for which the pressures even at large densities are small; argon, the 18.39" isotherm of Onnes and Crommelin; hydrogen, the data of Crommelin and Swallow (Leiden) which could not be correlated with the rest of the field, and the measurements of Verschoyle and Bartlett who made no observations below about 50 atmospheres; nitrogen, the 5 cc. per gram isometric of Smith and Taylor, which is possibly in error; and air, the −130, −135, −140 and −145° isotherms of Witkowski, which show large deviations from the rest of the field.

In order to determine the values of the equation of state constants for a substance, it is necessary to have data in the form of isometrics. Most investigators present their results in the form of isothermals; that is, they list a series of pressure–volume products together with the corresponding pressures (or volumes) for each of several different temperatures. To convert these results into isometrics, the quantity $[pV - RT]$ was calculated for each measurement on a given isothermal. A straight line was passed through the point of zero density (where $[pV - RT]$ is zero) and the highest measured density on the isotherm. Deviations of the observed values from those calculated by the linear equation were plotted against the density on a large scale. By use of the linear equation and the plot, values of $[pV - RT]$ and hence of the pressure (which are considered as the "observed pressures") could be interpolated for a set of evenly spaced densities, the same densities being used at each isotherm. Thus all of the original data were transformed into isometrics by a procedure which smooths with respect to volume; but no attempt was made to smooth for temperature, all of the original isotherms being preserved.

It has long been known[13] that at constant volume the pressure of a gas varies almost linearly with the temperature, and many equations of state which make use of this property have been proposed. The experimental work indicates that the curvature $(\partial^2 p/\partial T^2)_V$ is always negative in the

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[7] Witkowski, *Krakauer Anzeiger*, 305 (1905); Landolt-Börnstein, "Tabellen," 1923, p. 105.

[8] Witkowski, *Phil.* Mag., [5] 41, 288 (1896).

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

[10] Koch, *Ann. Physik*, *27*, 31 (1908).

[11] Amagat, *Ann. chim. phys.*, [6] 29, 68 (1893).

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

[13] Amagat, *Compt. rend.*, 94, 847 (1882).

gas region,[14] but that the isometrics approach linearity as the density decreases, and as the temperature increases.[15] It has been shown that the curvatures of the isometrics of nitrogen,[15] ethyl ether,[16] carbon dioxide,[17] and methane[18] could be represented by introducing into the Keyes[19] equation of state a logarithmic function of the temperature.

The method used for the determination of the values of the constants of the new equation of state can be indicated by rearranging (1) into the form

$$p' = p + \frac{c\psi(V)}{VT^2} = T\psi(V) - \phi(V) \qquad (2)$$

where $\psi(V) = R[V + B]/V^2$ and $\phi(V) = A/V^2$ both being functions of the volume alone. The quantity p' will be called the "corrected pressure." When c is positive, Equation 2 expresses the experimental findings concerning the curvature $(\partial^2 p/\partial T^2)_V$ mentioned above. If the volume and temperature functions used in (2) are satisfactory, there is one value of c which will cause the corrected pressure p' (calculated from p, c, and the volume and temperature functions given) to vary linearly with the temperature for all isometrics; this provides a method for determining c. With a chosen value for this parameter, the corrected pressures are calculated for a representative density; if too small a value of c has been used, all of the curvature is not removed from the corrected isometric, while too large a value causes the curvature of the p', T lines to change sign. Ordinarily two or three approximations are sufficient to select a satisfactory value of c even when correlating different sets of data. This provisional value of c is then verified by a study of the linearity of the corrected isometrics over the entire density field. It is generaliy true that measurements by two different observers give isometrics having different curvatures over the same temperature range; hence the value of c chosen represents a compromise.

From each corrected isometric there is obtained a value of $\psi(V)$ and of $\phi(V)$ which appear as the slope and intercept on the p' axis, respectively, of the linear p', T line. Since $V + B = V^2\,\psi(V)/R$, and $A = V^2\,\phi(V)$, it is possible to calculate a value of B and A for each isometric, and a plot of B against $1/V$ should give a straight line, the slope and intercept

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[14] (a) Keyes and Felsing, THIS JOURNAL, 41, 589 (1919); (b) Keyes, Smith and Joubert, *J. Math. Phys., M. I.* T., 1, 191,211 (1922) [methane]; (c) Smith and Taylor, THIS JOURNAL, 45,2107 (1923); (d) *ibid.*, 48,3122 (1926) [nitrogen]; (e) Beattie, *ibid.*, 46,342 (1924) [ethyl ether]; (f) Keyes and Burks, *ibid.*, 49, 1403 (1927) [methane].

[15] Keyes and Taylor, THIS JOURNAL, 49,896 (1927).

[16] Beattie, *ibid.*, 49, 1123 (1927).

[17] Bridgeman, *ibid.*, 49, 1130 (1927).

[18] Keyes and Burks, ref. 14 f.

[19] Keyes, *Amer. Soc. Refrig. Eng. Jour.*, 1, 9 (1914); *Proc. Nat. Acad. Sci.*, **3.** 323 (1917); Phillips, *J. Math. Phys., M. I. T.*, **1,** 1 (1921).

of which are B_0b and B_0, while A should also vary linearly with $1/V$, the slope and intercept being A_0a and A_0. Thus, with the exception of c, all of the adjustable constants appear as the slopes or intercepts of straight lines in which all of the measured data are given weight.

The values of the constants for the gases studied are given in Table I, where for comparison those for ethyl ether and carbon dioxide are included. In the units chosen, R has the same value for all gases, namely, 0.08206, and T_0 was taken as 273.13. It was found necessary to use different values of the constants for the data of Smith and Taylor on nitrogen, which are very consistent among themselves but could not be correlated with the determinations of the other investigators. Therefore, in the Tables, N_2^a applies only to the Smith and Taylor data, while N_2 includes all of the other data; these latter are the accepted constants for nitrogen.

TABLE I

CONSTANTS OR THE EQUATION OF STATE ROR TEN GASES

$p = [RT(1 - \epsilon)]/V^2\,[V + B] - (A/V^2)$. $A = A_0(1 - a/V)$. $B = B_0(1 - b/V)$. $\epsilon = c/VT^3$. R = 0.08206 for all gases. Units: pressures in atmospheres, volumes in liters per mole, temperatures in degrees Kelvin. $T°K = t°C + 273.13$.

Gas	A_0	a	B_0	b	c
He	0.0216	0.05984	0 01400	0.0	0.004 × 10^4
Ne	0 2125	,02196	.02060	.0	0.101 × 10^4
A	1.2907	,02328	.03931	.0	5.99 × 10^4
H_2	0.1975	− .00506	.02096	− .04359	0.0504 × 10^4
N_2	1 3445	,02617	,05046	− .00691	4.20 × 10^4
N_2^a	1.1440	.01788	.04314	− .01608	5.60 × 10^4
O_2	1.4911	.02562	.04624	,004208	4.80 × 10^4
Air	1 3012	,01931	.04611	− ,01101	4.34 × 10^4
CO_2	5.0065	,07132	.10476	,07235	66.00 × 10^4
CH_4	2 2769	.01855	,05587	− .01587	12.83 × 10^4
$(C_2H_5)_2O$	31 278	,12426	,45446	.11954	33.33 × 10'

[a] Constants for Smith and Taylor's data alone.

In Table II is given a summary of the comparisons of the pressures calculated from the equation of state, using the constants listed in Table I, with the observed pressures. In this comparison the entire measured temperature range is included for all gases, with the few exceptions mentioned above. For some of the gases the entire measured density range at the lower temperatures was not used. This was partly due to the fact that in the low temperature high density region the data were too fragmentary to define the isotherm sufficiently to allow smoothed values of the pressure to be obtained, and partly to the difficulty of correlating this region with the rest of the field due to the large experimental error. In every case all of the isotherms were extended to the maximum density listed in Table II when any data existed.

The second and third columns of Table II give the average deviations in atmospheres and percentage between the observed and calculated

Table II

Summary of the Deviations Between Observed and Calculated Pressures for Ten Gases

Gas	Av. dev. to $1/V = 5.0$ Atm.	%	Av. dev. over entire density range Atm.	%	Max. press., atm.	Max. density, moles/liter	Temp. range, °C.	No. of observers	No. of points
He	0.067	0.133	0.071	0.133	102	10	400 to −252	2	183
Ne	.053	.147	.081	.209	106	8 5	400 to −217	2	229
A	.059	.170	,078	.203	114	6	400 to −150	2	209
H_2	,053	.199	.068	.203	103	10	200 to −244	3	362
N_2	.061	.155	.072	.190	134	5 5	400 to −149	4	214
N_2[a]	.033	.040	.033	.040	213	5.0	200 to 0	1	50
O_2	.025	,069	.051	.115	103	9	100 to −117	2	137
Air	,095	.197	.113	.198	177	8	200 to −145	5	171
CO_2	.079	.144	.128	,203	111	5 5	100 to 0	2	148
CH4	.039	.048	.045	.049	243	6	200 to 0	1	60
$(C_2H_5)_2O$	...	...	.023	.076	90	2.7	325 to 150	1	64
Grand average	,060	.155	.077	.178					

[a] Deviations for Smith and Taylor's data alone. These are not included in the grand averages; to do so would make the grand average deviations smaller.

pressures over the complete temperature range and to a density of 5 moles per liter, which corresponds to an Amagat density of approximately 110, that is, 110 times as dense as at 0° and 1 atmosphere. The fourth and fifth columns contain the same information over the total range of temperature and density considered, these ranges being given in the succeeding columns. The last two columns give the number of different investigators whose data were correlated and the total number of points at which comparisons of observed and calculated pressures were made.

In the evaluation of the constants for the gases and in the comparisons given in Table II, the data of all observers on any particular gas were correlated, if possible, since a better average was thus obtained. For this reason the errors between observed and calculated pressures were larger than if separate equations were used for each group of results. It is in general true that the consistency of one set of data taken by the same observer is much greater than the agreement between two different sets. In fact, the deviations shown in Table II would be about halved if separate equations were used for the measurements of each observer. This can be seen from the results on methane, ethyl ether and Smith and Taylor's nitrogen, which are obtained from the work of the individual investigators and, further, the derivation of individual equations for one experimenter's data in the case of some of the other gases has verified this conclusion. The values of the constants obtained from a consideration of all the data were about the mean of those derived from the individual sets of measurements and are thus the best values that can now be assigned to them. In the cases in which the constants were determined from a consideration of the results of several investigators, the deviations between the observed and calculated values can be taken as an approximate estimate of the accuracy of the available data.

Summary

The new equation of state has been applied to the compressibility measurements on helium, neon, argon, hydrogen, oxygen, nitrogen, air and methane, and the values of the constants are given for these gases and for carbon dioxide and ethyl ether. A method is outlined for transforming the experimental pressure–volume–temperature data into isometric form, and a brief description of the procedure for evaluating the constants of the equation of state is given. Comparison of the observed pressures and those calculated from the equation have been made at 1777 points for these ten gases, the average deviation being **0.08** atmosphere or 0.18% over the entire temperature and density range considered. The average deviation is 0.06 atmosphere or 0.16% over the experimental temperature range and to a density of 5 moles per liter (an Amagat density of approximately 110).

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE BIOCHEMICAL LABORATORY OF VALIO, HELSINKI, FINLAND]

THE VOLATILITY WITH STEAM OF WATER-SOLUBLE ORGANIC SUBSTANCES.

BY ARTTURI I. VIRTANEN AND L. PULKKI

RECEIVED MAY 24, 1928 PUBLISHED DECEMBER 10, 1928

Investigations on the determination of volatile fatty acids by means of steam (which from an analytical point of view is a very important mode of procedure) have in many ways explained our opinion as to the quantitative course of distillation by steam and have rendered it possible to express quantitatively in a simple manner the volatility of water-soluble substances with steam. When boiling the diluted solutions of fatty acids a certain percentage of acid is always distilled into a certain quantity of water, this percentage being different in the case of different acids. If there are several acids in the same diluted solution of acid, each acid is distilled independently of the others. Duclaux's[1] well known and purely empiric mode of procedure for the determination of volatile fatty acids is based on these facts. This procedure is, however, complicated and requires definite tables; it also applies only to fatty acids.

Among the investigations, the purpose of which has been to derive simple mathematical formulas in order to follow the course of distillation, should be mentioned Barrel, Thomas and Sidney Young's[2] differential equations,

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[1] **Duclaux,** *Traité de Microbiologie,* 3,384 (1900); 4,685 (1901).

[2] Barrel, Thomas and Young, *Phil. Mag. and J. of Science, (V)37,* 8 (1894).

which are based upon Brown's[3] work and of a later time upon Richmond's[4] and Wiegner's[5] logarithmical equations, which have evidently been derived independently.

From Brown's equation $dy/dx = ky/x$, where y is the weight of the volatile substance in the liquid and x is the weight of the water in the liquid, Wiegner has derived a simple logarithmical equation

$$\log y = k \log x + 2 - 2k$$

which is very well applicable in practice. If the quantity of water at the beginning of the distillation is denoted by x_1 and at the end by x_2, and the substance to be distilled at the beginning by y_1, and when completed by y_2, we get the following equation

$$\frac{\log y_1 - \log y_2}{\log x_1 - \log x_2} = k$$

k is a constant which according to the above equation is easily calculable from the observations.

k, which we may call the constant of distillation, is a very practical means of indicating the volatility of the substance. If the solution is diluted with regard to the volatile substance to be investigated and if the distillation is made so that the condensation of steam is completely prevented, the value of k is constant for each volatile substance. Now it is impossible in practice completely to prevent the condensation of steam on the walls of the retort, but it may, however, be reduced so much that practically constant values may be obtained for k.

An ordinary steam distillation by blowing steam through the solution is not applicable to quantitative analyses since it is difficult to keep the volume of the solution perfectly constant during the time of distillation and the steam bubbles may be too large in passing through the solution, in which case an exact state of equilibrium between the composition of the steam and the composition of the solution is not obtainable. In practical laboratory work it is in many respects very important to know the volatility of different substances.

First, it is in many cases possible by means of fractional distillation to decide whether the substance is chemically pure or a mixture and thus the purity of the substance can be determined. If many fractions are distilled, k will have the same value in each fraction if the substance under investigation is pure.

Second, it is possible by means of steam distillation to obtain a quantitative analysis of volatile substances, as shown by the determinations mentioned below.

Third, it is possible on the basis of the value of k to decide in advance

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[3] Brown, *Trans.* Chem. *Soc.*, 1879,550; 49,304 (1880); 517 (1881).

[4] Richmond, *Analyst, 33,* 209, 305 (1907).

[5] **Wiegner,** ***Mitt. Gebiete Lebensmitteluntersuchung Hygiene,*** 10, Fasc. *3/6* **(1919).**

whether a substance can be separated from non-volatile substances by means of distillation, whether in such cases neutral salts must be added or whether it is necessary to use altogether different methods.

Taking all of the above-mentioned circumstances into consideration, it is important that the values of k should be found for all substances volatile with steam and that these values should be stated in the handbooks.

Volatility could be expressed not only by distillation constants but also simply by using the number which indicates the percentage of each substance distilled, when a certain volume (half, for instance) is distilled. By means of these values of semi- or quarter-distillations, it is easy to calculate k and *vice versa.*

In this investigation we have determined the value of k for numerous compounds which represent different groups of substances. For quantitative determinations it is important to know how different circumstances influence the value of k and therefore we have investigated by using certain fatty acids, the influence of some factors on the course of the distillation. At the same time we have made minute distillations with mixtures containing two or three different substances.

The influence of salts upon the distillation of substances by steam has been previously investigated by one of us.[6] With a view to theoretically explaining this question we have made additional investigations, which we shall present in this article.

Methods

In the quantitative distillation by steam the only exact procedure is by the method of boiling. For this purpose the solution of the'substance in water to be investigated is distilled without leading steam through the solution, the volume of the solution thus steadily diminishing. While employing the method of boiling it is important that attention be paid to the size of the vessel used in order to prevent the steam from becoming condensed uselessly. For the same reason the tube which unites the retort with the condenser must be sufficiently large and as low as possible. In our experiments we have used a 300cc. Erlenmeyer flask, the volume of the solution being 200 cc. The dimensions of our apparatus are shown in Fig. 1. It is necessary to be certain that the volume of the flask really is precisely 300 cc.

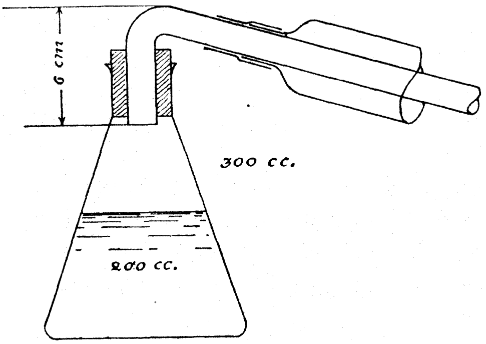

Fig. 1.

The flask was placed upon a network of asbestos and heated by means of an or-

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[6] Virtanen, *Suomen Kemistiseuran Tiedonantoja (Publications from the Chemical Society of Finland),* **1921,** 9.

dinary Bunsen burner. Calibrated volumetric flasks were used as receivers. The acids were determined by titration with $N/20$ sodium hydroxide, with phenolphthalein as indicator; the amines were determined by $N/10$ sulfuric acid with Congo red as indicator. The determination of other substances will be mentioned separately.

There are several circumstances which influence the course of the distillations of these substances in cases where the constant is very great or on the contrary very small. The concentration of the solution is of great importance even if the solution is very much diluted. (Table I.) According to Duclaux, his method of distillation is applicable up to solutions of 2%. Our determinations show that the differences of concentration in solutions with this dilution have a remarkable influence upon the value of k for a number of substances. The time of distillation, upon which the condensation of steam depends, must also be taken into consideration. Below are given a few examples which show the effects of these factors. (Table II.)

TABLE I

THE EFFECT OF CONCENTRATION UPON THE VALUE OF k

60-minute distillations in all experiments

Concentration %	Concentration N	k	Semi-dist. value, %	Concentration %	Concentration N	k	Semi-dist. value, %
Formic Acid (Kahlbaum)				Propionic Acid (Kahlbaum)			
0.02	0.0049	0.364	22.3	0.07	0.0088	1.235	57.5
.07	.0151	.370	22.6	.09	.0115	1.239	57.6
.24	.0521	.388	23.5	.13	.0169	1.239	57.6
.42	.0920	.390	23.7	1.32	.1785	1.270	58.5
.53	.1154	.398	24.1	Butyric Acid (Kahlbaum)			
Acetic Acid[a] (Kahlbaum)				0.05	0.0058	1.92	73.5
0.09	0.0150	0.657	36.6	.16	.0181	1.96	74.4
.51	.0843	.657	36.6	.29	.0332	1.99	74.8
				.88	.1000	2.00	75.0
				2.29	.2600	2.02	75.3

[a] The effect of the concentration of acetic acid is very small. For solutions of 2% and for more concentrated solutions, the value of k is almost the same as in the above distillations.

TABLE II

THE INFLUENCE OF THE TIME OF DISTILLATION UPON THE VALUE OF k

The time is that which elapsed in distilling from 200 to 100 cc.

Concn., %	Minutes	k	Semi-dist. value, %	Concn., %	Minutes	k	Semi-dist., value, %
Formic Acid				Propionic Acid			
0.39	59	0.389	23.7	0.12	60	1.239	57.6
.39	125	.325	20.2	.12	75	1.245	57.9
Acetic Acid				Butyric Acid			
0.12	41	0.668	37.0	0.15	36	1.940	73.9
.12	51	.659	36.7	.15	60	1.964	74.4
.12	58	.658	36.6	.15	88	2.035	75.6
.12	78	.641	35.9				
.12	135	.608	34.4				

From the above values of distillation it is evident that the time used for distillation has a remarkable effect upon k, especially with formic and butyric acids. A rapidity of distillation is, in our opinion, most conveniently used when half of 200 cc. is distilled in sixty minutes. In order to obtain identical values the same rate of distillation should always be used.

The Use of Method of Distillation in Analyzing Mixtures of Volatile Substances

The aforesaid experiences concerning the course of distillation as influenced by the concentration and the time used for distillation are facts to be noted in the quantitative analysis of volatile substances. Previous investigators have not paid attention to these facts but have generalized their method for solutions of fatty acids of 2% at most. In all analyses the differences in concentration may in most cases be passed over, but the results in such cases may be comparatively inexact. By taking the conditions of concentration into consideration it is possible to determine the volatile substances with surprising accuracy by using the method of distillation, as is evident from the determinations mentioned below.

Wiegner has suggested, in his valuable investigation in which fractional steam distillation is theoretically treated, a method to be put into use according to which the solution to he investigated, if containing two volatile fatty acids, is first half distilled; an equal quantity of water is then added to the remainder and the solution is again distilled to a semi-volume. For safety's sake this treatment is repeated for the third time. From the first and second distillations equations will be obtained by which the quantities of acids in the solution may be determined. The third equation may be used as control.

As the conditions of concentration always exercise, according to our determinations, a great influence upon the values of k, it is evident that by using this method the first distillation gives values which are different from those of the second. The third distillation can by no means be compared to the first. One of the authors[7] has previously presented a much simpler method for analyzing a solution containing two volatile acids.

Exactly half of the solution, the total quantity of acid in which is known, is distilled and the quantity of acid in the distillate is determined by titration. If the wanted quantities of acids in the solution are A and B and the value of A's semi-distillation is marked with a and that of B's semi-distillation with b, it is possible to determine the quantities of acids by means of one single distillation. The total quantity of acid may be z and the quantity of acid distilled in the semi-volume Z_1. Thus we obtain the following equations

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[7] Virtanen, *Soc. Scient. Fennica, Comm. Physico-Mathemat.*, **1**, 36 (1923).

$$A + B = z$$

$$\frac{a}{100} A + \frac{b}{100} B = z_1$$

The accuracy of this method is evident from the following example.

Experiment 1.—In 200 cc. there was acetic acid corresponding to 47.4 cc. of $N/20$ acid and propionic acid corresponding to 17.6 cc. of $N/20$ acid. The whole solution thus corresponded to 65.0 cc. of $N/20$ sodium hydroxide. The distillate of 100 cc. used 27.55 cc. of $N/20$ sodium hydroxide. The value of the semi-distillation of acetic acid (A) being 36.6% and that of the propionic acid (P) 57.7%, we obtain the equations $A + P = 65.0$ and $0.366\ A + 0.577\ P = 27.55$, which give $A = 47.2$ cc. of $N/20$ acid and $P = 17.8$ cc. of $N/20$ acid. The error in the acetic acid is −0.4% and that for the propionic acid, +1.1%.

Experiment 2.—In 200 cc. there was 23.6 cc. of $N/20$ acetic acid, 13.7 cc. of $N/20$ propionic acid and 24.0 cc. of $N/20$ butyric acid. Two fractions of 50 cc. were distilled, one of which consumed 18.5 cc. and the other 15.7 cc. of $N/20$ sodium hydroxide. The values of the semi-distillation being 36.6% for acetic acid, 57.7% for propionic acid and 74.0% for butyric acid, and the values of the quarter-distillation being 17.2% for acetic acid, 30.0% for propionic acid and 43.0% for butyric acid, we find the equations $A + P + B = 61.3$, $0.172\ A + 0.3\ P + 0.43\ B = 18.5$ and $0.366\ A + 0.577\ P + 0.74\ B = 34.2$, of which $A = 23.2$ cc. of $N/20$ acid, $P = 14.4$ cc. of $N/20$ acid, and $B = 23.7$ cc. of $N/20$ acid. The error as to the acetic acid is −1.7%; propionic acid, +5.1%; and butyric acid, −1.3%.

The above experiments show that by using the method of distillation it is possible to determine with great accuracy two volatile substances in the same solution when the time of distillation and the effect of the concentrations upon the value of the semi-distillation are taken into consideration. From our determinations it is evident that the best results will be obtained when each component has a value of semi-distillation which corresponds to the total concentration of acids in the solution. Thus, if there are in the solution, for example, 70 cc. of $N/20$ acetic acid and 30 cc. of $N/20$ butyric acid, for each acid the value of semi-distillation which corresponds to the concentration of 100 cc. $N/20$ must be used.

If the solution contains, at the same time, three volatile substances, it is possible to determine them with a comparatively great accuracy as is evident from Experiment 2. If four different substances have to be determined in the same solution, the errors will be very great.

The method of distillation is applicable in general to the determination of volatile substances of which the constant of distillation is not very great. If the value of k exceeds 5, the errors become so great as to render quantitative determinations out of the question.

The volatile acids can be determined according to the method suggested above only in solutions which contain no other substances. Therefore, in analyzing the results of reactions the volatile substances must first be distilled over quantitatively by passing steam through the solution. In the case of a volatile substance which has a low constant of distillation it is advisable to add sodium chloride to the solution so as to promote the distillation (see last section). On the other hand, one must take into account that if there is present in the solution lactic acid, for instance, this also passes over to some extent with steam. In studying cultures of bacteria and similar solutions, it is most advantageous to proceed as follows.

The alcohols, aldehydes, etc., which may be present in the neutral solution are removed by evaporating to half the original volume. The solution is then rendered acid with sulfuric acid and the volatile acids are removed by a current of steam, measured quantities of distillate (200 cc. for example) being collected. If the solution contains such a substance as lactic acid, it, too, passes over after the volatile acids have been removed. The process is stopped when the last two or three distillates contain a constant small quantity of acid. In order to eliminate carbon dioxide, it is necessary to boil the first fraction under an upright reflux condenser. All of the distillates are titrated with barium hydroxide of known strength. The solutions are then united, concentrated in an evaporating dish to small volume and quantitatively transferred to a 250-cc. volumetric flask. The calculated amount of sulfuric acid to react with the barium is added and the flask is filled up to the mark with distilled water. After standing for some time to allow the barium sulfate to settle, 200 cc. of the clear liquid is taken for the analysis. If it is known in advance which acids are present in the solution it is possible to make the quantitative determination as explained above. In order to eliminate the lactic acid which may have distilled together with the others the volatile acids must be expelled quantitatively, by means of steam, from the residue left after 100 cc. has been distilled from the 200 cc. The concentration of the lactic acid is now so low that it does not distil over any more. In this way we determine the amount of volatile acids present in the residue and the calculations can be made according to the method explained above. In order to hasten the volatilization, an excess of sodium chloride must be added to the residue before steam distillation. This addition is absolutely necessary especially when formic acid is present in the solution, since it distils rather poorly from very dilute solutions.

If we do not know what volatile acids are present in the solution, then several fractions, for instance of 10 or 25 cc., must be distilled. From the constants of distillation calculated on a basis of different fractions it is usually possible to judge which acids are present in the solution. Depending on the solution and the acids present we can, of course, use other methods for the qualitative determination of the acids.

Some Constants of Different Organic Substances

In all of the determinations the above-mentioned apparatus was used. From 200 cc. either two fractions of 50 cc. or four fractions of 25 cc. were distilled. In this manner it has been possible to ascertain whether k has the same value in different fractions and, consequently, the substances to be investigated are pure. At the same time the influence of the concentration can be determined.

Organic Acids.—

Acid	Concn., N	k	Semi-dist. value, %	Acid	Concn., N	k	Semi-dist. value, %
Diethylacetic	0.018	4.57	95.4	*o*-Toluic	0.010	0.608	29.7
Chloro-acetic	.036	0.047	3.2	*m*-Toluic	.013	.420	25.2
Phenylacetic	.017	.070	4.8	*p*-Toluic	.009	.378	23.1
Pyruvic	.033	.074	5.0	Anisic	.006	.050	3.4

Acid	Concn., *N*	k	Semi-dist. value, %	Acid	Concn., *N*	k	Semi-dist. value, %
α-Crotonic	.012	.760	41.0	Cinnamic	.010	.102	7.4
Benzoic	.024	.270	17.1	o-Aminobenzoic	.020	.019	1.3
Salicylic	.020	.088	5.9				

Meta and p-aminobenzoic acids and a-, *m*- and *p*-nitrobenzoic acids are not volatile with steam. Levulinic, glycolic and lactic acids are distillable in small quantities but have no constants of distillation. The quantity of distilled acid does not increase in proportion to the concentration. This proves that the said acids are not, in the proper sense of the word, volatile acids. It is possible that anhydrides which are volatile are formed in the distillation.

According as the carbonic chain is prolonged and the solubility diminished, k increases in homologous series notwithstanding the rise of the boiling point. In the aromatic series the a-compounds distil best, then the meta. The *p*-compounds do not distil as well as the others.

Amines.—Many amines are so easily volatile as to be completely distilled by the removal of a half-volume. In these cases out of 200 cc. only *10* cc. was distilled and k was determined accordingly. In these cases an exact value for the constant could not be obtained. The amines were determined by titration with $N/10$ sulfuric acid with Congo Red as indicator.

Amine	Ammonia	Methyl	Ethyl	Propyl	Butyl	Diethyl
B. p.. °C.	−34	−6	+19	+50	+77	+56
Concn., N	0.02	0 02	0.03	0 02	0.02	0.02
k, approx.	13	11	20	30	40	43

An increase of one carbon atom in the homologous series of monovalent aliphatic amines raises the value of k by about 10 units.

Amine	Ethylene di-	Aniline	Methylaniline	Benzyl	Benzyl	a-Naphthyl
Concn., *N*	0.03	0.05	0.03	0.02	0.20	0.01
k	.02	5.51	16	3.27	3.25	1.05
Semi-dist., %	1.4	98.6	...	89.6	89.5	51.7

β-Naphthylamine evaporates copiously but solidifies in the condenser. The value of k could not be determined. In some of the experiments aniline was determined by titration with a solution of $N/10$ sodium nitrite (0°); in other experiments by determining nitrogen by the Kjeldahl method. Methylamine also was determined by the latter method.

Phenols.—

Compound	Phenol	*p*-Chloro-	*p*-Nitro-	m-Nitro-	Thymol
Concn., N	0.10	0.01	0.07	0.06	0.06
k	1.94	1.30	.005	.01	12
Semi-dist., %	74.1	59 *6*	.35	.85	...

Phenol, p-chlorophenol and thymol were determined by titration with a solution of bromine. The nitrophenols could be titrated with $N/20$ sodium hydroxide by using phenolphthalein as indicator.

It is evident from the values given above that chlorine in replacing hydrogen in the benzene ring does not exert a noteworthy influence upon the volatility. On the contrary the nitro-group diminishes the volatility enormously. Of the nitro compounds the m-derivative is distilled better than the para. The influence of the position of the substituent has been proved to be the same in the cases of other substances.

Aldehydes.—The aldehydes were determined by titration with potassium bisulfite and a solution of iodine.

Compound	Formaldehyde	Acetaldehyde	Benzaldehyde	Anisaldehyde
Concn., N	0.03	0.01	0.01	0.01
k	2.6	Above 40	18	**3.1**
Semi-dist., %	83.0	...	...	88.5

Alcohols.—

Alcohol	Methyl	Ethyl
Concn., % by weight	0.05	0.10
k	8.9	12.5

Methyl and ethyl alcohols were determined according to Kuriloff by oxidation with a solution of sulfuric acid and bichromate of potash, which oxidizes ethyl alcohol quantitatively to acetic acid and methyl alcohol to carbon dioxide. The solution to be investigated was heated for three hours at 100° together with an oxidizing solution in a closed pressure flask. The quantity of alcohol was calculated according to the quantity of bichromate used. The precision of the method is 1%.

From these investigations the conclusion is reached that volatility with steam of water-soluble substances depends to a large extent upon the degree of hydration of these substances in solution. The lower members of an homologous series (for example formic acid in the series of fatty acids) are distilled much less easily than the higher members, although from the boiling points the reverse would be expected to be true. Since the value of k in an homologous series shows a regular increment with each added carbon atom (0.6 for fatty acids, 10 for amines), this evidently depends upon the fact that the degree of hydration regularly decreases as the carbon chain is lengthened. This is verified by the diminution in solubility. It is evident then that the effect of neutral salts upon the steam distillation is one of diminution of hydration of the volatile substance. The subject is treated more fully in the following section.

The Effect of Salts upon the Volatility of Substances with Steam

Neutral salts have in general a stimulating effect upon the constant of distillation, the influence of each salt having a different force. The investigations previously made by Virtanen show that the effect of the anions is most important, while that of the cations is much weaker. The influence of the different salts upon the distillation of acetic acid in dilute solution is shown by the curves in Fig. **2**. In distilling acetic acid in a saturated sodium chloride solution a value of $k = 2.3$ is obtained and, consequently, in distilling the semi-volume of the solution a quantity of 80% is distilled (of a pure water solution 36.6%). In the aforesaid investigation it has already been shown that the influence of salts upon the distillation of different acids is different. Fig. **3** indicates the distillation of different acids from a sodium chloride solution. The curves of formic acid and of acetic acid (both entirely soluble in water) are fairly straight lines, while the curves of less soluble acids the solubilities of which are appreciably diminished by the salts, rise more or less.

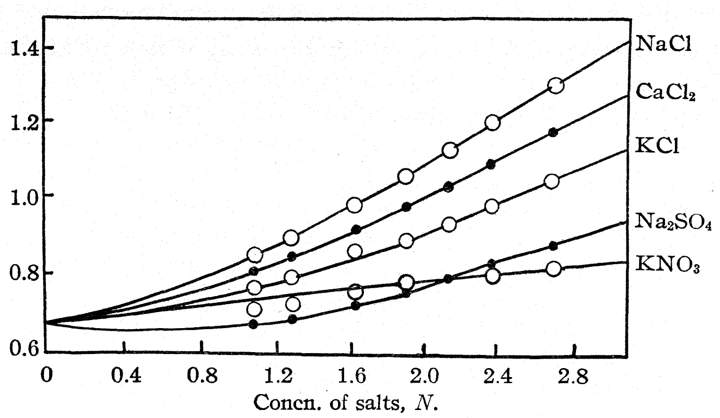

Fig. 2.—The curves indicate the influence of different salts upon the distillation of acetic acid.

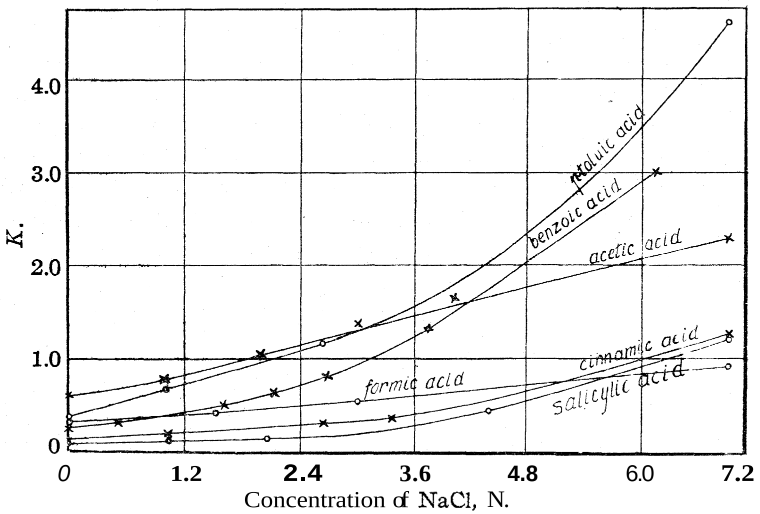

Fig. 3.—Influence of NaCl upon the distillation of some organic acids.

The question as to the real influence of the salts upon the distillation with steam has already been treated by Virtanen in a publication mentioned above. The rise in boiling point produced by the salt does not considerably alter the distillation. This is evident from the fact that several substances which are apt to raise the boiling point as much and even more than sodium chloride do not in a noteworthy degree raise the value of k. For example, the sodium acetate facilitates very little the distillation of acetic acid and glycerin does not in a noteworthy degree change the value of k, not even in a solution of 25%.

The volume mechanically taken up by the salts and the diminution of the quantity of water due thereto are not sufficient to explain the great influence of numerous salts. In 200 cc. of a solution of 1 *N* sodium chloride there are about 196.3 cc. of water at 20°. This small change in the volume of water cannot have much influence upon the value of k.

The only plausible explanation as to the influence of salts is that the salts in being hydrated or, in other words, in uniting themselves more or less firmly with the water molecules, diminish the hydration of the organic substances so that these substances detach themselves from the water molecules. Should this be the case, it is probable that the influence of the salts upon the solubility of volatile substances is, at least to some extent, to be compared to the influence of these salts in the distillation by steam. This appears, in general, to be the case, though unexpected exceptions are to be found, through the parallel determinations of the influence of some salts upon the solubility and upon the distillation of benzoic acid and salicylic acid. Fig. 5 shows the influence of the salts upon the volatility and upon the solubility of benzoic acid.

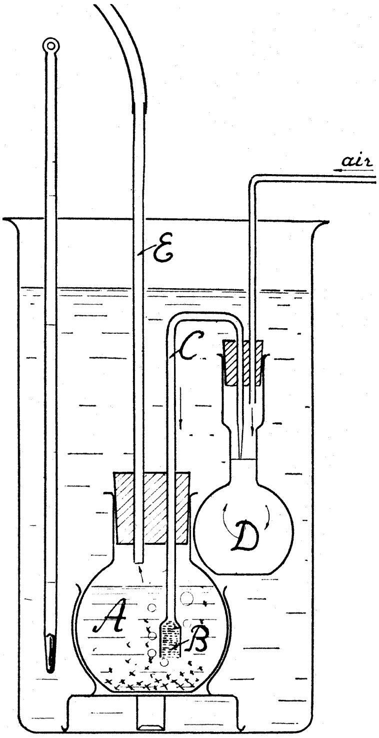

Fig. 4.

The distillation was determined so that out of 200 cc. one fraction of 25 cc. was always distilled. The determinations of solubility were made by using the apparatus shown in Fig. 4. The whole apparatus is submerged in boiling water (100"). The substance to be examined is dissolved in bottle **A.** From this the saturated solution is blown through the glass filter B and pipe C into the **25cc.** volumetric flask (D), from which the solution can be taken for titration. Stirring is effected by means of air flowing in the opposite direction, being forewarmed to 100° in the flask D. The pipe E leads to the vertical condenser, which prevents the water evaporating from the solution in the bottle A.

Of the salts investigated, sodium chloride most diminishes the solubility of benzoic acid. The influence of this salt upon the distillation of benzoic acid is also most effective. Sodium nitrate diminishes the solubility of benzoic acid to a less extent and correspondingly its effect upon the constant of distillation is also small. Sodium sulfate decreases the solubility more than sodium nitrate. In a weaker concentration, up to a normality of 2.5, sodium sulfate diminishes, strangely enough, the distillation of benzoic acid as well as that of other acids. To what this is due is, at present, inexplicable. Fig. 5 shows graphically the effect of sodium chloride, sodium sulfate and sodium nitrate upon the solubility and distillation of benzoic acid.

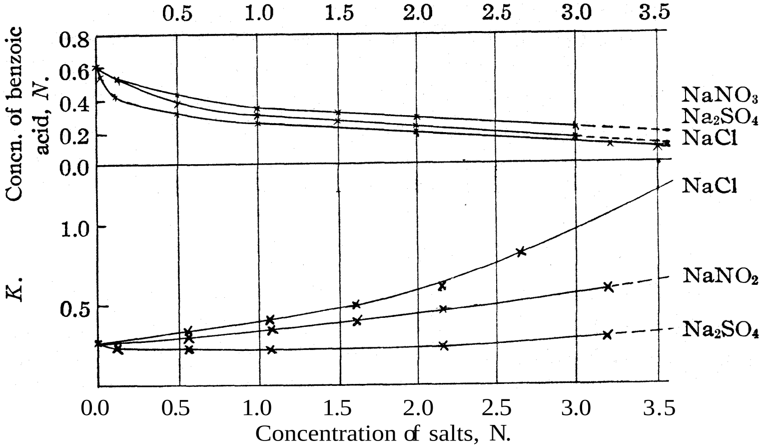

Fig. 5.—The curves in the upper figure indicate graphically the solubility of benzoic acid in NaCl, $NaNO_3$ and Na_2SO_4 solutions of different concentrations. The lower figure shows correspondingly the effect of the same salts upon the values of the distillation constant, k.

The hydration of acids has been shown to diminish at the same time that the degree of dissociation diminishes,[8] and it is to be concluded, accordingly, that the ions hydrate themselves. Since in the series of fatty acids the dissociation of acids diminishes at the same time that the molecular weight augments, it might be supposed that the weaker distillation of the first fatty acids would be due to their greater ionization in the diluted solutions. This opinion is, however, contradicted by the observation that if in the diluted solutions of acetic and formic acids alkaline salts of the same acids are added while the dissociation of acids diminishes to a minimum, the distillation of acids augments much less than through

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[8] Kendall, Booge and Andrews, THIS JOURNAL, **39**, **2303** (1917).

many other salts. On the contrary, the constant of the distillation of formic acid diminishes somewhat. As the great reduction in the dissociation of acetic and formic acids by no means essentially affects the distillation of these acids by steam, it is evident that it is chiefly through the hydration of the non-dissociated molecules of acids that the acids attach themselves to water.

The tendency of the electrolytes to unite molecules of water to themselves causes changes in the solutions which occur in many different ways. Especially have those changes been investigated which are caused by the neutral salts in the dissolution of the different substances.[9]

Wiegner, Magasanik and Virtanen[10] have investigated the influence of salts upon the adsorption of fatty acid by bone-charcoal and have found that the absorption becomes more effective, for example, through the influence of sodium chloride. We can in general find a great analogy in the influence of salts upon the distillation and adsorption of fatty acids. This is quite natural, for the detachment of acids from water through the influence of salts is the reason why acids escape more easily in steam and why they attach themselves more easily to adsorbent substances.

We will later on enlarge upon the question as to the distillation by steam of substances soluble in water and on the influence of salts.

Summary

The steam distillation of substances soluble in water and passing over with steam gives a possibility of determining whether the substance to be examined is pure or contains other substances belonging to the same group, for instance homologs. As a quantitative means of expression for the distillation of a substance with steam, either the distillation constant, k, or half-distillation, or one-fourth distillation value, respectively, can be employed.

By means of steam distillation volatile substances can be determined according to a very simple method. This mode of determination has been developed very accurately in this study. If there are in the same solution two substances belonging to the same group (for example, organic acids), they can be determined by means of a single fraction with considerable accuracy. If there are three substances, then the determination may be made by means of two fractions. The time of distillation and the variations of concentration in solutions have an appreciable effect on the course of distillation. If the volatility of the substance is so great that the value of the distillation constant k is above 5, the steam distillation cannot easily be used for the quantitative determination of the substance.

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[9] Geffken, *Z. physik. Chem.*, 49, 257 (1904); Euler, *ibid.*, 49, 303 (1909); Rothmund, *ibid.*, 40, 611 (1902).

[10] Wiegner, Magasanik and Virtanen, *Kolloid-Z.*, 28, 51 (1921).

Distillation constants have been determined for many organic substances belonging to different groups. In homologous series the value of k increases with the lengthening of the carbon chain. This is obviously due to the decline in hydration as the molecular weight increases.

The effect of salts upon the steam distillation is powerful. Among the salts studied sodium chloride has in the greatest degree raised the value of k. The influence of anions is obviously much more intense than that of cations.

The effect of the salts upon the distillation of different substances is variable (Fig. **3**). The curves indicating the dependency of k on salt concentration rise rather rectilinearly for those substances which dissolve indefinitely in salt solutions, while for those substances which do not dissolve indefinitely in water and which in part separate from water through the effect of salts, k rises with the increase in salt concentration so powerfully that the curve arches strongly upward.

The promoting effect of salts upon distillation is obviously due to the fact that they diminish the hydration of the substance, especially of undissociated molecules. The promoting effect of salts upon distillation can to a great extent be turned to advantage in distinguishing volatile from non-volatile compounds.

HELSINKI, FINLAND

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY,
MASSACHUSETTS INSTITUTE OR TECHNOLOGY, NO. 207]

A NEW EQUATION OF STATE FOR FLUIDS. III. THE NORMAL DENSITIES AND THE COMPRESSIBILITIES OF SEVERAL GASES AT 0°

BY JAMES A. BEATTIE AND OSCAR C. BRIDGEMAN[1]

RECEIVED JUNE 8, 1928 PUBLISHED DECEMBER 10, 1928

The compressibility of gases at 0° and at pressures up to one atmosphere is of great importance in the determination of the atomic weights of the inert gases from density measurements and for the calculation of the normal densities of those gases whose molecular weights can be determined by chemical analysis. The experimental evaluation of the ratio of the pressure–volume product at 0" and at one atmosphere, p_1V_1, to the product at zero pressure, p_0V_0, is difficult, and it is believed that this ratio can be obtained for any gas for which there are extensive p–V–T data with as great an accuracy from the equation of state.

The relations between these quantities are given by the equations

$$p_0V_0/p_1V_1 = 1 + \lambda \tag{1}$$

$$p_0V_0 = (m/M)\ RT_0 \tag{2}$$

$$d_n = \frac{m}{V_1} = \frac{M(1 + \lambda)}{RT_0} \tag{3}$$

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[1] **National Research Fellow in Chemistry.**

where λ is a constant for a given gas, M is its molecular weight, R is the gas constant per mole and T_0 is the value of 0° on the Kelvin scale. In Equation I the ratio p_0V_0/p_1V_1 can refer to any quantity of gas, but in Equation **2** the product p_0V_0 is taken for m grams. Combination of these relations leads to Equation **3,** in which d_n is the normal density of the gas, that is, the weight in grams of one liter of the gas at 0° and one atmosphere pressure.

Thus if RT_0 is known and a value of λ is available, the molecular weight of the gas can be calculated from the normal density. If, on the other hand, the molecular weight has been determined by chemical means, the normal density can be calculated.

Recently the authors have proposed a new equation of state[2]

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

$$A = A_0(1 - a/V). \quad B = B_0(1 - b/V). \quad \epsilon = c/VT^3 \qquad (4)$$

in which R is the gas constant and A_0, a, B_0, b and c are constants for each gas.

The values of these constants have been determined[3] for the ten gases helium, neon, argon, hydrogen, nitrogen, oxygen, air, carbon dioxide, methane and ether. The equation was found to reproduce the experimental pressure–volume–temperature data over wide ranges of temperature and density very satisfactorily. In the present article advantage is taken of this correlation to compute the values of p_0V_0/p_1V_1 and hence of λ for the nine of the above substances which are gases at 0° and one atmosphere; and then by use of Equation **3** to calculate the normal density of those gases for which the molecular weight can be determined by chemical means, and also to compute the molecular weights from the best values of the normal densities.

When working at constant temperature, it is more convenient to transform the Equation of state 4 into the virial form

$$\begin{aligned} pV &= RT + \beta/V + \gamma/V^2 + \delta/V^3 \\ \beta &= RTB_0 - A_0 - Rc/T^2 \\ \gamma &= -RTB_0b + A_0a - RB_0c/T^2 \\ \delta &= RB_0bc/T^2 \end{aligned} \qquad (5)$$

For the gases under consideration at 0° and one atmosphere, the term δ/V^3 is negligible, and on the average γ/V^2 affects the calculated value of p_1V_1 by one part in 300,000, while β/V contributes one part in 600. In the least favorable case—carbon dioxide—these last two terms are about three times as large. Thus if β is known to only 1%, the uncertainty introduced into p_1V_1 is on the average 0.002%, while for carbon dioxide it is 0.007%.

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[2] Beattie and Bridgeman, THIS JOURNAL, 49, *1665 (1927).*

[3] Beattie *and* Bridgeman, *ibid.*, 50, 3133 **(1928).**

In the determination of the equation of state constants from the pressure–volume–temperature data, the values of R and T_0 used were 0.08206 and 273.13 in units of international atmospheres for pressure, liters per mole for volume, and degrees Kelvin for temperature.[4] These give 22.4131 for RT_0, which is in good agreement with the value 22.4133 recently found by Baxter and Starkweather,[5] based on their determinations of the density of oxygen.

In Table I are listed the values at 0° of the parameters β, γ and δ calculated from the equation of state constants by means of the relations (5). It should be noted that these values are based on the correlation of the pressure–volume–temperature data of different investigators for each gas, over the whole temperature range and a wide density range, thus tending to eliminate both constant and accidental errors.

TABLE I

VIRIAL COEFFICIENTS AT 0° COMPUTED FROM THE EQUATION OF STATE

R = 0.08206; T_0 = 273.13; RT_0 = 22.4131 (g = 980.665). Units: international atmospheres, liters per mole, degrees Kelvin.

Gas	β	$\gamma \times 10^3$	$\delta \times 10^6$	Gas	β	$\gamma \times 10^3$	$\delta \times 10^6$
He	0.29214	1.292	....	N*	−0.23870	33.345	−42.7
Ne	,24810	4.644	....	O_2	− .50752	31.399	10.3
A	− .47553	27.457	....	CO_2	−3.38451	111.131	5502.6
H_2	.27172	19.467	− 0.5	CH_4	−1.16581	54.224	− 125.1
N_2	− .25974	40.669	− 16.1	Air	−0.31547	34.303	− 24.2

N* denotes values of the constants obtained from a consideration of the data of Smith and Taylor alone.

In Table II are given the details of the calculation of the ratio p_0V_0/p_1V_1 from the coefficients of Table I, by means of the relation

$$\frac{p_0V_0}{p_1V_1} = \frac{RT_0}{RT_0 + \beta/V_1 + \gamma/V_1^2 + \delta/V_1^3} = 1 + \lambda \qquad (6)$$

In the second column of this table are listed values of $p_1V_1 - RT_0$, that is, $\beta/V_1 + \gamma/V_1^2 + \delta/V_1^3$, which indicates the magnitude of the quantity which is obtained from the equation of state. In the third are given values of p_1V_1 calculated by use of Equation 5. Since the volume is contained implicitly in this relation, the perfect gas value, 22.41, was assumed for the first approximation. The convergence was very rapid, the next approximation giving the final value of p_1V_1. In the last two columns are listed the values of λ calculated from Equation 6 and those

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[4] This value of R is used in the "International Critical Tables" and was derived by Keyes, *Amer.* SoG. *Refrig. Eng J.*, *8*, 505 (1922); the value of T_0 was determined by Buckingham, *Bull. Bureau Standards*, 3, 237 (1907), and has been used for many years in this Laboratory.

[5] Baxter and Starkweather, *Proc.* Nat. *Acad. Sci.*, 10, 479 (1924); *ibid.*, 12, 699 (1926), give the value 22.4144 using 980.616 for *g*, and this was reduced to the international gravity, 980.665.

selected by Pickering.[6] It should be noted that the variations of the measured values obtained by different observers are large.

TABLE II

RATIO AT 0° OF THE pV PRODUCTS AT 0 AND 1 ATMOSPHERE

$RT_0 = 22.4131$ ($g = 980.665$)

Gas	$p_1V_1 - RT_0$	p_1V_1	$1 + \lambda$	$\lambda \times 10^3$, calcd.	$\lambda \times 10^3$, obs.[a]
He	0.01303	22.4261	0.99942	−0.58	-0.4_6
Ne	.01107	22.4242	.99950	− .50	−0.4
A	− .02118	22.3919	1.00095	+ .95	$+.9_0$
H_2	.01216	22.4253	0.99946	− .54	$-.6_1$
N_2	− .01151	22.4016	1.00051	+ .51	$+.4_7$
N*	− .01059	22.4025	1.00047	+ .47	
O_2	− .02260	22.3905	1.00101	+1.01	$+.9_4$
CO_2	− .15181	22.2613	1.00682	+6.82	$+7.0_6$
CH_4	− .05203	22.3611	1.00233	+2.33	+2.4
Air	− .01402	22.3991	1.00063	+0.63	$+0.6_1$

[a] Observed values are those given in "International Critical Tables," Vol. III, p. 3.

The values of λ calculated from the equation of state can be used to compute the normal density of those gases whose molecular weights can be determined by chemical means. The method of carrying out the calculation is evident from a consideration of Equation **3** and the results are given in Table III. The atomic weights given in "International Critical Tables," Vol. I, were used, and the resultant weights of a normal liter are compared with those selected by Blanchard and Pickering.[7]

TABLE III

COMPARISON OF OBSERVED AND CALCULATED WEIGHTS OF ONE LITER FOR SEVERAL GASES AT 0° AND 1 ATMOSPHERE

Gas	Int. crit. tables Mol. wt.	p_1V_1 (from Table II)	Wt. of liter, calcd.	Wt. of liter, obs[a]
H_2	2.0154	22.4253	0 08987	0.08988
N_2	28.016	22.4016	1.25062	1.2505_7
N*	28.016	22.4025	1 25057	
O_2	32.000	22 3905	1 42918	1 42904
CO_2	44.000	22 2613	1 97652	1 9769
CH_4	16.0308	22.3611	0.71691	$0\ 716_8$

[a] Observed values are those given in "International Critical Tables "

Recently Baxter and Starkweather[8] have determined the normal densities of helium, neon, argon, nitrogen and oxygen. These differ in some cases from the values selected by Blanchard and Pickering. In Table IV

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[6] Pickering, "International Critical Tables," McGraw-Hill Book Company, New York, 1928, Vol. III, p. 3.

[7] Blanchard and Pickering, *U. S. Bureau of Standards Scientific Paper*, No. 529, 1926; see also Pickering, "International Critical Tables," Vol. III, p. 3, 1928.

[8] Baxter and Starkweather, ref. 5; *Proc. Nat. Acad. Sci.*, **11**, 231 (1925); *ibid.*, **12, 20,** 703 (1926); *ibid.*, 14, 50, 57 (1928).

the measured values of Baxter and Starkweather (reduced to g = 980.665), and the selected values of Blanchard and Pickering (which only in the case of helium and oxygen include a consideration of the measurements of the former) are used in the computation of the molecular weights of the various gases. The results are compared with the values given in the "International Critical Tables," Vol. I. For those gases whose molecular weights can be determined by chemical analysis, this comparison is given as an indication of the consistency of the measured normal density and calculated X, with the molecular weight. The agreement in general is excellent.

TABLE IV

COMPUTATION OP THE MOLECULAR WEIGHT PROM THE WEIGHT OR A NORMAL LITER

Gas	Reference[a]	Exp. wt. of a normal liter	p_1V_1 (from Table II)	Mol. wt., calcd.,	Mol. wt., (Int. Crit. Tables)
He	B. and P.	0.1785	22.4261	4.003	4.00
He	B. and S.	.17847		4.002	
Ne	B. and P.	$.900_2$	22.4242	20.186	20.2
Ne	B. and S.	.89994		20.180	
A	B. and P.	1.7825	22.3919	39.914	39.91
A	B. and S.	1.78373		39.941	
H_2	B. and P.	0.08988	22.4253	2.0156	2.0154
N_2	B. and P.	1.2505_7	22.4016	28 015	28.016
N_2	B. and S.	1,25042		28.011	
O_2	B. and P.	1.4290_4	22.3905	31.997	32
O_2	B. and S.	1.42904		31.997	
Air	B. and P.	1,2929	22.3991	28.960	
CO_2	B. and P.	1.9769	22.2613	44.008	44.000
CH_4	B. and P.	0.716_3	22.3611	16.028	16.0308

[a] B. and P. = Blanchard and Pickering; B. and S. = Raxter and Starkweather.

The calculated values of X depend only on the equation of state constants of the various gases and the value of RT_0, and small errors in the latter evidently tend to cancel. The deviations between the observed and calculated values of X and of the normal densities and molecular weights shown in Tables II to IV are well within the variations between the determinations of different observers except for the gas oxygen. Thus, for instance, Moles[9] gives 1.25062 as the normal density of nitrogen, while the review of the normal densities of gases given by Blanchard and Pickering shows a rather wide variation in the experimental determinations. In the case of oxygen, however, the value of λ calculated from the equation of state seems to be too large, which gives too large a value for the normal density. The equation of state of oxygen reproduces the experimental compressibility data quite satisfactorily in the neighborhood of 0°. Moreover, since the values of λ calculated for other gases from the equation of state agree well with the experimental values, it seems reasonable to assume

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[9] Moles, *Gazz chim. ital.*, 56, 915 (1926). The value was reduced to g = 980.665,

that the discrepancy in the case of oxygen is due to an inconsistency between the compressibility and the normal density data.

The value of λ and the weight of a normal liter have been determined experimentally for carbon monoxide and nitrous oxide, but the compressibility data on these gases are too fragmentary to allow of the evaluation of their equation of state constants. Langmuir[10] has pointed out that the physical properties of CO and N_2O are very similar to those of N_2 and CO_2, respectively. He has postulated that the external arrangements of the electrons are the same in CO and N_2, and in N_2O and CO_2; and thus in each pair the electrical fields are quite similar. The constants of the equation of state are probably due largely to the external electrical fields and hence the constants of CO and N_2O should be close to those of N_2 and CO_2. In Table V the experimentally determined values of λ and of the weight of a normal liter of CO and N_2O selected by Blanchard and Pickering[7] are compared with those calculated from the equation of state, using the values of the constants of N_2 and CO_2, respectively. The agreement is good and indicates that at moderate pressures and at temperatures which are not too near the critical temperature, the thermodynamic properties of CO and N_2O can be calculated by use of the equation of state constants for N_2 and CO_2.

TABLE V

COMPARISON OF OBSERVED AND CALCULATED VALUES OF λ AND OF THE WEIGHT OF A NORMAL LITER OF CO AND N_2O

Gas	Mol. wt., I. C. T.	$\lambda \times 10^3$ (calcd.)	$\lambda \times 10^3$ (obs.)	Wt. of liter (calcd.)	Wt. of liter (obs.)
CO	28.000	+0.51	+0.5	1.2499	1.250_4
N_2O	44.016	+6.82	+7.4	1.9772	1.977_8

Calculated values are obtained by use of the equation of state constants for N_2 and CO_2, the isosteres of CO and N_2O. Observed values are those given in "International Critical Tables."

Summary

The equation of state proposed by the authors is used to calculate values of the ratio at 0° of the pV products at one atmosphere and at zero pressure for several gases, and a brief discussion is given concerning the merits of this particular method and its accuracy. These ratios are then employed to compute the weights of a normal liter of hydrogen, oxygen, nitrogen, carbon dioxide and methane, whose molecular weights can be determined by chemical means, and a good agreement is obtained with accepted values. The molecular weights of the gases named above and of helium, neon, argon and air are calculated from the normal densities, and the agreement with the "International Critical Tables" values is very good. The agreement obtained in these calculations indicates that the

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[10] Langmuir, THIS JOURNAL, 41, 868, 1543 (1919).

equation of state extrapolates to low pressures with a high degree of accuracy.

The values at 0° of the ratio of the pV product at one atmosphere to that at zero pressure, and the weights of a normal liter of CO and N_2O are calculated from their molecular weights and the values of the constants of the equation of state of their isosteres, namely N_2 and CO_2. The agreement with the observed values is very good, and indicates that for many thermodynamic calculations the constants of N_2 and CO_2 can be used for CO and N_2O, respectively.

CAMBRIDGE, MASSACHUSETTS

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

THE IONIC CONCENTRATIONS AND ACTIVITY COEFFICIENTS OF WEAK ELECTROLYTES IN CERTAIN SALT SOLUTIONS

BY HERBERT S. HARNED AND ROBERT A. ROBINSON[1]

RECEIVED JUNE 15, 1928 PUBLISHED DECEMBER 10, 1928

The electromotive forces of cells of the types

$$Ag \mid AgX \mid HX(m_0),\ MX(m) \mid H_2 \mid HX(m_0) \mid AgX \mid Ag$$

and

$$H_2 \mid MOH(m_0),\ MX(m) \mid M_xHg \mid MOH(m_0) \mid H_2$$

have proved very useful in determining the activity coefficients of some strong acids and hydroxides in certain salt solutions.[2] In the cases so far considered, this method has been applied to the class of strong acids and hydroxides. The question naturally arises as to whether measurements of this kind cannot be extended so as to determine the activity coefficients of weak acids and hydroxides in salt solutions of varying strengths as well as the hydrogen and hydroxyl ion concentrations of weak acids and hydroxides in these solutions.

It is the purpose of this study to show that this information may be acquired by measurements of cells without liquid junction potentials. Furthermore, this result can be accomplished with cells which contain easily reproducible electrodes such as the hydrogen and silver–silver chloride electrodes. The limitations of the method are for the most part experimental and depend on the difficulty of obtaining the reversible electro-

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[1] Commonwealth Fund Fellow, 1927–1929.

[2] (a) Harned, THIS JOURNAL, 38, 1986 (1916); (b) 42, 1808 (1920); (c) 47, 684 (1925); (d) 48, 326 (1926); (e) Loomis, Essex and Meacham, *ibid.*, 39, 1133 (1917); (f) Chow, *ibid.*, 42, 497 (1920); (g) Harned and Brumbaugh, *ibid.*, 44, 2729 (1922); (h) Åkerlöf, *ibid.*, 48, 1160 (1926); (i) Harned and Swindells, *ibid.*, 48, 126 (1926); (j) Harned and James, *J. Phys. Chem.*, *30*, 1060 (1926); (k) Harned and Åkerlöf, *Physik. Z.*, 27, 411 (1926); (l) Güntelberg, *Z. physik. Chem.*, *123*, 199 (1926); (m) Randall and Breckenridge, THIS JOURNAL, 49, 1435 (1927).

motive force of the hydrogen electrode in solutions containing hydrogen or hydroxyl ion at very low concentrations and salts at high concentrations.

This opens up a wide field for investigation, since we shall be able to study the effect of the powerful fields of electrolytic solutions upon the characteristic potentials of the organic cations and anions, and make preliminary attempts to parallel this property with the ion constitution. Further, these results may be compared with results obtained from catalytic data by Harned and Hawkins[3] and the values of the ionic activity coefficients of water in salt solutions.[4,2i,j]

Outline of the Method

The activity coefficient of a weak electrolyte may be defined in two ways. Assuming that the activity product, a_Ca_A, of the ions of a uni-univalent weak electrolyte has been determined, wc may define an activity coefficient by either

$$\text{(a)} \quad \gamma = \sqrt{\frac{a_Ca_A}{m_Cm_A}} \quad \text{or} \quad \text{(b)} \quad \gamma = \sqrt{\frac{a_Ca_A}{m_+m_-}}$$

In (a) m_C and m_A are the stoichiometrical molalities of the ion groups of the electrolyte which would be computed in just the same way as in the case of a strong electrolyte. Thus, in a solution of $HAc(m_1) + NaAc(m_2)$, m_C equals m_1 and m_A equals $(m_1 + m_2)$, and in a solution of $HAc(m_1) + NaCl(m_2)$, m_C equals m_A equals m_1.

In (b), m_+ and m_- are the true molal concentrations of the ionic species. It is the second of these quantities which is the subject of the present study. In fact, the second is the more important since this quantity is directly comparable to the activity coefficients of strong electrolytes and to the potentials of ionic solutions in general.

In the first place, we shall consider the determination of the activity coefficients of a weak acid in a salt solution. Let us consider the simple cells

$$H_2 \mid HAc(m_1),\ MX(m_2) \mid AgX \mid Ag \qquad (1)$$
$$H_2 \mid HX(m_0),\ MX(m_3) \mid AgX \mid Ag \qquad (2)$$

where HAc is a weak acid and HX is a strong acid. Subtract (2) from (1) and obtain

$$Ag \mid AgX \mid HX(m_0),\ MX(m_3) \mid H_2 \mid HAc(m_1),\ MX(m_2) \mid AgX \mid Ag \qquad (3)$$

The cell reaction of **(3)** represents the transfer of HX from the solution containing HX to the solution containing HAc. The electromotive force of **(3)** is therefore given by

$$\mathbf{E} = \mathbf{0.05915}\,\log \frac{\gamma_{H(2)}\gamma_{X(2)}\,m_0(m_3 + m_0)}{\gamma_{H(1)}\gamma_{X(1)}\,m_Hm_0} \qquad (4)$$

where $\gamma_{H(2)}\gamma_{X(2)}$ is the activity coefficient product of the ions in the solution

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[3] Harned **and** Hawkins, THIS JOURNAL, **50, 85** (1928).

[4] Harned, *ibid.*, **47, 930 (1925).**

containing HX only and $\gamma_{H(1)}\gamma_{X(1)}$ the same in the solution containing HAc; m_H is the stoichiometrical molality of the hydrogen ion.

We shall now consider the conditions under which $\gamma_{H(1)}\gamma_{X(1)}$ may be taken equal to $\gamma_{H(2)}\gamma_{X(2)}$. Throughout this discussion, let it be understood that the total ionic strengths of the two solutions are equal. Thus,

$$m_3 + m_0 = m_H + m_2$$

Assume that the molality of the weak acid is low enough so that the presence of the undissociated molecule of the acid causes no appreciable change in $\gamma_{H(1)}\gamma_{X(1)}$. It has been shown for mixtures of strong electrolytes of these types that a constant total molality of the ions

$$\log \gamma_{HX} = \alpha m_{HX} + \log \gamma_0 \qquad (5)$$

where α is a constant, γ_{HX} equals $\sqrt{\gamma_H\gamma_X}$ and γ_0 equals γ_{HX} when m_{HX} equals zero.[2d,1] The values of the constants α for the different salt solutions are such that γ_{HX} practically becomes independent of the acid concentration in solutions containing less than 0.01 M HX. This is illustrated in Fig. 1 in which γ_{HCl} in a potassium chloride solution is plotted against the logarithm of the acid concentration. The total concentration of the acid and the salt is 3 M. Thus at concentrations below 0.01 M hydrochloric acid, the plot becomes parallel to the abscissa. To be exact, at 0.01 M, γ_{HCl} equals 0.860, and at 0.001 M it equals 0.859, corresponding to a difference of less than 0.1 mv. Thus, if $m_{H(1)}$ and m_0 are 0.01 M or less, $\gamma_{H(1)}\gamma_{Cl(1)}$ may be taken equal to $\gamma_{H(2)}\gamma_{Cl(2)}$ without introducing an error greater than the experimental. Equation 4 becomes

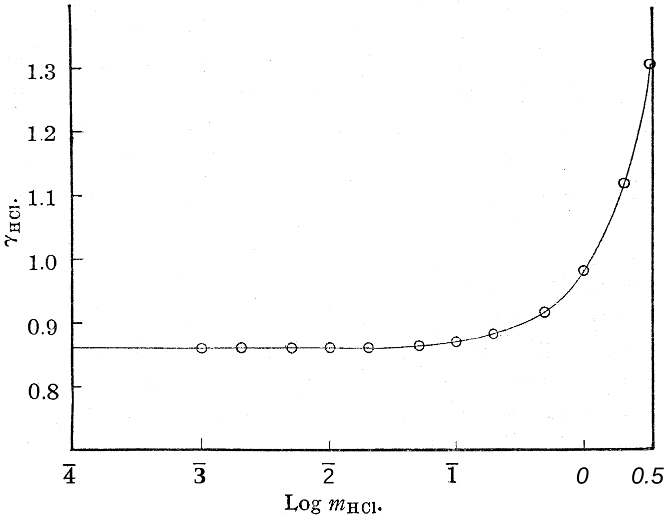

Fig. 1.—γ–log m plot of hydrochloric acid in potassium chloride solutions at a constant total molality of 3.

$$E = 0.05915 \log \frac{m_0(m_0 + m_3)}{m_H m_2} \tag{6}$$

and since m_0, m_2 and m_3 are known, m_H may be computed.

After having computed m_H by Equation 4 or Equation 6, the calculation of $\gamma_H\gamma_{Ac}/\gamma_{HAc}$ becomes a simple matter since the thermodynamic equation for the dissociation of HAc is

$$K = \frac{\gamma_H\gamma_{Ac}}{\gamma_{HAc}} \frac{m_H^2}{m_1 - m_H} \tag{7}$$

and K, m_1 and m_H are known.

That exactly similar considerations will apply to the determination of the activity coefficient products of weak hydroxides in salt solutions from measurements of cells of the type

$$H_2 \mid MOH(m_0),\ MX(m_3) \mid M_xHg \mid BOH(m_1),\ MX(m_2) \mid H_2 \tag{3a}$$

where MOH is a strong and BOH a weak hydroxide, may readily be shown.

For this case, the equation corresponding to Equation 4 will **be**

$$E = 0.05915 \log \frac{\gamma_{M(2)}\gamma_{OH(2)}\ m_0(m_3 + m_0)\ a_{H_2O(1)}}{\gamma_{M(1)}\gamma_{OH(1)}\ m_{OH}\ m_2\ a_{H_2O(2)}} \tag{4a}$$

where the subscript (2) refers to the solution containing the strong, and (1) to that containing the weak hydroxide. Since the ratio of the activity of water in the two solutions will be unity, and since for low concentrations of the weak base we may take the activity coefficient ratio in the two solutions as unity, we obtain

$$E = 0.05915 \log \frac{m_0(m_3 + m_0)}{m_{OH}\ m_2} \tag{6a}$$

which corresponds to Equation 6.

In many cases it may be simpler from the point of view of experiment to measure cells with salt bridges such as

$H_2 \mid HX(m_0),\ MX(m_3) \mid$ sat. KCl $\mid HAc(m_1),\ MX(m_2) \mid H_2$
$H_2 \mid MOH(m_0),\ MX(m_3) \mid$ sat. KCl $\mid BOH(m_1),\ MX(m_2) \mid$ *Ha*

In the case of the latter cells, the difference in the two liquid junction potentials will be very small provided that the hydrogen-ion concentrations in the first and the hydroxyl-ion concentrations in the second are the same on both sides of the salt bridge. If we apply the above considerations to these cells, then at small concentrations of HAc and BOH (not above 0.5 M), the electromotive force is a measure of the ratio of the hydrogen or hydroxyl-ion concentrations in the two electrode compartments.

So far we have assumed that the concentration of the undissociated molecule, HAc, is so low that it has only a negligible effect on $\gamma_{H(1)}\ \gamma_{X(1)}$. At higher concentrations of HAc, the absolute value of $\gamma_{H(1)}\ \gamma_{X(1)}$ relative to pure aqueous solution will increase with increasing concentration of the undissociated molecule. Thus, Harned and Fleysher[5] have found that

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[5] Harned and Fleysher, THIS JOURNAL, 47, 82 (1925).

$\gamma_H\gamma_{Cl}$ in a 0.01 M acid solution in water increases 3 1 times its initial value on the addition of 25 mole per cent. of ethyl alcohol. From the nature of the plot of their results, the presence of 0.1 M ethyl alcohol would cause an increase of somewhat less than 0.5% in $\gamma_{H(1)}\gamma_{X(1)}$. Consequently, Equation 6 is only exactly valid at zero concentration of HAc, but is valid to within less than 1.2% for solutions containing 0.2 M HAc or less, if we presume that the effect of undissociated acetic acid upon the activity coefficient is not greater than that of ethyl alcohol. Equation 6 will be strictly valid in the case of the cells

$$\mathrm{Ag} \mid \mathrm{AgCl} \mid \mathrm{HX}(m_0),\ \mathrm{M}(m_4),\ \mathrm{MX}(m_3) \mid H_2 \mid \mathrm{HAc}(m_1),\ \mathrm{MX}(m_2) \mid \mathrm{AgCl} \mid \mathrm{Ag}$$

provided that **M** is an undissociated molecule at a concentration $m_4 = (m_1 - m_H)$ which produces the same effect on $\gamma_{H(1)}\gamma_{X(1)}$ as does the undissociated acetic acid.

Since the present study contains extensive determinations of $\gamma_H\gamma_{Ac}/\gamma_{HAc}$ and $\gamma_B\gamma_{OH}/\gamma_{BOH}$ in aqueous solutions, we have not thoroughly investigated the above effect at this time. We have, however, obtained a few series of results with acetic acid at high concentrations in sodium chloride solutions which we shall use to illustrate the magnitude of this effect.

Part 1. The Ionic Concentrations and Activity Coefficients of Acetic Acid in Salt Solutions

Experimental Results and Method of Numerical Calculation.—The cells measured were of the type

$$\mathrm{H_2} \mid \mathrm{HAc}(m_1),\ \mathrm{MX}(m_2) \mid \mathrm{AgCl} \mid \mathrm{Ag} \qquad (8)$$

Extended series of measurements of cells containing 0.1, 0.2, 0.5, 1.0, 5.0 and 10 M acetic acid were made in each of which sodium chloride was varied over a concentration range of 0.02 to 3 M. Further, a series of determinations of cells containing acetic acid at a concentration of 0 2 M and potassium, lithium and barium chlorides of varying strengths was made, as well as a series of cells with 0.1 M acetic acid and potassium chloride. The acetic acid and salts were of a high grade of purity. The potassium and sodium salts were dried at a suitable temperature, barium chloride was used in the form of the dihydrate and the lithium chloride solutions were made by dilution of an analyzed concentrated solution.

The silver–silver chloride electrodes were of the spiral type. The silver oxide paste was heated at 500° on the platinum spiral. No electrolytic silver was deposited on the spiral previous to this operation. Electrodes made in this way have the same potential as those made by the Noyes and Ellis method.

The hydrogen electrodes were of the usual platinum foil type and were found to give reproducible results in all cases except those of the cells containing 0.1 M acetic acid. In the latter case, with cells containing either sodium or potassium chlorides, it was found impossible to obtain electromotive forces corresponding to reasonable values of the activity coefficient of acetic acid unless the platinum foils were coated with an extremely thin film of platinum black. With this additional precaution, potential readings were obtained which are thought to be reasonably close to the correct ones, but a high degree of accuracy is not claimed. This source of error is in accord with the experiments of Harned.[2d] He found that in solutions containing hydrochloric acid and sodium or potassium chlorides (of constant total molality) the hydrogen electrode as usually prepared was unreliable at acid concentrations below 0.002 M to 0.005 M. He showed that very thinly coated electrodes improved the situation but did not completely eliminate the error when the salt to acid ratio was very high. Our observations agreed with his, since the error was found to be the greater. the higher the salt concentrations.

In the cells containing acetic acid at 0.2 M or higher, the reproducibility was approximately ±0.2 mv. if the salt concentrations were at 0.05 M or higher. Attempts were made to obtain results in solutions of 0.02 M salt but they were successful in only a few cases.

Instead of comparing the electromotive force of the cell containing acetic acid with that of the cell containing hydrochloric acid in salt solution of the same total molality according to the Scheme **3** and Equation 4 it was found more convenient to proceed as follows.

If the cell

$$Ag \mid AgCl \mid HCl(m_0),\ MCl(m_3) \mid H_2 \mid HCl(0.01) \mid AgCl \mid Ag \tag{9}$$

be subtracted from **(3)** for the case where X equals chlorine, the cell

$$Ag \mid AgCl \mid HCl(0.01) \mid H_2 \mid HAc(m_1),\ MCl(m_2) \mid AgCl \mid Ag \tag{10}$$

is obtained. But this cell is also obtained by subtracting

$$H_2 \mid HCl(0.01) \mid AgCl \mid Ag \tag{11}$$

from the cells measured, namely

$$H_2 \mid HAc(m_1),\ MCl(m_2) \mid AgCl \mid Ag \tag{12}$$

Let E' equal the electromotive force of cells (12)[2g,i] and 0.4644 be the electromotive force of (11), then

$$E' - 0.4644 = 0.05915 \log \frac{(0.902)^2(0.01)^2}{\gamma_{H(1)}\gamma_{X(1)}\, m_H m_2} \tag{13}$$

if 0.902 be taken as the activity coefficient of hydrochloric acid in water at 0.01 M. Equation 13 reduces to

$$E' - 0.2225 = -0.05915 \log \gamma_{H(1)}\gamma_{Cl(1)}\, m_H m_2 \tag{14}$$

Neglecting for the present any correction involving the change in solvent caused by the presence of undissociated acetic acid, we let $\gamma_{H(1)}\gamma_{Cl(1)}$ equal $\gamma_{H(2)}\gamma_{Cl(2)}$, which latter data were obtained from cells of the type (2) containing hydrochloric acid and a chloride.

The experimental data as well as the calculated hydrogen-ion concentrations and activity coefficients are given in Table I; m_1 is the molal concentration of the acetic acid, m_2 the molal concentration of added salt and E' the measured values of the electromotive forces, The values of $\gamma_{H(2)}\gamma_{Cl(2)}$ or $\gamma_{H(1)}\gamma_{Cl(1)}$ were read off plots of the data taken from the tables of Harned and Åkerlöf.[2k] m_H is the hydrogen or acetate-ion concentration calculated by Equation 14. The next column gives the values of $\sqrt{\gamma_A}$ computed by Equation 8 from the values of m_H. The value employed for the dissociation constant of acetic acid[6] was 1.85×10^{-5}. All measurements were made at 25°. Since m_H was unknown in the most dilute solutions,

TABLE I

HYDROGEN OR ACETATE-ION CONCENTRATIONS AND ACTIVITY COEFFICIENTS OF ACETIC ACID IN CHLORIDE SOLUTIONS

A. Potassium Chloride

(1) m_1 = 0.1005 M HAc. Correction for E' = $0.0001 (0.44%)

m_2	E'	$\gamma_{HCl(H_2O)}$	m_H	$\sqrt{\gamma_A}$	$m_{H(corr)}$	$\sqrt{\gamma_A}$(corr)
0.05	0.4754	0.810	0 001616	0.837	0.001609	0.841
.1	.4589	.781	.001652	.818	,001645	,822
.2	.4423	.747	.001723	.785	.001716	.788
.5	.4206	.711	.001771	.763	.001763	.766
1.5	.3935	.736	,001582	.855	.001575	.859
2.0	.3857	.777	.001442	.939	.001436	.943
3.0	.3736	.859	.001260	1.075	.001255	1.080

(2) m_1 = 0.2001 M HAc. Correction for E' = $0.0003 (1.16%)

m_2	E'	$\gamma_{HCl(H_2O)}$	m_H	$\sqrt{\gamma_A}$	$m_{H(corr)}$	$\sqrt{\gamma_A}$(corr)
0.05	0.4655	0.810	0 002376	0.805	0.002349	0.814
.1	.4492	.781	.002410	.794	,002382	.803
.194	.4336	.749	.002479	.771	.002451	.780
.5	.4113	.711	,002543	.752	,002514	.761
1.0	.3945	.712	,002438	.785	.002410	.795
1.5	.3840	.736	.002290	.835	,002264	.845
2.0	.3761	.777	,002096	.913	.002072	.924
3.0	.3645	.859	,001795	1 067	,001774	1.079

B. Sodium Chloride

(1) m_1 = 0.1 M HAc. Correction For E' = +0.0001 (0 44%)

m_1	m_2	E'	$\gamma_{HCl(H_2O)}$	m_H	A	$m_{H(corr)}$	$\sqrt{\gamma_A}$(corr.
0.0997	0.02	0.4972	0.864	0.001520	0.887	0.001513	0.891
.0992	.05	.4747	.815	.001640	.819	,001633	.823
.1003	.05	.4744	.815	.001660	.814	.001653	.818
.0991	.1	.4581	.785	.001687	.796	.001680	.799
.1004	.1985	.4415	.752	.001767	.764	.001759	.767
.0991	.2	.4417	.752	.001741	.771	.001733	.774
.1006	.5	.4184	.729	.001835	.753	,001827	.756
.0997	.486	.4197	.729	.001795	.750	.001787	.753
.1050	1.0	.3986	.764	.001806	.765	.001798	.768
.1050	1.489	.3874	.810	.001668	.829	.001661	.833
.1050	2.0	.3773	.891	.001521	.910	.001514	.914
.1003	2.95	.3624	1.085	,001242	1.090	.001237	1.095

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

TABLE I (Continued)

(2) m_1 = 0.2 M HAc. **Correction for** E' = +0.0003 (1.16%)

m_1	m_2	E'	$\gamma_{HCl(H_2O)}$	m_H	$\sqrt{\gamma_A}$	$m_{H(corr.)}$	$\sqrt{\gamma_A}$(corr.)
0.1965	0.05	0.4653	0.812	0.002382	0.796	0.002350	0.805
.2018	.1	.4484	.782	.002480	.774	.002452	.783
.2018	.2	.4317	.752	.002569	.747	.002540	.756
.2018	.5	.4088	.729	.002666	.720	.002635	.728
.2026	1.066	.3877	.771	.002542	.757	.002513	.766
.2018	1.5	.3777	.817	.002375	.809	.002348	.818
.2018	2.0	.3682	.891	.002176	.883	.002151	.893
.2018	3.0	.3519	1.085	.001838	1.047	.001817	1.059

(3) m_1 = 0.519 M HAc. **Correction for** E' = +0.0008 (3.16%)

m_2	E	$\gamma_{HCl(H_2O)}$	m_H	$\sqrt{\gamma_A}$	$m_{H(corr.)}$	$\sqrt{\gamma_A}$(corr)
0.02	0.4746	0.859	0.003706	0.833	0.003593	0.859
.05	.4522	.815	.003939	.784	.003819	.809
.0957	.4362	.784	.004146	.744	.004019	.768
,2285	.4152	.747	.004331	.713	.004198	.736
.614	.3902	.732	.004443	.695	.004307	.717
1.0	,3765	.764	.004268	.723	.004137	.746
1.5	.3646	.811	.004013	.769	.003890	.793
1.54[a]	.3640	.811	.003952	.768	.003831	.792
1.995	.3551	.891	.003619	.853	.003508	.880
2.993	.3387	1.085	.003080	1.003	.002986	1.035

[a] m_1 = 0.502.

(4) m_1 = 1.002 M HAc. **Correction for** E' = +0.0019 (7.67%)

0.01997	0.4646	0.859	0.005478	0.784	0.005088	0.844
.049	.4429	.815	.005772	.744	.005362	.801
.1	.4255	.780	.006079	.706	.005646	.760
.222	.4061	.748	.006337	.678	.005886	.730
.2	.4085	.752	.006338	.677	.005886	.729
.5	.3865	.729	.006352	.676	.005899	.728
1.0	.3672	.764	.006130	.700	.005677	.754
1.3[a]	.3596	.792	.005898	.726	.005478	.782
2.43	.3377	.960	.005039	.852	.004647	.917
2.96[a]	.3300	1.074	.004455	.963	.004138	1.037

[a] m_1 = 0.998.

(5) m_1 = 5.4 M HAc. **Correction for** E' = +0.0107 (51.7%)

m_1	m_2	E'	$\gamma_{HCl(H_2O)}$	m_H	$\sqrt{\gamma_A}$	$m_{H(corr.)}$	$\sqrt{\gamma_A}$(corr.)
5.41	0.05	0.4092	0.800	0.02180	0.458	0.01438	0.695
5.41	.1	.3923	.774	.02248	.445	.01482	.675
5.39	.2	.3758	.748	.02288	.436	.01509	.661
5.41	.5	.3535	.729	.02295	.436	.01513	.661
5.41	1.0	.3337	.766	.02247	.445	.01481	.675
5.37	1.5	.3237	.812	.01967	.506	.01297	.785
5.39	1.5	.3233	.812	.01998	.499	.01317	.757
5.39	2.0	.3138	.872	.01881	.530	.01240	.804
5.39	3.0	.2990	1.088	.01433	.696	.01189	1.056

TABLE I *(Concluded)*

(6) m_1 = 10.2 M HAc

m_2	E'	$\gamma_{HCl(H_2O)}$	m_H	$\sqrt{\gamma_A}$
0.05	0.3888	0.782	0.05048	0.272
.0992	.3726	.765	.04995	.274
.257	.3509	.738	.04821	.284
.5	.3351	.730	.04685	.293
1.0	.3181	.766	.04124	.332
1.49	.3057	.814	.03972	.345
2.0	.2975	.885	.03444	.398
2.96	.2814	1.085	.02897	.474

C. Lithium Chloride

(1) m_1 = 0.2 M HAc. **Correction for E'** = +0.0003 (1.16%)

m_1	m_2	E'	$\gamma_{HCl(H_2O)}$	m_H	A	$m_{H(corr.)}$	$\sqrt{\gamma_A}$(corr)
0.2122	0.04467	0.4669	0.817	0.002475	0.796	0.002477	0.805
.2090	.08933	.4501	.788	.002559	.764	.002530	.773
.2107	.2	.4301	.760	.002677	.733	.002646	.741
.2037	.5	.4059	.751	.002813	.685	.002781	.693
.2145	1.0	.3842	.804	.002856	.689	.002823	.697
.2110	1.568	.3674	.902	.002783	.705	.002751	.713
.2100	2.069	.3541	1.027	.002730	.717	.002699	.725
.2081	3.112	.3313	1.340	.002590	.753	.002560	.762
.2037	4.533	.2993	2.115	.002481	.778	.002453	.787

D. Barium Chloride

(1) **Cells of the type** (2). m_0 = 0.01 M HCl.

m_0	m_2	$\sqrt{\mu}$	E	γ_{HCl}	mo	m_2	$\sqrt{\mu}$	E	γ_{HCl}
0.01	0.02	0.27	0.4295	0.796	0.00936	0.466	1.19	0.3615	0.712
,00991	.0257	.295	.4249	.790	.01	.463	1.19	.3600	.711
.01	.05143	.405	.4109	.760	.00944	.941	1.67	.3363	.817
.01	.0926	.537	.3991	.728	.01	1.0	1.74	.3330	.821
.00931	,1870	.750	.3856	.700	.00952	1.423	2.07	.3166	.970
.01	.1852	.752	.3838	.702	.01	1.5	2.12	.3128	.994

(2) m_1 = 0.2035 M HAc. **Correction for E'** = +0.0003 (1.16%)

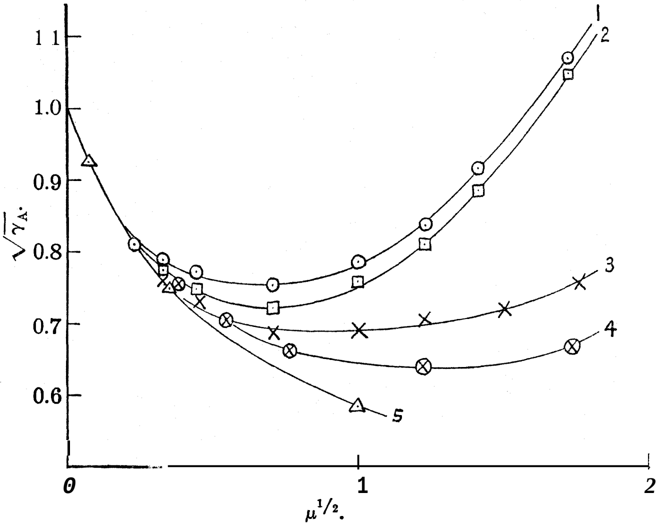
m_2		$\gamma_{HCl(H_2O)}$	m_H	$\sqrt{\gamma_A}$	$m_{H(corr)}$	$\sqrt{\gamma_A}$(corr.)
0.01984	0.4712	0.803	0.002440	0.791	0.002412	0.800
.0496	.4493	.761	.002549	.757	.002520	.766
.0992	.4323	.725	.002721	.708	.002690	.716
.1984	.4147	.699	.002905	.663	.002872	.671
.496	.3891	.714	.003017	.638	.002983	.645
.992	.3651	.822	.002897	.665	.002864	.673
1.484	.3478	.990	.002618	.736	.002588	.744
1.5	.3471	.994	.002640	.730	.002610	.738

and therefore the total molality was unknown, γ_{HCl} or $\gamma_{H(1)}\gamma_{Cl(1)}$ was obtained approximately by trial and a first rough value of m_H determined. From this a more accurate value of the total ionic molality was computed and a more accurate value of γ_{HCl} was obtained; m_H could then be calculated with certainty.

It was found necessary to determine γ_{HCl} in 0.01 *M* hydrochloric acid–barium chloride mixtures by means of cells of type (2). These are included in the table and will be found to agree excellently with some recent values of Randall and Breckenridge.[2m]

Discussion of the Properties of the Acetic Acid–Salt Systems

(a) General Considerations.—From the data in Table I, it is obvious from the behavior of m_H that in all cases the first addition of salt increases the dissociation of the acid. As the concentration of the added salt increases this dissociation reaches a maximum, and in the more concentrated solutions decreases with increasing salt concentration. On the other hand, γ_A decreases, passes through a minimum and then increases upon the addition of the salt. This latter behavior is in accord with that of all strong acids in salt solutions, of the ionic activity coefficient product of water in salt solutions, and of the ionic activity coefficient of the mono- and dichloro-acetic acids as computed from catalytic data.

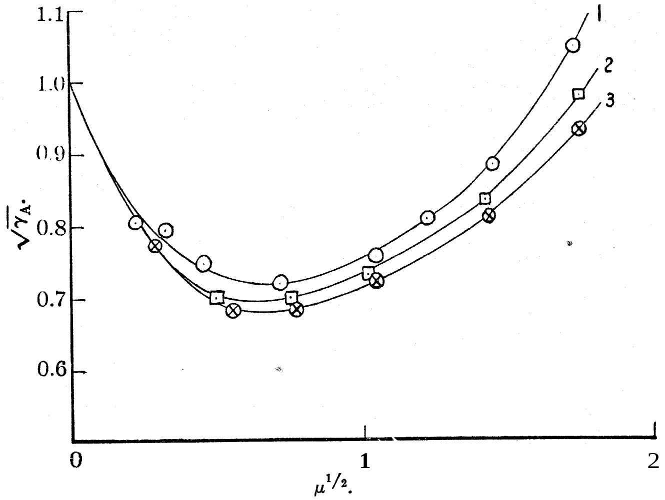


1, KCl; 2, NaCl; 3, LiCl; 4, $BaCl_2$; 5, Debye and Hückel theory.

Fig. 2.—The ionic activity coefficients of 0.2 M acetic acid in salt solutions.

Figure 2 contains plots of $\sqrt{\gamma_A}$ in the four salt solutions against the square root of the ionic strength, $\mu^{1/2}$. These were obtained from the cells containing 0.2 *M* acetic acid. Since for the present we have neglected the effect of the change in solvent due to the presence of the undissociated molecule, these results for $\sqrt{\gamma_A}$ may all be low to the extent of approximately 0.5%. Exactly the same order and approximately the same arrangement of results is obtained as was found by Harned[4,7] in the case of the ion activity coefficient of water, of strong hydroxides in the corresponding chloride solutions, of formic acid in salt solutions, and by Harned and Hawkins[3] in the case of the mono- and dichloro-acetic acids in halide solutions.

In Fig. 3, the values of $\sqrt{\gamma_A}$ for acetic acid and dichloro-acetic acid in potassium and sodium chloride solutions are plotted. Since in the case of the dichloro-acetic acid a greater curvature appears at the lower concentration, it would seem that its activity coefficient should always lie below that of the acetic acid. The values of γ_A have therefore been taken as calculated by Harned and Hawkins. The value of γ_A of monochloro-acetic acid in sodium chloride solutions is also given. Thus, in aqueous salt solutions, it would appear that γ_A decreases as the chlorine substitution increases up to the formation of dichloro-acetic acid. The plots in the upper part of Pig. 4 show the effect of change of concentration of the acetic acid on the activity coefficients relative to unity at infinite dilution of the pure aqueous solutions and calculated according to Equation 14. It is interesting to note that the upper four plots are parallel.



1, CH_3COOH; 2, $CH_2ClCOOH$; 3, $CHCl_2COOH$.

Fig. 3.—The ionic activity coefficients of acetic, mono- and dichloro-acetic acids in sodium chloride solutions.

As previously pointed out, Equation 6 is not valid in the case where considerable concentrations of undissociated acetic acid are present and, therefore, to compute the activity coefficients relative to unity at infinite dilution for each separate solvent, cells equivalent to those represented by (8) are necessary. Equation 14 would be valid in the form

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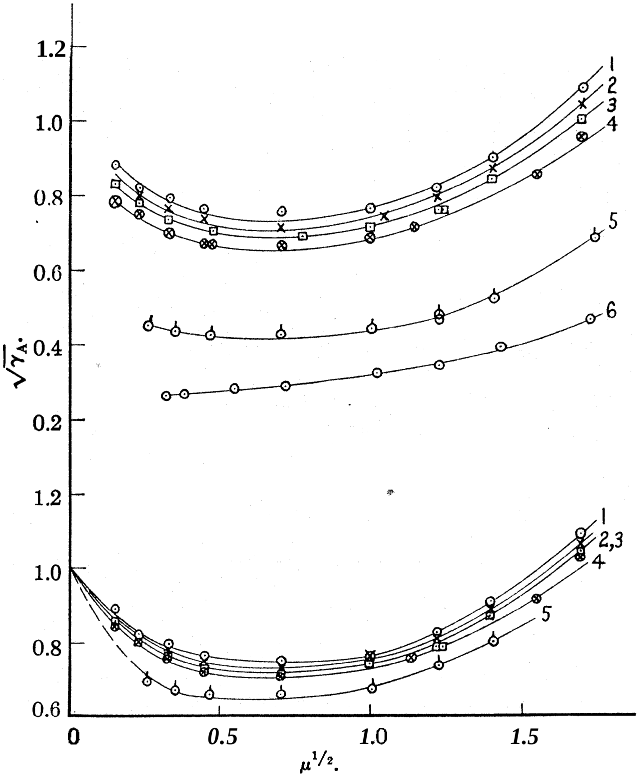
[7] Harned, THIS JOURNAL, 49, 1 (1927).

$$\begin{aligned} E' - 0.2225 &= -0.05915 \log \gamma'_{\mathrm{H}(1)}\gamma'_{\mathrm{Cl}(1)}\, m_{\mathrm{H}} m_2 \\ &= -0.05915 \log \gamma_{\mathrm{H}(1)}\gamma_{\mathrm{Cl}(1)}\, m_{\mathrm{H}} m_2 - 0.05915 \log \frac{\gamma'_{\mathrm{H}(1)}\gamma'_{\mathrm{Cl}(1)}}{\gamma_{\mathrm{H}(1)}\gamma_{\mathrm{Cl}(1)}} \qquad (14a) \end{aligned}$$

where $\gamma'_{(\mathrm{H}1)}\gamma'_{\mathrm{Cl}(1)}$ is the activity coefficient of hydrochloric acid in a solution containing the acetic acid and salt relative to $\gamma_{\mathrm{H}(1)}\gamma_{\mathrm{Cl}(1)}$ in the salt solution in pure water. The second member on the right is, therefore, the correction term for the electromotive force E which will take into account the change in solvent.



1, 0.1 *M*; 2, 0.2 *M*; 3, 0.5 *M*; 4, 1.0 *M*; 5, 5.4 *M*; 6, 10.2 *M*.

Fig. 4.—The ionic activity coefficients of acetic acid at different molalities, *M*, in sodium chloride solutions.

To correct for this change in solvent, we have used a method which, although approximate, yields results of the right magnitude and illustrates the effect of the correction. We make the assumption that up to 5.4 M concentration the effect of the undissociated acetic acid on the activity coefficient of the hydrochloric acid is the same as that of ethyl alcohol. Further, owing to the parallel nature of the plots in Fig. 4, we assume that at a given acetic-acid concentration the correction is independent of the salt concentration. To this end we have plotted the electromotive forces of the cells

$$H_2 \mid HCl(0.01) \mid AgCl \mid Ag$$

in water and water–alcohol mixtures against the mole per cent. of alcohol, and have read off this plot the changes in electromotive forces produced by the addition of 0.1, 0.2, 0.5, 1 and 5.4 M alcohol. These were found to be 0.1, 0.3, 0.8, 1.9 and 10.7 millivolts, respectively. These corrections, which correspond to the second member on the right of Equation 14a, we have added to E'. Subsequently, m_H was recalculated and $\sqrt{\gamma_A}$ computed by Equation 7. The corrected results are given in the last columns of Table I, and the corrected values of $\sqrt{\gamma_A}$ are plotted in the lower part of Fig. 4. It is obvious upon inspection of these curves that this correction brings the curves much closer together. The distribution is also what is to be expected from the change in the dielectric constant produced by the addition of the undissociated acid.

Since acetic acid has a dielectric constant lower than that of water, the value of the ionic activity coefficient product of the acid relative to unity in infinite dilution in a given solvent will decrease with increasing acetic-acid concentration. The extent of the variation may be calculated approximately in the case of dilute solutions by the equation

$$\frac{\log \sqrt{\gamma_{A(1)}}}{\log \sqrt{\gamma_{A(2)}}} = \left(\frac{D_2}{D_1}\right)^{3/2} \qquad (14b)$$

derivable from the Debye and Hückel theory. This calculation requires a knowledge of the dielectric constants of acetic acid–water mixtures. These data are not available, although we find that the dielectric constant of pure acetic acid is 9.7.[8] Assuming that the dielectric constant of acetic-acid–water mixtures varies in the same way as that of alcohol–water mixtures, and taking the dielectric constant of pure water as 81, we obtain 80, 78, 75 and 58 for the dielectric constants of 0.2, 0.5, 1 and 5.4 M acetic-acid solutions, respectively. We now select a concentration (0.3μ) at which $\sqrt{\gamma_A}$ equals 0.800 in pure water. Substituting the values of the above dielectric constants in Equation 14b, we obtain the values of $\sqrt{\gamma_A}$ in the different solvents which are given in the third line of Table II. These may be compared with the values read off the curves in the lower part of Fig. 4, which are given in the second line.

TABLE II

COMPARISON OF THE OBSERVED ACTIVITY COEFFICIENTS WITH THOSE COMPUTED BY EQUATION 14b

HAc concn.	0.0	0.2	0.5	1.0	5.4
$\sqrt{\gamma_A}$ (obs.)	0 800	0.796	0.79	0.77	0.69
$\sqrt{\gamma_A}$ (calcd.)	0.800	0.796	0.79	0.78	0.70

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[8] Francke, Wied. Ann., 50, 163 (1893).

These results show that the procedure which we have adopted and which is necessarily an approximation, gives results of the correct order of magnitude and illustrate very well the influence of the various factors which come into force when the nature of the solvent medium is altered.

Part 2. The Ionic Concentrations and Activity Coefficients of Ammonia and its Methyl Derivatives in Salt Solutions

Experimental

As this investigation is intended as a preliminary survey of the possibilities of determining the activity coefficients of weak electrolytes in salt solutions rather than a very accurate determination of such activity coefficients, it was considered advisable to employ cells with liquid junctions, rather than cells of the type (3a), in the determination of the activity coefficients of the weak hydroxides. Cells of the type (3a) can undoubtedly be used for the accurate determination of these activity coefficients (provided that there is no reaction between the amalgam and the cation of the base), but cells of the type

$$H_2 \mid MOH(m_0),\ MX(m_2) \underset{A}{\mid} MX(m_2) \mid AgCl \mid Ag \mid AgCl \mid MX(m_2) \underset{B}{\mid} BOH(m_1),\ MX(m_2) \mid H_2 \qquad (15)$$

obtained by difference of the half-cells

$$H_2 \mid MOH(m_0),\ MX(m_2) \mid MX(m_2) \mid AgCl \mid Ag \qquad (16)$$

$$H_2 \mid BOH(m_1),\ MX(m_2) \mid MX(m_2) \mid AgCl \mid Ag \qquad (17)$$

which can be constructed with greater ease and rapidity, probably give quite accurate results.[9]

Cells of this type were therefore constructed, in which MOH was sodium hydroxide at a concentration of 0.01 M and MX was sodium chloride at concentrations varying between 0.02 and 3.0 M. Five bases were used, as follows: ammonia, mono-, di- and trimethylamines, and tetramethyl ammonium hydroxide. BOH therefore represents one of these hydroxides in a sodium chloride solution of the same concentration as that in the left half of the cell (15). Junction between these two solutions was made by means of silver–silver chloride electrodes in solutions of sodium chloride at the same concentration as in the hydroxide solutions. In practice the two halves of the cell were measured separately.

In this case two liquid junctions are encountered, at A and B. Virtually, however, this reduces to one liquid junction, namely, that at the boundary

$$NaOH(m_0),\ NaCl(m_2) \mid BOH(m_1),\ NaCl(m_2) \qquad (18)$$

When the concentration of the sodium chloride is great compared with that of the hydroxide, the liquid junction potential must be very small

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[9] *Note that we have made* $(m_0 + m_2)$ *equal* to $(m_{OH} + m_2)$ *so that the* ionic *strengths* in *each are* **equal.**

and, indeed, negligible. Even in the lowest sodium-chloride concentrations which were used (0.02 M), the liquid junction potential must be very small, since we endeavored to work with concentrations of the weak hydroxide such that its hydroxyl-ion concentration was around 0.01 *M*, that is, nearly that of the sodium hydroxide in the left half of cell (15).

The mono- and dimethylamines were used at a concentration of approximately 0.2 M. The ammonia was 0.5 M, giving a hydroxyl-ion concentration of about 0.005 M. Trimethylamine was used at 0.2 M, giving a hydroxyl-ion concentration of between 0.005 M and 0.01 M. Tetramethylammonium hydroxide was used at 0.01 M, since we were able to show that in all probability it belongs to the class of "completely dissociated" electrolytes.

Two difficulties were encountered. In the first place, preliminary measurements of sodium-chloride solutions of sodium hydroxide at low concentrations of the latter (0.0025 M) showed that the hydrogen electrode would not give accurate potentials at this concentration of hydroxyl ion. This is in accordance with our experience with the hydrogen electrode in acetic-acid solution, as previously described.

Secondly, in the 0.02 *M* and 0.05 *M* sodium-chloride solutions of ammonia and trimethylamine, difficulty was experienced in determining the potentials accurately. This is probably due to one of two causes. (1) Diminution of the salt concentration lowers the hydroxyl-ion concentration. It may be, therefore, that in the above two salt concentrations we are approaching the limit of the hydroxyl-ion concentration at which the hydrogen electrode will work efficiently. (2) The liquid junction according to the scheme (18) will probably no longer be of negligible magnitude if the sodium-hydroxide concentration is 0.01 *M* and the hydroxyl-ion concentration of the weak hydroxide is approximately 0.005 M. As the salt concentration increases, most of the ionic transference is due to the sodium and chloride ions, and therefore it is likely that for solutions of concentrations 0.1 M sodium chloride and greater, the liquid junction potential may be neglected with safety. We have therefore omitted measurements in 0.02 M and 0.05 M sodium-chloride solutions of ammonia and trimethylamine.

Cells were also measured containing potassium chloride and either ammonia or methylamine against cells containing 0.01 *M* potassium hydroxide in potassium chloride solutions, and also similar series with lithium chloride as salt.

The electrodes were of the type already described. Measurements were made at 25°. The liquid junctions were of the static type, a capillary tube containing the hydroxide–salt solution being dipped into a cup containing the pure salt solution.

Calculation of Results

Table III gives the electromotive forces of the half-cells (16) and (17) measured, that is, cells containing 0.01 M sodium, potassium or lithium hydroxides in the respective salt solutions,-the five hydroxides in sodium-chloride solution, and ammonia and methylamine in potassium- and lithium-chloride solutions.

TABLE III

ELECTROMOTIVE FORCES OF CELLS (16) AND (17) CONTAINING HYDROXIDES AND ALKALI CHLORIDES

A. Sodium Chloride

Salt concn.	0.01 M NaOH	0.5030 M NH_3	0.1989 M CH_3NH_2	0.1987 M $(CH_3)_2NH$	0.1891 M $(CH_3)_3N$	0.01 M $(CH_3)_4NOH$
0.02	1.0197	....	1.0221	1.0239	....	....
.05	1.0015	....	1.0060	1.0077	....	....
.1	.9858	0.9646	.9924	.9945	0.9653	0.9855
.2	.9689	.9494	.9781	.9813	.9515	.9692
.5	.9452	.9282	.9583	.9614	.9332	.9467
1.0	.9273	.9125	.9432	.9476	.9192	.9285
1.5	.9166	.9025	.9342	.9390	.9113	.9181
2.0	.9086	.8946	.9277	.9330	.9048	.9099
3.0	.8973	.8835	.9177	.9240	.8973	.8985

B. Potassium Chloride

Salt concn.	0.01 M KOH	0.1910 M CH_3NH_2	0.5030 M NH_3	Salt concn.	0.01 M KOH	0.1910 M CH_3NH_2	0.5030 M NH_3
0.02	1.0207	1.0235	....	1.0	0.9380	0.9511	0.9199
.05	1.0044	1.0090	....	1.5	.9294	.9437	.9119
.1	.9900	.9967	0.9688	2.0	.9226	.9378	.9055
.2	.9749	.9832	.9546	3.0	.9140	.9304	.8969
.5	.9537	.9647	.9347				

C. Lithium Chloride

Salt concn.	0.01 M LiOH	0.5030 M NH_3	0.1910 M CH_3NH_2	Salt concn.	0.01 M LiOH	0.5030 M NH_3	0.1910 M CH_3NH_2
0.02	1.0167	....	1.0207	1.0	0.9145	0.9016	0.9343
.05	.9974	....	1.0040	1.5	.8981	.8888	.9219
.1	.9801	0.9590	.9896	2.0	.8866	.8781	.9125
.2	.9624	.9433	.9739	3.0	.8667	.8613	.8974
.5	.9371	.9208	.9528				

Considerations similar to those which led to Equation 4 will show that the electromotive forces of the cells (15) are given by

$$E = 0.05915 \log \frac{\gamma_{H(2)}\gamma_{X(2)}\ C_{H(2)}\ m_2}{\gamma_{H(1)}\gamma_{X(1)}\ C_{H(w)}\ m_2} = 0.05915 \log \frac{\gamma_{OH(1)}\gamma_{X(2)}\ a_{H_2O(2)}\ m_2 m_{OH}}{\gamma_{OH(2)}\gamma_{X(1)}\ a_{H_2O(1)}\ m_2 m_0} \quad (19)$$

Since the concentrations of BOH have been taken low enough to render the dielectric constant correction negligible, the activity and activity coefficient ratios may again be taken as unity. Equation 19 becomes

$$E = 0.05915 \log \frac{m_{OH}}{m_0} \quad (20)$$

which is comparable to Equation 6. We can therefore calculate m_{OH}

from a knowledge of the difference of the two half-cells (16) and (17), one containing the strong base and the other the weak base. Table IV contains the hydroxyl-ion concentrations of the weak hydroxides in sodium, potassium and lithium-chloride solutions, calculated by Equation 20.

TABLE IV

HYDROXYL-ION CONCENTRATIONS OF WEAK HYDROXIDES IN SALT SOLUTION

A. **Sodium Chloride**

Salt concn.	0.5030 M NH_3	0.1989 M CH_3NH_2	0.1987 M $(CH_3)_2NH$	0.1891 M $(CH_3)_3N$
0.02	......	0.01098	0.01178	......
.05	......	.01191	.01273	......
.1	0.004382	.01293	.01403	0.004502
.2	.004683	.01431	.01620	.005080
.5	.005159	.01665	.01879	.006268
1.0	.005621	.01857	.02204	.007296
1.5	.005776	.01984	.02410	.008136
2.0	.005821	.02103	.02585	.008625
3.0	.005844	.02212	.02827	.010000

B. **Potassium Chloride**

Salt concn.	0.5030 M NH_3	0.1910 M CH_3NH_2
0.02	......	0.01085
.05	......	.01196
.1	0.004382	.01298
.2	.004537	.01381
.5	.004773	.01534
1.0	.004943	.01665
1.5	.005060	.01745
2.0	.005139	.01807
3.0	.005139	.01893

C. **Lithium Chloride**

Salt concn.	0.5030 M NH_3	0.1910 M CH_3NH_2
0.02	......	0.01124
.05	......	.01293
.1	0.004398	.01448
.2	.004754	.01564
.5	.005300	.01843
1.0	.006052	.02161
1.5	.006964	.02526
2.0	.007183	.02741
3.0	.008104	.03304

$\gamma_B\gamma_{OH}/\gamma_{BOH}$ or γ_R may be computed from m_{OH} by

$$K = \frac{\gamma_B\gamma_{OH}}{\gamma_{BOH}} \frac{m_{OH}^2}{m_1 - m_{OH}} \tag{21}$$

employing the law of mass action in a manner identical with that previously used in the case of acetic acid (compare Equation 8).

In the case of ammonia,[10] the dissociation constant was taken to be 1.85×10^{-5}. In the case of mono- and dimethylamines, it was assumed that in 0.02 M sodium-chloride solution, the value of $\sqrt{\gamma_B\gamma_{OH}/\gamma_{BOH}}$ or $\sqrt{\gamma_R}$ was equal to the activity coefficient of sodium hydroxide in this concentration of sodium chloride, that is, 0.830. On this assumption a value of K was calculated. In the case of trimethylamine, as the variation of $\sqrt{\gamma_R}$ with the sodium-chloride concentration was very similar to the corresponding variation of $\sqrt{\gamma_R}$ in the case of dimethylamine, we assumed that the values of $\sqrt{\gamma_R}$ for these two bases are identical at a sodium chlor-

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[10] Lundén, *J. chim.* phys., 5, 574 (1907); Noyes, Kato and Sosman, *Z. physik. Chem.*, 73, 1 (1910).

ide concentration of 0.1 M, that is, 0.709. It is to be realized that the choice of a reference point for the calculation of K is a somewhat arbitrary matter, and therefore the values of K used in the calculation of $\sqrt{\gamma_R}$ are to be considered tentative and subject to revision should more accurate values be forthcoming.

Table V contains the values of K calculated in the above manner, compared with the values obtained by Bredig from conductivity measurements.[11]

TABLE V

DISSOCIATION CONSTANTS OF AMINES AT 25°

Base	Present authors	Bredig
Monomethylamine	4.42×10^{-4}	5.0×10^{-4}
Dimethylamine	5.12×10^{-4}	7.4×10^{-4}
Trimethylamine	5.27×10^{-5}	7.4×10^{-5}

Using these values of K, $\sqrt{\gamma_R}$ was calculated and these values are given in Table VI.

TABLE VI

ACTIVITY COEFFICIENTS OF WEAK HYDROXIDES IN SALT SOLUTION

A. Sodium Chloride

Salt concn.	0.5030 M NH_3	0.1989 M CH_3NH_2	0.1987 M $(CH_3)_2NH$	0.1891 M $(CH_3)_3N$
0.02	...	0.830	0.830	...
.05	...	.763	.767	...
.1	0.693	.701	.693	0.693
.2	.648	.631	.597	.613
.5	.588	.539	.511	.495
1.0	.540	.481	.432	.424
1.5	.525	.448	.394	.380
2.0	.521	.422	.364	.358
3.0	.519	.400	.330	.307

B. Potassium Chloride

Salt concn.	0.5030 M NH_3	0.1910 M CH_3NH_2
0.02	...	0.822
.05	...	.744
.1	0.693	.683
.2	.669	.641
.5	.636	.574
1.0	.614	.527
1.5	.600	.502
2.0	.591	.484
3.0	.591	.461

C. Lithium Chloride

Salt concn.	0.5030 M NH_3	0.1910 M CH_3NH_2
0.02	...	0.793
.05	...	.686
.1	0.691	.610
.2	.639	.563
.5	.573	.474
1.0	.501	.417
1.5	.435	.339
2.0	.422	.310
3.0	.373	.253

Discussion of the Properties of the Hydroxide–Salt Systems

In Fig. 5 the activity coefficients of four bases in sodium chloride solutions are plotted against $\mu^{1/2}$. It appears that as substitution of the am-

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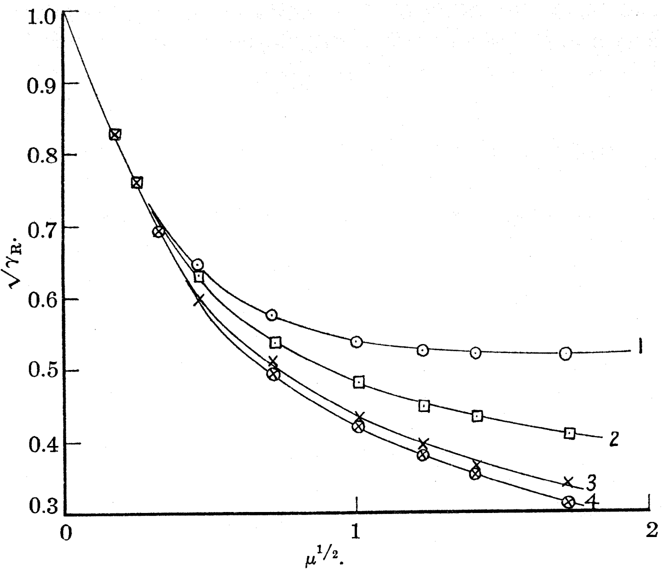
[11] Bredig, Z. *physik. Chem.*, 13, 191 (1894).

monium ion by the methyl groups occurs, lower values for the activity coefficients are obtained. This is in accord with our results on acetic acid and the chloro-substituted acetic acids. The results are of the expected order of magnitude but no great accuracy can be claimed, particularly in the dilute solutions where errors due to small liquid junction potentials are possible.

That the order of the salt effects corresponds to that of acetic acid in the simple halide solutions is shown by the plots in Fig. 6.



1, NH_4OH; 2, CH_3NH_3OH; 3, $(CH_3)_2NH_2OH$; 4, $(CH_3)_3NHOH$.

Fig. 5.—The ionic activity coefficients of ammonia and amines in sodium chloride solutions.

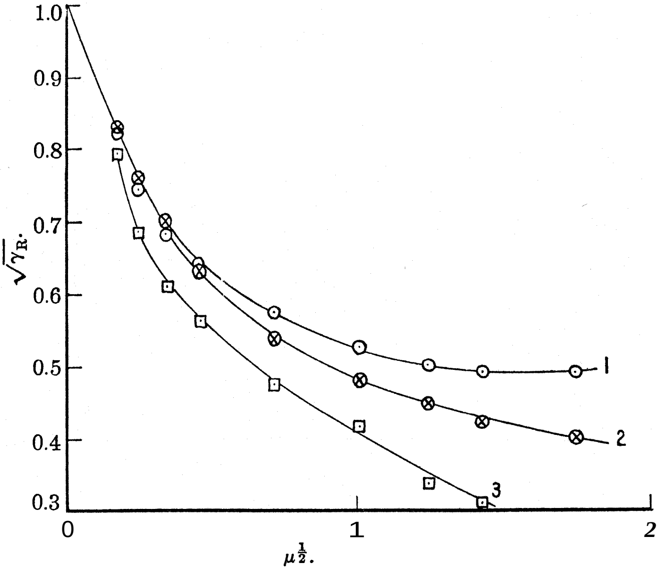
The activity coefficients of tetramethylammonium hydroxide cannot be determined by this method but it is of very great interest to note that our measurements show that, in the presence of sodium chloride, this hydroxide is more highly dissociated than sodium hydroxide. The ratios of hydroxyl-ion molalities, $m_{OH(T)}/m_{OH(NaOH)}$, at the various salt concentrations computed by Equation 20, are given in Table VII.

TABLE VII

HYDROXYL-ION CONCENTRATION RATIOS OF TETRAMETHYLAMMONIUM HYDROXIDE TO SODIUM HYDROXIDE IN SODIUM-CHLORIDE SOLUTIONS

Salt concn.	0.1	0.2	0.5	1.0	1.5	2.0	3.0
$m_{OH(T)}/m_{OH(NaOH)}$	0.988	1.012	1.052	1.048	1.060	1.052	1.048

Since the stoichiometrical concentrations of the hydroxides were both 0.01 M, the liquid junction potential must indeed be small at 0.1 M salt concentration, and certainly negligible at high salt concentrations. Thus, at 0.5 M sodium chloride and higher the amine is between 4.8 and 6% more strongly dissociated than the sodium hydroxide. At 0.1 M salt, it appears to be somewhat less dissociated. Since the amine possesses a high dissociation constant, the addition of salt would increase its dissociation somewhat due to the decrease in γ_R. If γ_R decreases more rapidly than $\gamma_{Na}\gamma_{OH}$ upon salt addition, and if sodium hydroxide is not completely dissociated, we may account for this observation. That sodium and lithium hydroxides are probably not dissociated to the extent of the halides of the alkali metals has already been pointed out by Harned.[12]



1, KCl; 2, NaCl; 3, LiCl.

Fig. 6.—The ionic activity coefficient of methylamine in potassium, sodium and lithium chloride solutions.

We desire to take this opportunity of expressing our thanks to the Commonwealth Fund for the grant of a Fellowship, which has made this joint contribution possible.

General Considerations and Summary

1. A method has been discussed whereby the activity coefficients and dissociation of weak acids and bases in salt solutions may be computed from the electromotive forces of cells without liquid junctions containing easily reproducible electrodes.

2. This method has been employed to obtain the activity coefficient of

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[12] Harned, *Z. physik. Chem.*, **117**, 1 (1925).

acetic acid in potassium, sodium, lithium- and barium-chloride solutions. In this case, the cells employed were

$$H_2 \mid HX(m_0),\ MX(m_3) \mid AgX \mid Ag$$
$$H_2 \mid HAc(m_1),\ MX(m_2) \mid AgX \mid Ag$$

Measurements of the second type have been made.

3. A modified method employing cells with negligible liquid junction potentials was employed for the determination of the activity coefficients of the bases. In this case, the cells measured were

$$H_2 \mid MOH(m_0),\ MX(m_2) \mid MX(m_2) \mid AgX \mid Ag$$
$$H_2 \mid BOH(m_1),\ MX(m_2) \mid MX(m_2) \mid AgX \mid Ag$$

where MOH is a strong and BOH a weak hydroxide.

4. The dissociation constant of a weak electrolyte in a given solvent or in salt solutions in this solvent, is given by $K = (C_C C_A/C_{CA})(\gamma_C \gamma_A/\gamma_{CA}) = K_c\gamma^2$. When the electrolyte is at infinite dilution so that γ^2 equals unity, K equals K,. Thus, ***K*** is a constant which measures the dissociation of the weak electrolyte in the pure solvent. γ^2 is a measure of the effect of the presence of the attractive and repulsive forces of the electrical field produced by the addition of the salts on the electrical potentials of the ions of the weak electrolyte. K_c is an absolute measure of the dissociation of the weak electrolyte under varying conditions of salt concentration. Although the change of K_c upon salt addition depends upon the variation of γ^2, its absolute value does not. This is shown clearly by the behavior of the methyl derivatives of ammonia. Thus, K_c increases in the order ammonia, tri-, mono-, dimethylamine, whereas, at a given salt concentration, γ^2 increases in the order tri-, di-, monomethylamine, ammonia.

5. We may generalize our results of the specific relative salt actions by the following brief rules. *A.* The ionic activity coefficients of acetic, mono- and dichloro-acetic acids are less in the solution of a given strength of that salt which possesses the higher activity coefficient in pure water. B. The same is true for ammonia and monomethylamine. It seems highly probable that it would also be the case for di- and trimethylamine. This order agrees with that found for the ionic activity coefficients of water, and is the reverse of the order found for the activity coefficients of halide acids in salt solutions.

6. Our results show that a 0.01 M solution of tetramethylammonium hydroxide containing 0.1 M sodium chloride has a slightly lower hydroxyl-ion concentration than that of an identical salt solution containing sodium hydroxide. At higher salt concentrations, however, sodium hydroxide is about 6% less dissociated.

7. The effect of the change in the solvent caused by large quantities of the undissociated molecules has been discussed, and approximately computed.

8. The method here employed, as well as the results, should prove very useful for studying salt effects in organic and biological media. It is far more sound from a kinetic or a thermodynamic point of view than the usual method which employs single electrodes and ordinary salt bridges.

PHILADELPHIA, PENNSYLVANIA

[CONTRIBUTION FROM THE RESEARCH LABORATORY, GENERAL ELECTRIC COMPANY]

THE FORMATION OF OZONE BY CATHODE RAYS

BY ABRAHAM LINCOLN MARSHALL

RECEIVED JUNE 23, 1928 PUBLISHED DECEMBER 10, 1928

The purpose of this investigation was to secure quantitative data on a supposedly simple reaction, the production of ozone from oxygen under the influence of high velocity electrons, which could be used in the interpretation of more complicated reactions. It has been found, however, due to the secondary decomposition of the ozone formed, that an analysis of the results is far from simple. The cathode ray tube recently described by Coolidge[1] was used, which allows one to obtain an intense source of very high velocity electrons. The various controllable variables, such as duration of exposure, average velocity and number of electrons, size and shape of the reaction chamber, were studied separately.

Not much work has been reported in the literature on the chemical effects of high velocity electrons in gaseous systems. Kriiger and Moeller[2] have studied the formation of ozone with very low intensity, low velocity electrons and their work has been subsequently very materially amplified by Kriiger and Utesch.[3] The latter worked with a hot cathode tube as a source of electrons and used an aluminum foil, 0.011 to 0.005 mm. thick, supported on a brass plate containing 65 holes 0.8 mm. in diameter as a window through which they obtained electrons from their tube. The source of voltage was a 500-cycle, high voltage transformer with a single kenotron rectifier giving peak voltages up to 60 kv. The largest current used in the tube was 0.4 milliampere. With a tube current of 3×10^{-4} ampere, 4.5×10^{-5} ampere was incident on the aluminum foil and of this 2.0×10^{-6} ampere passed through into the reaction chamber. The maximum amount of energy entering the reaction vessel in any experiment was estimated to be 0.12 watt. In one set of experiments a vessel containing two condenser plates placed 26 mm. apart was fastened to the window end of the tube. The plates were 4×2.5 cm. The diameter of the cathode ray beam at the window was 19 mm. and the authors be-

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[1] *(a)* Coolidge, J. *Franklin Inst.*, December, 1926, p. 693; (b) *Am. J. Rontgenol. Radium Therapy*, *19*, 313 (1928).

[2] Kriiger and Moeller, *Physik. Z.*, 13, 1040 (1912).

[3] Krüger and Utesch, *Ann. Physik*, 78, 113 (1925).

lieve that none of the primary electrons hit the condenser plates. With the tube operating, and oxygen at atmospheric pressure in the cell, voltage was applied to the condenser plates. At about 3000 volts, saturation current was reached and this current was taken as a measure of the intensity of ionization. The amount of ozone formed with the tube operating under the same conditions was determined and it was then possible to calculate the ratio of the number of molecules of ozone formed to the number of ions formed. The values obtained for this ratio range from 12 to 40. Any uncertainty in this value comes from the measurement of the saturation current, and in view of the importance of the value of this ratio in developing the theory of these reactions the measurements should be further substantiated. In their experiments oxygen was circulated through the reaction vessel at varying rates up to 15 liters per hour, and it was found that the amount of ozone formed increased up to a circulation of 10 liters per hour and then remained roughly constant. From the results it was calculated that 6–11% of the energy put into the gas was used to form ozone, from 2–4% caused ionization and the remainder heated up the gas. Their conclusion was that the formation of ozone by cathode rays was not connected with ionization of oxygen but with activation. The larger fraction of the energy absorbed from the electron stream was taken up in small amounts which produce excited oxygen molecules and these subsequently react to form ozone.

Experimental Method

The cathode ray tube was operated from a 200-kv. transformer which in turn was fed from a 1:1 transformer having a secondary insulated for 100 kv. As the case of the high voltage transformer was insulated from ground and connected to its primary and to the middle of the secondary, this method of operation enabled one to ground the anode end of the tube.[4] Since the cathode ray tube only imposes a half-wave load on the line, the inverse or non-useful voltage would normally be higher than the useful. This imposes an unnecessary strain on the tube and high voltage transformer and renders difficult a measurement of the voltage usefully employed. To obviate this difficulty, the wave form is distorted on the low voltage side of the transformer by connecting a half-wave load to the line, in the form of a mercury arc, on that half of the wave not used by the cathode ray tube. This load is made much greater than that of the tube and thus causes the inverse voltage to fall below the useful Voltage was measnred by means of a regulation sphere gap using the standard tables of the A. I. E. E. lor calibration. A large ballast resistance was placed in the primary circuit of the 1:1 transformer which was connected to a 550-volt, 60-cycle supply. The ballast resistance limited the energy input if for any reason the high voltage insulation broke down.

The tube used was modified slightly from that described by Coolidge, to enable one to fasten the reaction vessel directly to the anode arm of the tube. An invar ring one inch wide was brazed onto the end of the invar sleeve which constitutes part of the anode structure of the tube. The cell was fastened to a similar ring and the two were

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[4] **Ref. 1*a*, p. 707.**

clamped together with a rubber gasket between them. This made a gas-tight joint which could be easily assembled and aided greatly in all subsequent manipulation.

The bulb of the tube was **30.5** cm. in diameter and the tube was 89 cm., overall length. **A** detailed description of this particular type of tube which is the best available at present for operation in air has been given by Coolidge.[1b]

The tube and high voltage source were placed in a lead house having 1/8" to 1/4" thick walls and very thick lead glass windows. This gave complete protection from both x-rays and high voltage; the former was very necessary in an investigation of this nature where the tube was to be operated almost continuously. A remote control device was inserted in the power line supplying the high voltage transformer. Safety switches were placed on all the doors of the house so that it was impossible to come in contact with the high voltage circuit when the power was on. The filament of the cathode ray tube was operated from a storage battery in order to obtain **very** steady discharge currents. To avoid corona losses the battery was placed in an iron box having all the corners and edges rounded and the high voltage leads, which were kept very short, were made of **2**" brass tubing with 4" spheres placed at all right angle bends.

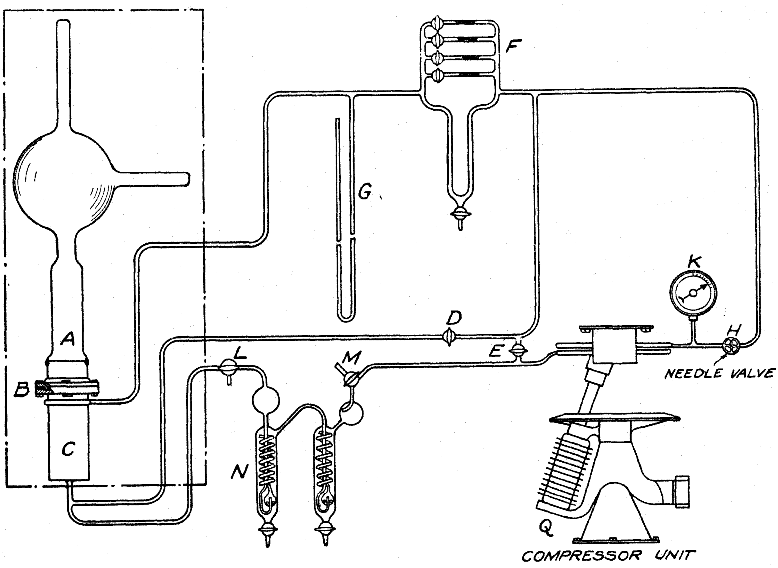


Fig. 1.

The window material employed was **resistal**,[1b] which is an alloy consisting of 18 parts by weight of chromium, **3** parts of silicon, **0.2** of carbon, 4–3.8 of iron and **35** of nickel. The window thickness varied from 0.50–0.57 of a mil.

A cooling coil of copper was soldered around the metal sleeve of the anode through which water was circulated. With this cooling it was possible to operate the tube continuously at 180 kv. and 1 milliampere.

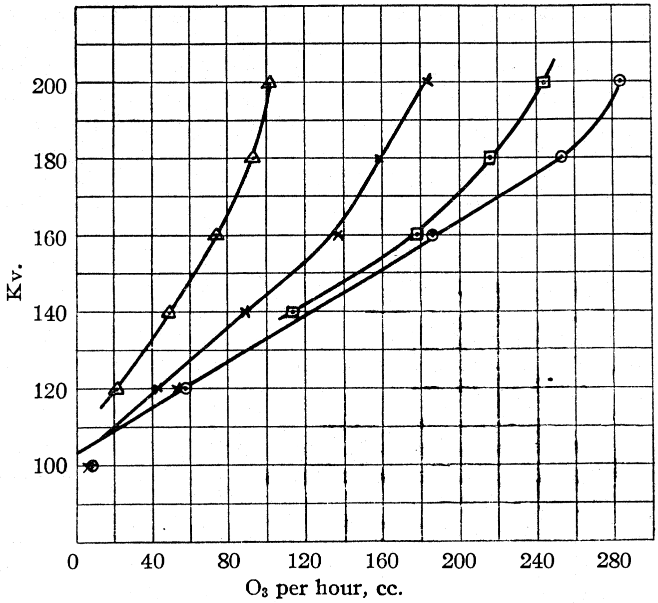
A closed system, illustrated in Fig. 1, was used at first and pure oxygen made by the electrolysis of a solution of potassium hydroxide was circulated by means of a compressor **Q.** The compressor unit was designed by J. G. deRemer and is described in the *Proc. Am. Soc.* Mech. *Eng.* for **1926.** It operated on the principle of Archimedes' screw using mercury as the compressing fluid. The pump is of all steel construction and contains no stuffing-boxes, so that there is no opportunity for oxygen to be contaminated with grease or to leak from the system. The oxygen always contained traces of mercury vapor coming from the mercury in the pump and water vapor from the gas scrubbers. The high pressure side of the unit was kept at 39 lbs. above atmospheric by means of the needle valve H, the pressure being measured on the gage K. The maximum rate of flow from the compressor was 1200 liters per hour measured at one atmosphere pressure. The rate of flow through the cell C was measured on the flowmeter F and controlled by means of the by-pass D. In this it was possible to vary the rate of flow through the reaction vessel from 20 to 1200 liters per hour and keep the pressure in the cell C always at one atmosphere. After being exposed in the reaction vessel the oxygen was passed through two scrubbing bottles, N, to remove any ozone formed. These scrubbers contained an alkaline solution of potassium iodide (50 g. KI, 25 g. KOH, per liter) and ozone could not be detected in the effluent gases when circulating at 1200 liters per hour. The full flow of gas from the compressor was sent through the scrubbers in order to minimize as much as possible any momentary pressure inequalities in the system due to the method of flow through the goose-neck of the scrubber and thus ensure a steady flow of gas through the reaction vessel. After an experiment the stopcock at E was opened and then L and M were opened to the atmosphere. The solution was removed from N and replaced; pure oxygen was bubbled through to displace the air and then the wash bottles were reconnected to the system for the next experiment. These operations required from five to ten minutes so that it was quite feasible to make a large number of experiments in a day with a single filling of the whole system.

Experimental Results

Surface Effects.—A series of experiments was made to determine whether an extension of the surface exposed in the glass reaction vessel had any effect on the amount of ozone formed. A cell 87 mm. in diameter and 20 mm. long was filled with loosely packed glass wool which came in contact with the tube window. The presence of the glass wool modified greatly the method of flow of the oxygen in the cell and tended to form pockets where the gas would be moving slowly. In ten minutes with circulation at the rate of 1200 liters per hour, 180 kv. and 1 milliampere, 11.2 *cc.* of ozone was formed. Blank experiments without glass wool gave 21.3 and 18.7 cc. in the same time interval. The glass wool was then replaced and 10.7 cc. of ozone was formed. A number of experiments were also performed with a cell 250mm. long filled loosely with glass wool to within 50 mm. of the tube window. About 35 cc. of ozone was formed in both this experiment and the control without glass wool. A fine network of tungsten wire was used to fill the cell and this apparently produced only a very minor effect.

In order to determine whether the "resistal" window was exercising an effect on the course of the reaction, it was completely covered with a sheet of mica 0.5 mil thick which was kept in close contact with the window by a brass ring. Three consecutive experiments with oxygen circulating at 1200 liters per hour, 200 kv. and 1 milliampere gave 39.2, 38.9 and 38.1 cc. of ozone in a ten-minute interval, while a blank without the mica gave 40.4 cc. of ozone.

The nature of these results indicates that the amount of ozone formed is almost entirely independent of the nature or extent of surface exposed during raying, and the ozonization of oxygen by cathode rays is a homogeneous gas phase reaction. This does not mean, of course, that there are no complications introduced by the walls due to reflection of primary and emission of secondary electrons during bombardment.



Cell length: △, 5 mm.; ×, 24 mm.; ⊡, 56 mm.; ⊙, 247 mm. Tube current, 1 milliampere. Pressure, 1 atmosphere. Rate of circulation, 1200 liters per hour.

Fig. 2.

Variation in Yield with Voltage and Cell Length.—The results given in Table I for three different cells show in part the reproducibility of the results for a given set of conditions and are tabulated to show how the yield varies with the voltage applied to the tube. The rate of circulation was 1200 liters per hour with a tube current of 1 milliampere.

TABLE I

OZONE FORMED PER HOUR, CC.

Kv. (max.) applied	Cell length, cm.		
	10	25	2
200	(257,264, 261) 261	282	177
180	(239,234, 232) 235	242	161
160	183	198	137
140	120	132	99
120	57.8	70	49.7
100	12.7	11.4	10.7

Air was used in the 10-cm. cell in one experiment at 180 kv. and 177 cc. of ozone was formed as compared with **235** cc. with pure oxygen. The above results were all with glass cells. Fig. 2 illustrates the results of a more detailed study with copper reaction vessels varying in length from 5 to 247 mm. Copper cells were used wherever possible in all subsequent work since the glass did not stand up well under the intense bombardment and would often crack badly after only short use. In Fig. **3** the yield for a given voltage is shown as a function of the cell length. These results are for **1** milliampere tube current and oxygen circulating at 1200 liters per hour.

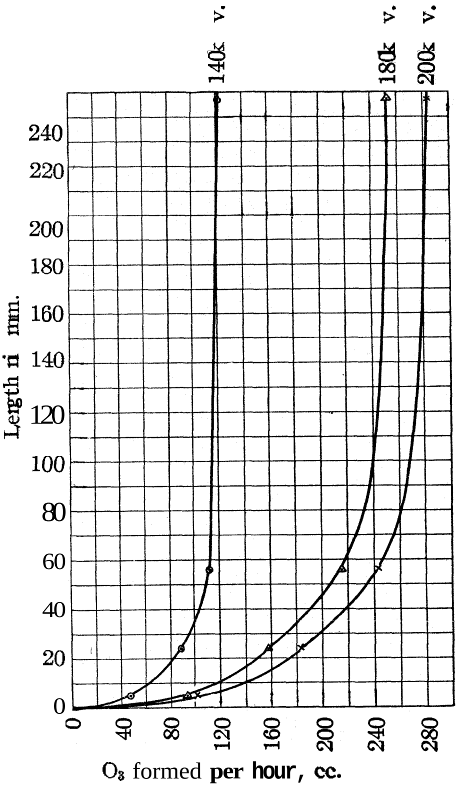


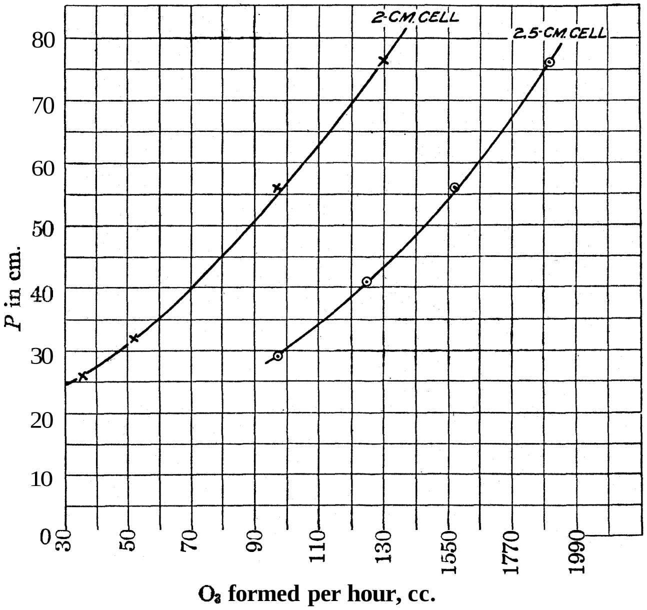
Fig. 3.

Pressure Variable.—Experiments were made with two cells on the effect on the yield of varying the oxygen pressure. The tube was operated at 180 kv., **1** milliampere and oxygen circulated at the rate of 655 liters per hour, the volume circulated being measured at the pressure under consideration. Fig. 4 illustrates the results obtained; the relationship is not a linear one and shows that at high pressures the yield for a given cell becomes independent of pressure.

Rate of Flow.—In connection with the investigation of the effect of varying the rate of flow of oxygen through the cell, a large number of preliminary experiments were made while determining the best method of carrying out the experiments. From studying these results, a purely empirical result was discovered, namely, that there appeared to be an approximately linear relationship between the logarithm of the rate of flow and the yield of ozone for a given time of raying. At low tube currents this relationship appeared to be very real over the whole range of circulation employed but deviations became large at higher currents. Fig. 5 illustrates the general trend of all these results. So far no theoretical significance has been obtained for this relationship, but it proved quite useful in the early stages of the experimental work in detecting gross errors in results obtained. A similar result was obtained when the tube current was varied.

The yield for a given rate of circulation is a linear function of the logarithm of the tube current.

In the experiments using the mercury compressor, it was noticed that a film of mercuric oxide deposited on the walls of the tubing leading away from the reaction chamber. The mercury could be removed from the gas stream by circulating through a trap immersed in carbon dioxide–ether mush. It was found that the yield of ozone was about 1 cc. greater in a fifteen minute period when the mercury was removed. Calculation showed that about 0.8 cc. of mercury vapor measured at N.T.P. would pass through the system in this period and apparently it was all oxidized.

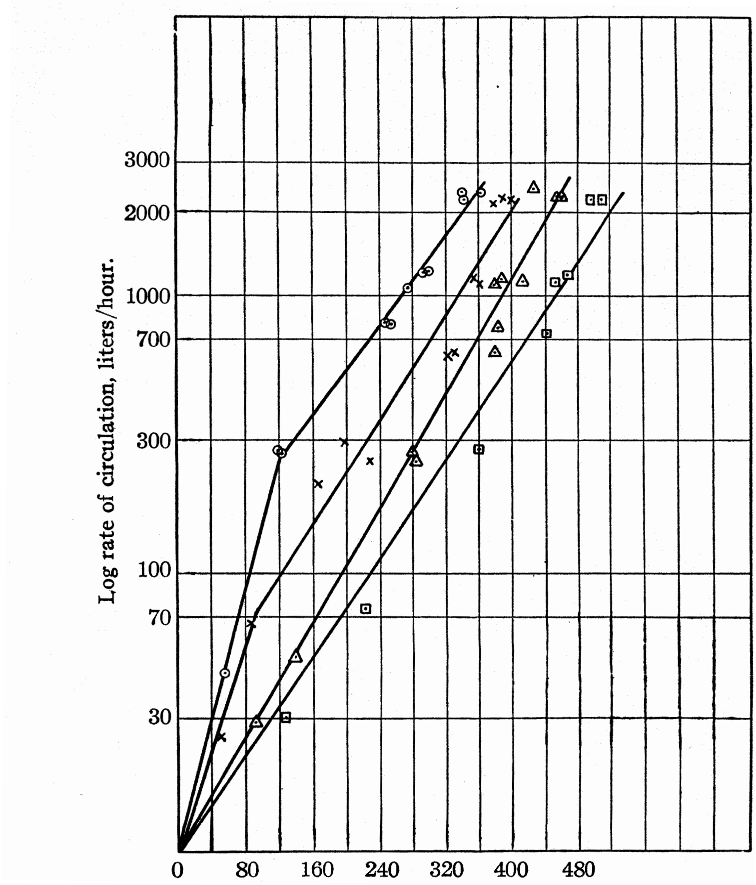


180 kv., 1 milliampere. Rate of circulation, 655 liters per hour.

Fig. 4.

At about this stage in the work a number of experiments were made with the electrolytic oxygen which we have on tap throughout the laboratory. This contains small quantities of hydrogen, nitrogen and water vapor with a trace of carbon dioxide. It was found that the results obtained with this supply of oxygen agreed very well indeed with those obtained from the specially purified gas used previously. All subsequent experiments were therefore made with oxygen from the line. In order to be able to pass oxygen through the system at rates of flow up to 2400 liters per hour and discharge the effluent gas into the atmosphere, it was necessary to operate in the cell at pressures above one atmosphere, and all subsequent experiments were carried out at a pressure of about 91 cm. of mercury.

Several thousand experiments were made with two sizes of cell, namely, 162 cc. and 1520 cc. at various currents, voltages and rates of circulation in order to obtain reliable data for quantitative treatment. The results for the 1520-cc. cell are given in Table II for a tube voltage of 180 kv. and varying currents. Each figure is the average of 4 to 5 experiments and the various experiments were made in random order to detect any source of error that might creep in during the course of a series of experiments.



Volume of cell, 162 cc.; voltage, 180 kv.; pressure, 91 cm.; current, ⊙, 1.00 ma.; ×, 0.50 ma.; △, 0.20 ma.; ⊡, 0.10 ma.

Fig. 5.

In treating these results, it will be more convenient to deal in terms of concentration of ozone and time of exposure rather than rate of flow and amount of ozone formed and these are calculated in the third and fourth columns of the table. In order to make this transformation, the assumption is made that the concentration of ozone is uniform in the cell as the gas passes through. This may be approximately correct at high rates of passage where the flow through the cell is turbulent and the gas is stirred up very rapidly. At lower rates of circulation, however, the concentration

TABLE II

VARIATION OF OZONE YIELD WITH CIRCULATION

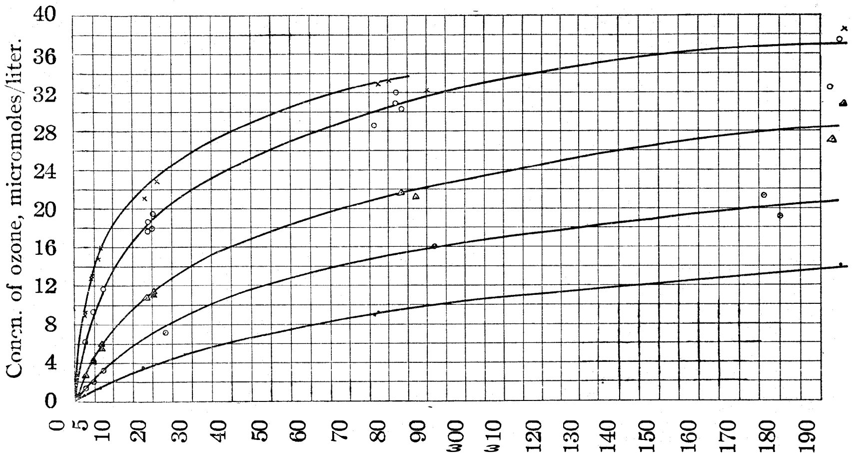
Circn., liters/hr.	O_3 per hour, cc.	I, sec.	Concn. ozone, micro-moles/-liter
1 Milliampere Current			
870	289	6.2	14.8
1210	353	4.46	13.0
2136	428	2.53	8.94
288	146	18.7	22.7
60	49.6	90.0	37.0
27.6	22.4	196	36.3
No circn.		600	37.2
No circn.		600	35.0
27.0	23.4	200	38.8
61	43.6	89	32.0
280	141	19.3	22.5
816	292	6.62	16.0
69	51.4	78	33.2
1266	363	4.26	12.8
2124	436	2.54	9.2
300	142	18	21.1
70.8	52	76	32.8
260	139	20.8	23.8
0.5 Milliampere Current			
No circn.	6.6	600	31.9
28.5	20.8	192	32.5
67	46.4	82	30.9
288	120	19	18.6
750	196	7.3	11.7
1134	237	4.83	9.35
1164	245	4.71	9.4
2100	291	2.61	6.19
798	209	6.87	11.7
270	118	20.3	19.5
66.6	47.7	82	32.0
28.3	23.7	193	37.4
No circn.		600	38.2
26.7	21.9	205	36.5
2120	294	2.58	6.19
1218	242	4.50	8.6
786	206	6 97	11.7
270	118	20.3	19.6
306	117	18.0	17.6
72	46.1	76.3	28.6

Concn., liters/hr.	O_3 per hour, cc.	*t*, sec.	Concn. ozone, micro-moles/-liter
276	110	19.9	17.9
66	45	83.4	30.3
0.20 Milliampere Current			
270	69	20.3	11.4
66	32	83	21.6
26.4	18	207	30.7
No circn.		600	20.4
786	97	6.97	5.53
1122	112	4.88	4.44
2100	124	2.61	2.63
1120	112	4.89	4.47
768	103	7.13	5.99
294	71	18.6	10.8
63	30	8.7	21.2
28.2	17	194	27.1
No circn.		600	29.2
2040	124	2.68	2.72
270	67	20.3	11.1
1200	112	4.58	4.17
270	70	10.3	11.6
66	32	83.4	22.0
28.8	16	190	24.8
0.10 Milliampere Current			
744	53	7.40	3.24
1146	51.4	4.80	2.00
1920	59.8	2.86	1.39
744	52.1	7.40	3.13
258	41.3	21.3	7.15
1140	54	4.82	2.11
2075	60.5	2.65	1.30
60	21.5	92	16.0
60	21.5	92	16.0
31.2	14.8	176	21.3
30.5	13.0	180	19.1
No circn.		600	25.3
No circn.		600	22.3
258	41.9	21.3	7.24
780	54.7	7.06	3.12
1170	61.8	4.69	2.36
1968	66.5	2.79	1.51

TABLE II (*Concluded*)

Circn , liters/hr.	O_3 per hour, cc.	t, sec.	Concn. ozone. micro-moles/-liter	Concn , liters/hr.	O_3 per hour, cc.	*t*, sec.	Concn. ozone, micro-moles/-liter
1164	59.5	4.73	2.28	72	13.8	76.4	**8.9**
1950	66.2	2.82	1.51	70.8	14.6	77.6	**9.2**
				27	8.5	203	**14.0**
0.05 Milliampere Current				310	24	17.7	3.5
2100	30.9	2.61	0.66	1110	29.6	4.95	1.19
1130	28.2	4.85	1.11	2100	33.3	2.62	0.71
840	25.2	6.55	1.34	870	28.6	6.32	1.46
300	24.9	18.0	3.7	294	24	18.3	3.65

may vary greatly from point to point through the cell. The entering gas contains no ozone and meets the highest electron density at the window of the tube. At the exit the ozone concentration is high and the rate of production much lower. The concentration should be much more uniform in a short cell than in a long one. The time is taken as the average time that a molecule is present in the cell; if there is any tendency to form pockets in the cell when the gas is moving more slowly, the calculated time will be incorrect and again the factor will be more important at the slower rates of flow.



1520-cc. cell. 180 kv. X, 1 00 ma.; ⊙, 0.50 ma.; △, 0.20 ma.; ⊖, 0.10 ma.; ●, 0.05 ma.

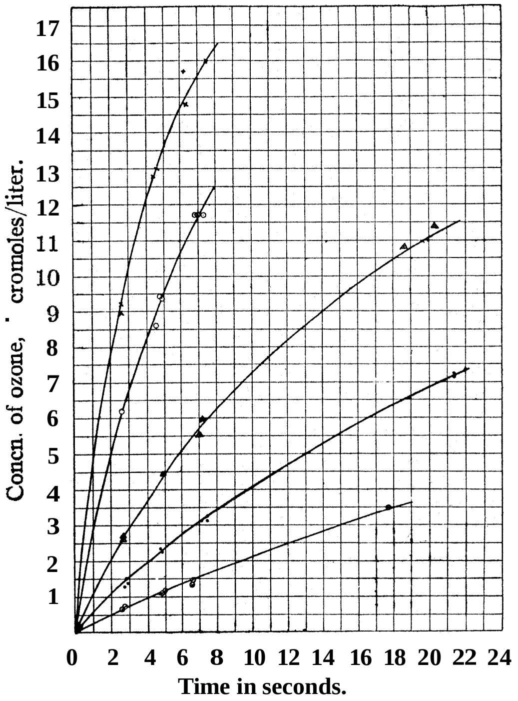
Fig. 6.

$$C_{O_3} \text{ (in micromoles per liter)} = \frac{\text{Cc. of ozone formed in } t \text{ minutes}}{\text{rate of flow in liters/hour}} \times \frac{60}{t} \times \frac{1}{22{,}400}$$

$$t \text{ in seconds} = \frac{3600 \times \text{volume of cell in liters}}{\text{rate of flow in liters/hour}}$$

where *t* is time of exposure.

Some of the results which have been obtained are presented graphically in Figs. 6, 7 and 8. One at once observes that the rate of increase of concentration with time is decreasing rapidly and that a steady state is soon reached. The concentration of ozone in the steady state is about 1 molecule of ozone to 1700 of oxygen. At first sight it did not appear probable that ozone at such a low concentration was being decomposed as fast as it was formed and an alternative explanation was advanced: an intermediate product is formed initially by the cathode rays and is able to break down in two ways—either reverting to oxygen or forming ozone. A study of the reaction between hydrogen and oxygen, however, gave definite evidence in support of the instability of ozone at this low concentration. This will be reported in a subsequent paper.



1520-cc. cell. 180 kv. X, 1.00 ma.; ○, 0.50 ma.; △, 0.20 ma.; ●, 0.10 ma.; ⊖, 0.05 ma.

Fig. 7.

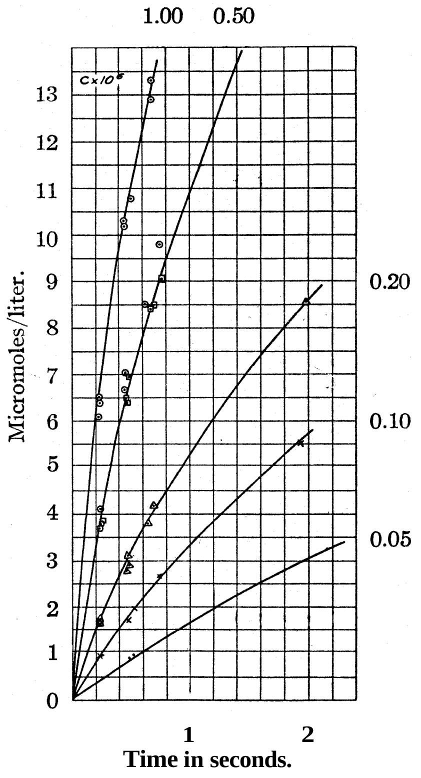


Fig. 8.—Volume, 162 cc.

Warburg[5] and Warburg and Leithauser[6] have studied the rate of formation of ozone in the silent discharge by both static and dynamic methods. In this case also the rate of formation of ozone falls off rapidly with in-

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[5] Warburg, Ann. *Physik,* [4] 9, 781 (1902).

[6] Warburg and Leithäuser, *ibid.,* [4] 28, 24 (1909).

creased time of exposure. Table II illustrates some of the results which they obtained with a glass ozonizer having electrodes 1.4 mm. apart and operating on 50 cycles with a current of 1.15 milliamperes. The pressure was 764 mm. and the temperature 19.5°.

TABLE III

PRODUCTION OF OZONE BY SILENT DISCHARGE

Concn. O_3, mml./liter	341	513	660	689	907	1176	1381	1514	1785
O_3, cc. at N.T.P. per ma./hr. obs.	204	202	195	193	186	175	172	168	159
O_3, cc. at N.T.P. per ma./hr. calcd.	207	202	197	196	189	180	173	168	159

The calculated yield of ozone at zero concentration was 218 cc. per milliampere hour and the concentration of ozone in the steady state which was obtained by a separate experiment in a static system was 3720 micromoles per liter. The striking part of these results as compared with those obtained with cathode rays is the much greater concentrations of ozone obtained. In this case one molecule in twelve is converted to ozone in the steady state, where with cathode rays the concentration was one in seventeen hundred. There is a very marked increase indeed in the stability of ozone in silent discharge as compared with the cathode ray stream.

They have discussed their results theoretically on the basis of an equation involving both formation and decomposition of ozone and have obtained good quantitative agreement with experiment. The amount of ozone formed in time dt is proportional to the current I and to the oxygen concentration. The amount of ozone decomposed is taken as proportional to the current and the ozone concentration

$$\frac{\mathrm{d}(n_{O_3})}{\mathrm{d}t} = I(k_1c_{O_2} - k_2c_{O_3})$$

where n_{O_3} is the number of molecules of ozone formed in time dt. If there is no ozone present the rate of formation is given by

$$\frac{\mathrm{d}(n_{O_3})}{\mathrm{d}t} = k_1Ic_{O_2}$$

and the amount of ozone formed per ampere hour is

$$A^0 = \frac{\mathrm{d}(n_{O_3})}{Idt} = k_1c'_{O_2}$$

where c'_{O_2} is the initial concentration of oxygen and $c'_{O_2} - c_{O_2} = 3/2c_{O_3}$.

$$\frac{\mathrm{d}(n_{O_3})}{Idt} = A_0 - k_1(c'_{O_2} - c_{O_2}) - k_2c_{O_3}$$

The concentration of ozone in the steady state is given by

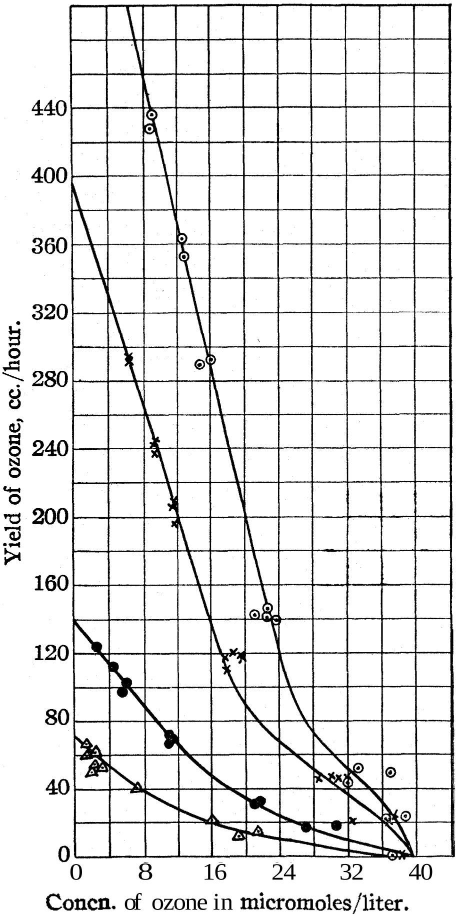
$$Ao = (3/2\,k_1 + k_2)c'_{O_3}$$

Hence the concentration in the steady state is independent within certain limits at least of the current. The current strength determines the velocity at which equilibrium is attained, but not the equilibrium concentration.

$$A = \frac{\mathrm{d}(n_{O_3})}{I\mathrm{d}t} = A_0 - k_1(c'_{O_2} - c_{O_2}) - k_2c_{O_3}$$
$$= A_0 1 - \left\{\frac{c_{O_3}}{A_0}(3/2\ k_1 + k_2)\right\}$$
$$= A_0\left(1 - \frac{c_{O_3}}{c'_{O_3}}\right)$$

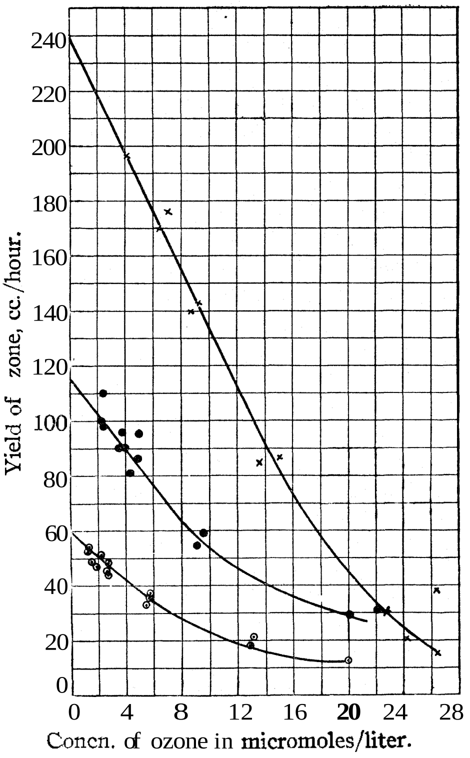
A_0 and A are the moles of ozone formed per ampere hour at $t = 0$ and $t = t$.

From this result, it is evident that the yield of ozone should be a linear function of the concentration of ozone in the gas. The results given in Table II and Figs. 6, 7 and 8 and also others obtained with 130 kv. applied to the tube have been treated in this way in Figs. 9–12. One notices at once that at the higher concentrations of ozone, which represent experimentally the slower rates of flow, the linear relationship breaks down and the yield approaches zero



180 kv., 1520 cc. volume. ⊙, 1.00 ma.; **X, 0.50 ma.; ●, 0.20 ma.**; △, 0.10 ma.

Fig. 9.



130 kv., 1520 cc. volume. X, 1.00 ma.; ●, 0.50 ma.; ⊙, 0.20 ma.

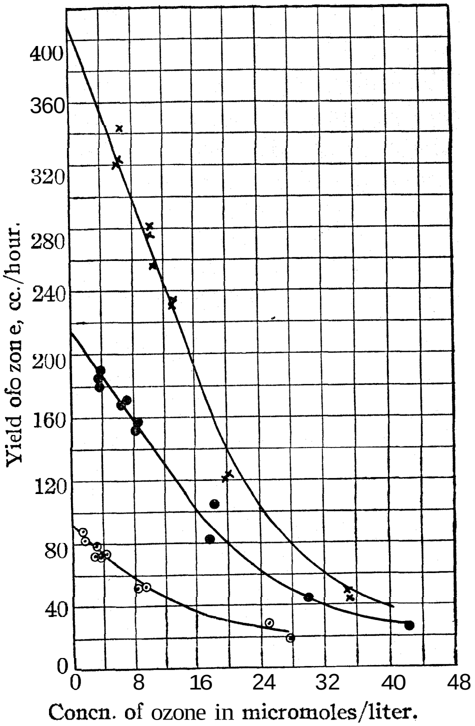
Fig. 10.

more slowly than predicted. This may be due in part to the fact that the values calculated for the concentration are much more inaccurate at the higher concentrations. These portions of the curve have not been treated theoretically since the variation in concentration of ozone throughout the cell is unknown and the radiation density is so far from uniform.

There are two methods available for determining the maximum yield of ozone for a given voltage and tube current. One can draw tangents to the curves in Figs. 5 and 8 at zero time. These give a measure of the actual rate of ozone production when none is present to be decomposed. The other method is to extrapolate the straight lines of Figs. 9–12 to zero concentration of ozone.

The results obtained by the use of these two methods with the data given in Fig. 7 are tabulated in Table IV.

The result for 0.50 milliampere is apparently too large; the discrepancy was not noticed at the time and it has not been possible to recheck this value. When one attempts to draw tangents to the curves at the origin one soon realizes that the results in Cols. 2 and 3 are well within the experimental error and that the extrapolation method is more likely to give a reliable result.



180 kv., 162 cc. volume. ×, 1.00 ma.; ●, 0.50 ma.; ⊙, 0.20 ma.

Fig. 11.

TABLE IV

MAXIMUM RATE OF OZONE FORMATION

Curr., milliampere	Yield from tangents in Fig. 7	Yield from extrapolation in Fig. 9	Yield per milliampere
1.00	746	640	640
0.50	422	382	764
.20	135	139	695
.10	73.5	70	700
.05	37	..	740

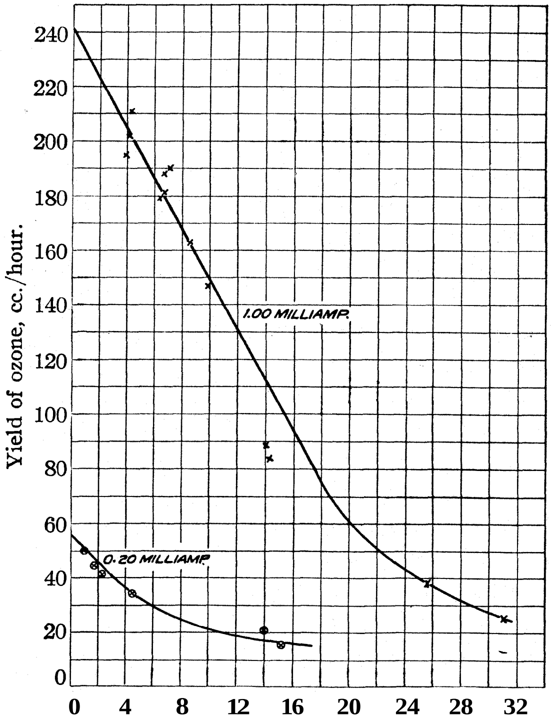
A similar set of results has been obtained with the data from the 163-cc. cell and these are given in Table V.

TABLE V

MAXIMUM RATE OF OZONE FORMATION

Current, milliampere	Yield from tangents in Fig. 8	Yield from extrapolation in Fig. 11	Yield per milliampere
1.00	392	407	407
0.50	202	215	430
.20	91	92	460
.10	49	49	490
.05	24	24	480

The rate of formation of ozone, expressed in micromoles per second, for various times of exposure has been plotted in Fig. 13 as a function of the tube current. For zero time the rate is a linear function of the tube current within the experimental error, but for all actual experiments it deviates from this ideal result due to secondary decomposition of ozone, the deviation being greater the longer the time of exposure and the greater the electron density.



Concn. of ozone in micromoles/liter.
130 kv., 162 *cc.* volume.
Fig. 12.

A series of experiments was carried out with a large spherical reaction vessel of twelve liters capacity in an attempt to find out what additional effect would be obtained by allowing the electrons to scatter laterally; it was also hoped to obtain more exact data on the concentration of ozone in the steady state. The results are given in Table VI; the voltage used was 180 kv. and the current 0.80 milliampere.

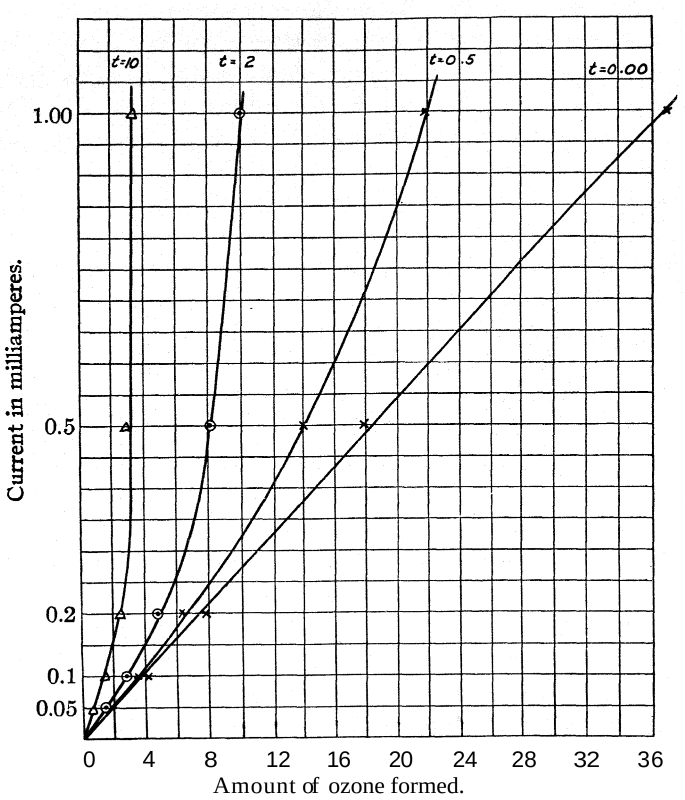


Fig. 13.—All calculated on the basis of one second.

TABLE VI

FORMATION OF OZONE WITH 12-LITER VESSEL

Rate of circulation	O_3 formed per hour, cc.	Time, sec.	Concn. of ozone, micromoles/-liter	$c \times 10^6$ (corr.)
2400	378	18	7.04	7.0
1350	293	32	9.7	9.4
660	183	65.5	12.4	11.7
300	128	144	19.0	16.8
75	69	580	41	26.4
Static	..	300	21.5	..
Static	..	600	26.4	..
Static	..	900	26.4	
Static	..	1800	26.4	

The calculated concentrations given in Col. 4 are too large, due to the experimental conditions. The oxygen in this case is passing through a vessel of 12 liters capacity. After the exposure the vessel is still filled with partially rayed oxygen, which, however, has been rayed during the period of the exposure; the amount of gas rayed is thus greater than that passing through the cell during the duration of the experiment. In the case where oxygen was circulating at 75 liters per hour one knows from the static experiments that the ozone concentration is 26.4×10^{-6} mole per liter and this enables one to calculate the actual concentration in all the experiments. When these results are plotted with the ozone yield as a function of its concentration and extrapolated to zero concentration, the maximum yield is found to be 660 cc. per hour for 0.8 milliampere or 825 cc. per hour per milliampere. This result is to be compared with the value of 640–700 cc. of ozone obtained with the cylindrical cell of 1520-cc. volume and 410490 cc. obtained with the 162-cc. cell. It appears that approximately half of the energy in the electron stream can be expended in a cell 26 mm. deep and 89 mm. in diameter as measured by its ability to produce ozone. Of course, there is considerable reflection of electrons from the walls of the cell, which helps to increase the yield, and the fraction might be much lower if the walls were completely transparent to electrons.

Experiments with an Applied Electric Field

In discussing the work of Krüger and Utesch, the main criticism was launched against their method of determining ionization. If their result is valid and there are as many as 40 molecules of ozone formed per ion, then the conclusions of Lind[7] on the mechanism of these reaction is incorrect. The ozonization of oxygen is a reaction which proceeds with a free energy increase and it would be impossible for one ion to initiate a chain of reactions producing many molecules of ozone. An attempt was made to see if it is possible to obtain saturation currents under somewhat similar experimental conditions to those used by Kriiger and Utesch. A copper plate with a slit 1 cm. wide by 5 cm. long was fastened over the window of the tube. This permitted about 20% of those electrons to enter the gas which would have entered in the absence of the shield. Two condenser plates 6 cm. X 8 cm. were placed in the reaction vessel so that they were symmetrically mounted with respect to the slit. The upper edges of the plates were 3 cm. distant from the window of the tube. They were placed either 2.4 cm. or 6.3 cm. apart.

A 10-kw., 60,000-volt DC outfit consisting of transformer, full wave rectifier and condensers was used as a source of voltage; the mid-point of the condenser bank was grounded so that the voltage drop between the window and each of the plates in the reaction vessel was the same.

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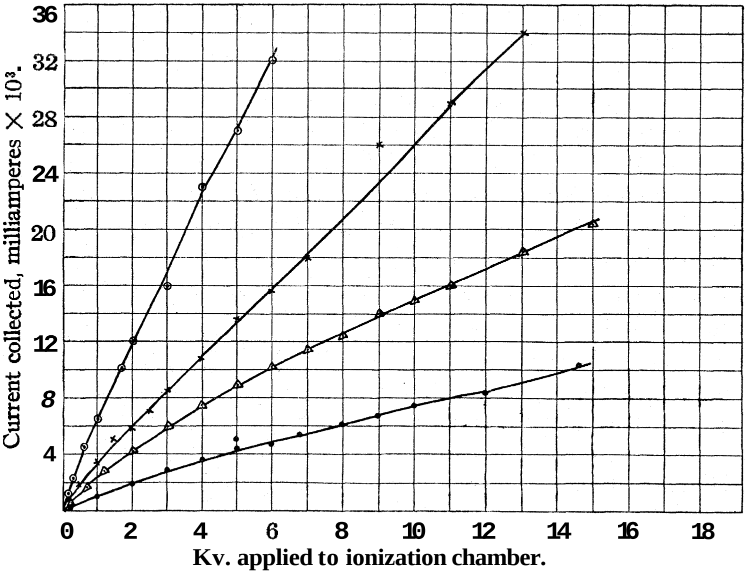
[7] Lind, "Chemical Effects of Alpha Particles," The Chemical Catalog Co., Inc., New York, 1928.

Experiments were first made with and without the field applied, circulating oxygen through the cell and determining the amount of ozone formed. With 180 kv. and 0.50 milliampere, two experiments without applied field gave 46.5 and 55.5 cc. of ozone formed per hour. With the plates 5 cm. apart, 16 kv. applied and a current of 1.3 milliamperes flowing in the ionization chamber, 69 cc. of ozone was formed. With the plates 2 cm. apart, 16 kv. applied and 2.6 milliamperes flowing, 205 cc. of ozone was formed.

A second set of experiments was made with much lower power. The tube was operated at 106 kv. with a current of 0.10 milliampere. A blank experiment without applied field gave 1.6 cc. of ozone formed per hour. With the electrodes 2 cm. apart and 16 kv. applied, a current of 0.11–0.14 milliampere was collected and 3.4 cc. of ozone was formed. The electrodes were than placed 5 cm. apart, 24.5 kv. applied, the same current collected and the same yield obtained. When a voltage gradient as high as 8 kv. per cm. is applied, it is evident that a considerable increase in ionization is obtained, as measured by ozone production; about 3000 volts per cm. is the highest which can be used without causing an increase in the ozone yield. In terms of saturation current phenomena, 3000 volts per cm. should produce saturation and higher voltage should cause increased ionization due to the kinetic energy of the ions becoming sufficient to ionize the gas molecules by impact.

Kriiger and Utesch estimated that the maximum current which they had entering their reaction chamber was 2×10^{-6} ampere. The yields of ozone reported in their experiments where ionization was studied varied from 0.3 to 66 cc. of ozone per hour. These are of the same magnitude as those reported above. In Fig. 14 the currents collected in the ionization chamber are plotted as a function of the applied voltage. There is no indication whatever of a saturation current; the curves in some cases were continued up to 40 kv. and were perfectly continuous. In one case with 0.010 milliampere, the yield of ozone would have been of the order of 0.10–0.20 cc. per hour. With 83 kv. applied to the tube, the current collected at 15 kv. was less than 0.0001 milliampere; at 90 kv. applied to the cathode ray tube, it amounted to 0.0013 milliampere, but here also there was no indication of saturation being attained.

The experiments reported above differ, however, in one respect from those of Kriiger and Utesch; they used 500-cycle power to operate their cathode ray tube while 60-cycle power was used in this investigation. It is difficult to see how this could affect the current collected in the ionization chamber. The average velocities of the electrons were approximately the same in the two cases. In order to be certain that the absence of a saturation current was not due to some ionization being produced outside the region of the applied field from which an increasing number of ions was drawn as the field increased, the ionization chamber was re-designed. The copper plate over the window of the tube was covered with mica, the condenser plates were moved up in the cell until their upper edges touched this mica and they were enclosed in a mica box. In this way all the ionization occurred in the space between the plates. Within the experimental error, the results were the same as those already described. These results render the values for the ratio of molecules produced to ions collected, as reported by Krüger and Utesch, very doubtful and the real value for this quantity will remain an open question until a more reliable method is devised for measuring the rate of ion production at high intensities of ionization.



Tube current—with plates 2.4 cm. apart: ⊙, 0.10 ma.; X, 0.03 ma.; △, 0.01 ma.—with plates 6.3 cm. apart: ●, 0.01 ma.

Fig. 14.

Summary

A cathode ray tube installation has been described which can be conveniently used for studying the effects of high velocity electrons on pure and mixed gases.

The tube can be operated continuously with a current of 0.0010 ampere and 200 kv.

A detailed study has been made of the ozonization of oxygen. The reaction has been shown to occur wholly in the gas phase and to be uninfluenced by the nature of the walls of the containing vessel.

Fifty per cent. of the reaction takes place in a volume within 2 cm. of the tube window, although the cathode rays have a range of 20 cm. under these conditions. This corresponds to the roughly exponential manner in which the energy of the beam falls off as one proceeds away from the window of the tube.

Ozone is both formed and decomposed under the influence of cathode rays. With continued raying a steady state is reached with an ozone concentration of 1 molecule to 1700 of oxygen. This concentration is independent of the tube current. This value compares with the concentration of 1 in 12 obtained with the silent discharge. Cathode rays have a much greater decomposing action than the silent discharge.

The maximum yield of ozone is 825 cc. of gas, measured under standard conditions and obtained with a tube current of 0.0010 ampere at 180 kv.

It has not been possible to check the results of Krüger and Utesch, who determined the amount of ionization by a saturation current method. Saturation was never observed in any of the experiments—the current in the ionization chamber increasing regularly as the applied field increased.

SCHENECTADY, NEW YORK

[CONTRIBUTION FROM THE RESEARCH LABORATORY, GENERAL ELECTRIC COMPANY]

COMBINATION OF HYDROGEN AND OXYGEN UNDER THE INFLUENCE OF CATHODE RAYS

BY ABRAHAM LINCOLN MARSHALL

RECEIVED JUNE 23, 1928 PUBLISHED DECEMBER 10, 1928

The reaction between hydrogen and oxygen presented itself as the simplest oxidation reaction occurring in the gas phase which could be investigated. Hinshelwood and Thompson[1] have shown that it is possible to study a homogeneous thermal reaction between these substances in the range 550–600° with velocities increasing in rate up to explosions. It is well known that when flames of hydrogen and oxygen impinge on a cold surface hydrogen peroxide can be detected as one of the products of reaction. Marshall[2] has found that in the case of the photochemical reaction sensitized by mercury vapor the reaction proceeds by way of the peroxide stage and that this product can be obtained in the pure state. Scheuer[3] has studied the combination of hydrogen and oxygen (electrolytic gas) under the influence of α-particles and in all cases reported hydrogen peroxide as one of the products of the reaction, amounting in one case to 16% of the combined hydrogen.

In a previous paper[4] on the ozonization of oxygen the cathode ray tube

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[1] Hinshelwood and Thompson, Proc. Roy. *Soc.*, 118, 170 (1928).

[2] Marshall, *J. Phys. Chem.*, 30, 1078 (1926).

[3] Scheuer, *Compt. rend.*, 159, 423 (1914).

[4] Marshall. THIS JOURNAL, 49, 2763 (1927).

installation and general technique for high voltage work was described. One point, however, which is important for the technical success of this investigation was not mentioned, namely, the temperature of the window during the operation. Coolidge[6] reports a few measurements on window temperature during operation; with 200 kv. and 0.6 milliampere, the window reached 132° in five seconds, and with 1.3 milliamperes it reached 340° in ten seconds. Mixtures of hydrogen and oxygen explode when heated to about 600° so that one is strictly limited as to the amount of energy one can use for successful operation by the temperature of the window. If the filament does not give a uniform distribution of energy over the focal area, it is quite possible for a very small area to be receiving considerably more than its quota of electrons and to form a hot spot on the window. During the early part of the investigation, the tube was operated at 180 kv. and 1 milliampere, and on several occasions, due to a slight increase in current, disastrous explosions occurred. The system was finally operated at 180 kv. and 0.80 milliampere and was stabilized by means of a very sensitive relay connected in the grounded side of the high voltage line. This relay opened the remote control in the power line supplying the transformers when the tube current rose to 0.90–1.00 milliampere. During several months' work it functioned on a number of occasions and no further troubles were experienced from this source.

The reacting gases were taken from the high pressure supply lines of electrolytic hydrogen and oxygen available in the Laboratory and were used without further purification. It was possible to obtain rates of flow up to 1500 liters per hour of each gas. They were circulated through a cylindrical glass cell 3½″ in diameter by 10″ long. In all the experiments the pressure was kept at 91 cm. of mercury. The effluent gases were analyzed for hydrogen peroxide, water vapor and ozone. In order to make this analysis, it was necessary to dry the gases as completely as possible before use. It was found that the use of liquid-air traps for this purpose was entirely ineffective; the moisture was frozen out in the trap in the form of snow which would then be blown out of the trap, due to the high rate of gas passage. The most effective drying agent was found to be concentrated sulfuric acid. Two large gas scrubbing bottles of the type used in the previous investigation for absorbing ozone were connected in series and filled with sulfuric acid. The first scrubber did practically all of the work even at the fastest rates of flow, the purpose of the second being to remove that water vapor which the first could not absorb, due to an increase in its aqueous tension brought about by dilution and heating. It was found after some time that a slight mist of sulfuric acid was being carried over from the scrubbers, which deposited on the walls of the reaction chamber and gave rise to erratic analytical results by absorbing

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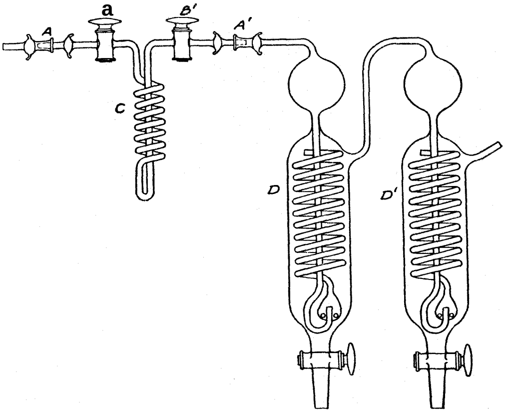
[5] Coolidge, *J. Franklin Inst.,* **December, 1926.**

some of the peroxide and water vapor formed in the reaction chamber. A long column of powdered potassium hydroxide was then introduced into the system and a plug of absorbent cotton, which was dehydrated by warming gently and passing a current of dry gas. Separate drying trains were used in each gas line. With this system it was possible to pass gas at 1500 liters per hour and collect less than 1 mg. of material in a liquid-air trap in the exit line over a fifteen minute period. This amount was within the experimental error of the analytical method used.

Method of Analysis

The gas mixture from the reaction vessel was led through a glass coil, C, in Fig. **1,** which was immersed in a carbon &oxide–ether mush to freeze out the hydrogen peroxide and water vapor formed during the reaction. The gas, before it entered the gas scrubbers D and D', was then passed through another spiral, not shown in the figure, which was immersed in warm water. D contained distilled water to absorb any peroxide not caught in C, and D′ alkaline potassium iodide to absorb ozone. The coil C was connected to the rest of the apparatus by means of two ground-glass joints, **A** and **A'.** After an experiment, the trap was disconnected at A and A' and while still in the cooling mixture, dry air was passed slowly through it to remove the hydrogen and oxygen. The stopcocks B and B' were then closed, the male parts of the ground joints carefully wiped free from grease and the coil warmed up to room temperature and dried in a blast of compressed air. The coil was then carefully wiped with a linen cloth and weighed. The coil weighed about **180 g.** and was balanced to the nearest milligram. During a series of experiments, the weight of the coil might drift **10–15** mg. but it was always found possible to check its weight to within one milligram when it was merely chilled, allowed to warm up and dried. It was absolutely necessary to displace the hydrogen and oxygen before weighing and to make sure that the coil was properly chilled before closing the stopcocks.



Pig. 1.

TABLE I

PROOF THAT RATIO H_2O_2/H_2O IS UNCHANGED BY PASSAGE THROUGH TRAP

Rate of circulation, **1400** liters/hour of H_2; **240** liters/hour of O_2

Coil 1		Coil 2			
Weight incr., g.	KMnO₄, cc.	**Weight incr., g.**	KMnO₄, cc.	**Ratio weight**	**Ratio titer**
0.089	27.6	0.011	1.3	8.1	21.2
.033	24.8	.002	2.0	16.5	12.4
Rate of circulation, **450** liters/hour of H_2; 60 liters/hour of O_2					
0.069	14.7	0.026	6.8	2.65	2.16
.034	14.3	.018	7.5	1.89	1.91
.030	13.9	.016	7.4	1.87	1.88

After weighing, the coil was washed out and the peroxide collected titrated with standard permanganate solution; any peroxide collected in D was then added and the total titer obtained. It was found that practically all of the material collected in Coil C was caught in the first two turns; however, some of this was blown through the coil in the form of snow and this was collected in D. From a knowledge of the two titers and the weight of material caught in C, it was possible to calculate the total amount of peroxide and water vapor formed. The physical properties of these two substances are almost identical and thus the ratio of peroxide to water in the coil was the same as that in the scrubber. To be certain of this point, a few experiments were made using a second coil; it was shown that the ratio of materials in Coil 2 was the same as in Coil 1. These results are tabulated in Table I.

The second experiment and the last two are the most reliable and in these it is easy to see that the ratios are the same within experimental error, which proves the desired point as only a small fraction of the material caught in the trap is peroxide.

Having obtained a reliable method of analysis, a study was next made of the effect of adding a small amount of water vapor on the yield of hydrogen peroxide. The results justify the conclusion that peroxide formation does not proceed *via* water vapor. Hydrogen, from an electrolytic generator producing 12.5 liters per hour, was passed through a water saturator at 22° and then led into the dry gas stream on its way to the reaction vessel. The gases were streaming at the rate of 1400 liters per hour of hydrogen and 240 liters per hour of oxygen. In blank experiments about 0.045 g. of water was collected in the coil in 15 minutes; with the tube operating the total material collected averaged 0.081 g., whereas without the water added 0.033 g. were collected. This latter consisted of approximately 85% hydrogen peroxide, so that the addition of the saturator has increased the water vapor concentration about ten-fold. The average of 6 experiments without water addition gave 41.2 cc. of hydrogen peroxide formed in fifteen minutes and the same amount was formed in the presence of the added water vapor.

Several series of experiments were performed using approximately the same concentrations of hydrogen and oxygen throughout the series but varying the rate of circulation. The results given in Table II are taken from the earlier part of the work and are not so reliable as those in Table III, which, however, are for a different concentration.

TABLE II

VARIATION IN REACTION PRODUCTS WITH RATE OF FLOW

Rate of circulation, liters per hour		Product formed in one hour, cc.			
H_2	O_2	H_2O_2	H_2O	O_3	$H_2O_2 + H_2O$
1400	240	116.8	166.0	13.6	282.8
800	120	100.8	188.8	11.2	289.6
1400	240	115.2	164.4	..	279.6
450	60	83.2	218.8	8.0	302.0
800	120	97.2	211.2	..	308.4
1400	240	114.0	167.6	..	281.6

Each set of values is the average of 4 or 5 experiments and while the peroxide determinations are easily reproducible, those for the water vapor in some cases show considerable divergences, typical sets of data being 44.7, 46.2, 37.0, 36.6 and 55.2, 46.0, 41.4, 46.2. This, however, is to be expected, since all the errors of the analysis are placed on the water vapor value, which is obtained by a difference method.

The second half of Table III gives a résumé of all the data obtained for a single set of conditions and is typical of all the results to be reported in this paper.

TABLE III

VARIATION IN REACTION PRODUCTS WITH RATE OF FLOW

Rate of circulation, liters per hour		Product formed in one hour, cc.			
H_2	O_2	H_2O_2	H_2O	O_3	$H_2O_2 + H_2O$
1450	1280	214.0	293.6	108.4	507.6
865	780	198.4	304.4	103.2	502.8
345	300	153.6	353.6	70.0	507.2
865	780	214.0	313.2	122.0	
		212.0	360.0	122.4	
		187.6	306.8	91.6	
		192.0	272.8	92.0	
		174.6	302.4	71.2	
		206.4	316.8	121.6	
		193.1	254.8	92.4	
		193.9	284.2	96.0	
		212.2	327.8	118.8	

It will be noted that the yield of peroxide for a given concentration of hydrogen and oxygen decreases as the rate of flow is decreased. There is a roughly linear relation between the concentration decreases and the water vapor increases, the sum of the two remaining constant. This means that at the lower rates of flow where the concentration of the products is higher, some of the peroxide is decomposed forming water vapor. The total amount of reaction for a given energy input is constant and hence the sum of the peroxide plus water vapor formed is independent of the rate of flow. This is the best proof available that both peroxide and ozone are decomposed as well as formed by high velocity electrons. The amount of water vapor primarily formed by the radiation is constant, independent of the rate of circulation, and the observed increases at lower rates of flow are due to secondary decomposition of hydrogen peroxide.

Influence of Changing Concentrations

Another very interesting study in an investigation of this kind is the kinetics of the reaction. Five different concentrations were used and the gases were circulated at the fastest rate available in an attempt to avoid as much decomposition of hydrogen peroxide as possible. About twenty experiments were made at each concentration and the extreme values of the peroxide and ozone determinations did not vary more than (±)5% from the mean and, in most cases, agreed much closer than this; in the case of the water vapor determinations, the extremes were (±)18% in a few cases with most of the values coming within better than 10% of the mean. The results are given in Table IV.

TABLE IV

VARIATION IN REACTION PRODUCTS WITH CONCENTRATION

Rate of flow, liters per hour		Product formed in one hour, cc.			
H_2	O_2	H_2O_2	H_2O	O_3	$H_2O_2 + H_2O$
1450	300	173	128	24	301
865	1500	167	428	152	595
1450	780	199	211	68	410
345	2000	99	528	256	627
1450	1280	197	269	105	466

These results can be compared with those obtained by Lind[6] raying similar mixtures in a static system with α-particles. Lind gives values for

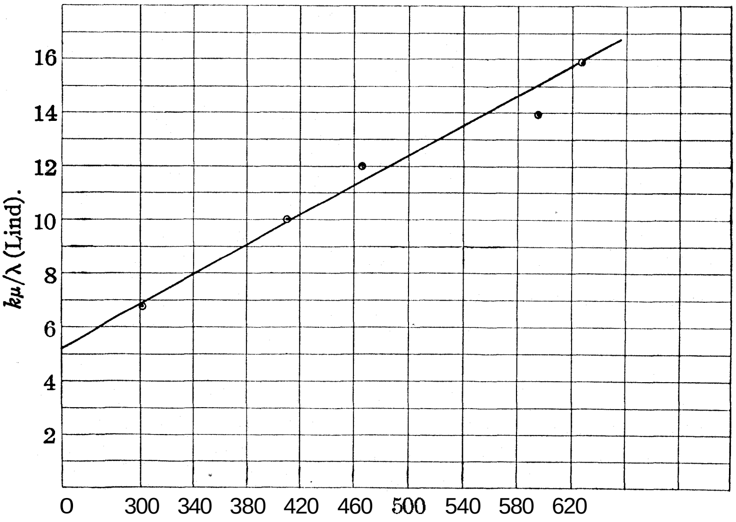


Fig. 2.

$k\mu/\lambda$, the velocity constant obtained with α-particles, for a number of concentrations of hydrogen and oxygen. These velocity constants are all reduced to values for a cell of given volume and plotted as a function of the concentration. This reduction is possible since Lind has shown that the velocity constant varies inversely as the square of the diameter of the sphere in which the reaction is proceeding. From the smoothed curve of

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[6] Lind, THIS JOURNAL, **41**, 543 (1919).

the reaction velocity–concentration diagram, values are read off corresponding to the concentrations used in this investigation. In Lind's experiments in a static system, the final product would be water vapor with only traces of peroxide and ozone; hence the sum of the peroxide and water vapor formed in a given time in the cathode ray experiments should be proportional to Lind's reaction velocity constant if the mechanism in the two cases is similar. The comparison is given in Fig. 2 and it is seen that any discrepancies lie well within the limits of experimental error in the two investigations.

The rate of peroxide formation is very insensitive to changes in concentration; at 15% hydrogen it has dropped to half the maximum value and at 83% hydrogen it has decreased 13% from the maximum. The rates of formation of water vapor and ozone seem to parallel one another very closely as evidenced by Fig. 3, which shows that over the range investigated the relationship is almost linear. We know that with pure oxygen the curve must return to zero amount of water vapor formed, so that it is possible to guess the result in the concentration region not investigated. This seems to indicate that the mechanisms responsible for water vapor and ozone formation are closely connected and quite different from that which produces hydrogen peroxide.

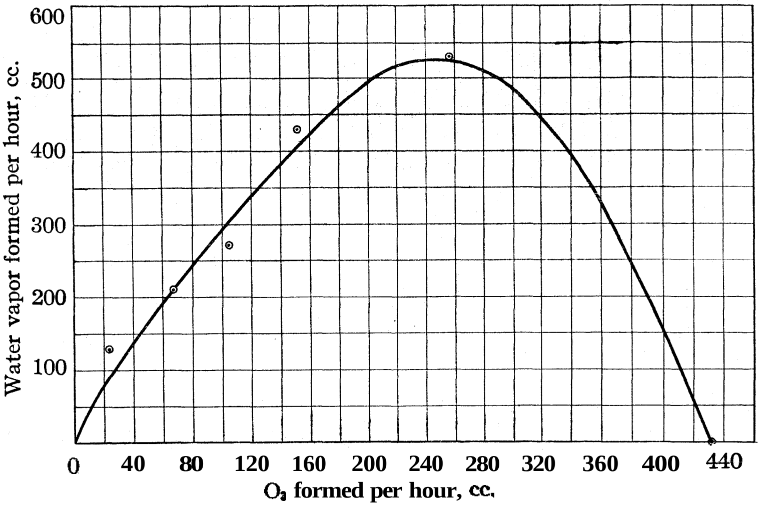


Fig. 3.

Summary

A method has been developed for analyzing gas mixtures containing small quantities of hydrogen peroxide, water vapor and ozone.

In the reaction between hydrogen and oxygen under the influence of cathode rays, it has been shown that peroxide, water vapor and ozone are formed as primary products.

A kinetic study at varying concentrations of hydrogen and oxygen shows that the rate of peroxide formation is almost independent of concentration, whereas the rate of water vapor formation varies over a five-fold range, and ozone over a ten-fold range.

The rates of formation of ozone and water vapor parallel one another very closely at all the concentrations studied, suggesting that the same primary mechanism is responsible for the formation of both.

The gross rate of reaction parallels that observed by Lind for the same reaction under the influence of a-particles.

SCHENECTADY, NEW YORK

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

THE CATALYTIC DECOMPOSITION OF HYDROGEN PEROXIDE IN AN ACID CHLORINE–CHLORIDE SOLUTION. II. AN INTERPRETATION OF THE RATE MEASUREMENTS IN CONCENTRATED SOLUTION

BY ROBERT LIVINGSTON

RECEIVED JUNE 29, 1928 PUBLISHED DECEMBER 10, 1928

The velocity of decomposition of hydrogen peroxide in an acid chlorine–chloride solution can be represented, with approximate accuracy, by the following equation[1]

$$v = \chi(H_2O_2)(H^+)(Cl^-)f^2_{HCl} \qquad (1)$$

where χ is a constant (0.00010) and f_{HCl} is the activity coefficient of hydrochloric acid. In dilute solutions the equation apparently represents the experimental data within the limits of error; in more concentrated solutions the value of χ decreases systematically to a value of 0.00005 at an ionic strength of 5μ. Equation 1 may be considered as a simplified form of the general reaction velocity equation, presented by J. N. Brönsted.[2] The exact form of the Bronsted equation for this reaction is

$$v = K\,H_2O_2(H^+)(Cl^-)f^2_{HCl} \cdot f_{H_2O_2}/f_x \qquad (2)$$

where f_x is the activity coefficient of the "reaction complex," ($H_2O_2 \cdot HCl$). If we assume that $f_{H_2O_2}/f_x$, the ratio of the activity coefficients of two neutral molecules, is equal to unity, Equation 2 reduces to the form of Equation 1.

It has been demonstrated, both on theoretical[3] and on experimental[4]

[1] Livingston and Bray, THIS JOURNAL, 47,2069 (1925); 48,405 (1926).

[2] (a) Bronsted, *Z. physik. Chem.*, 102, 169 (1922); (b) "The Velocity of Ionic Reactions," Columbia Press, 1927.

[3] Debye and McAuley, *Physik. Z.*, 26, 22 (1925).

[4] A review of existing data has been recently presented by Randall and Failey, *Chem. Reviews*, 4,271,285 (1927). This summary demonstrates that the formula holds

grounds, that the variation of the activity coefficient of a non-electrolyte in an aqueous salt solution may be represented by an equation of the following form

$$\log f_0/\mu = k \tag{3}$$

where f_0 is the activity coefficient of the non-electrolyte and k is a constant the value of which depends upon the properties of the salt and the non-electrolyte present.

Since both hydrogen peroxide and the reaction complex are neutral molecules, we may write

$$\log (f_{H_2O_2}/f_x) = \mu(k_{H_2O_2} - k_x) = \mu k' \tag{3a}$$

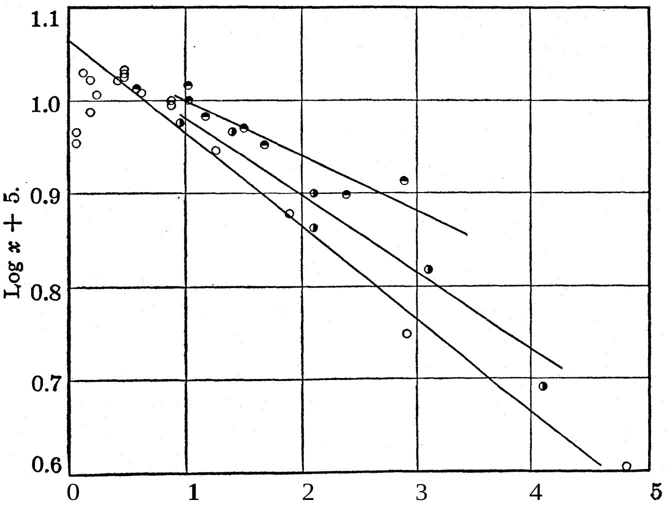
Substituting this relation in Equation 2, we obtain

$$v = K(H_2O_2)(H^+)(Cl^-)f^2_{HCl} \cdot 10^{\mu k'} \tag{4}$$

or

$$\log K = \log \chi - \mu k' \tag{4a}$$

We may test this relation by plotting log χ against μ. Such a plot is given in Fig. 1. The data are taken from Table I of reference 1. The points, representing experiments performed in hydrochloric acid solutions, fall on a straight line within the limits of experimental error. The experi-



Ionic strength.

○, HCl; ◑, HCl + NaCl; ◓, HCl + HClO$_4$.

Fig. 1.—The velocity of decomposition of hydrogen peroxide in an acid chlorine–chloride solution.

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with reasonable accuracy for all of the non-electrolytes investigated, even at high ionic strengths. Linderström-Lang, *Compt. rend. trav. lab. Carlsberg*, **15**, No. 4 (1924), measured the solubilities of quinone, hydroquinone, succinic acid and boric acid in the presence of varying concentrations of a number of different salts, and found that the ratio of the logarithm of the activity coefficient of the non-electrolyte to the equivalent concentration of the salt was practically constant.

ments at the lowest concentrations show a negative departure of 10 to 20%; however, this is probably due to experimental error, since the absolute values of these rates are very small.[5] The experiments performed in mixtures of hydrochloric acid and perchloric acid or sodium chloride may be also represented by straight lines the slopes of which differ from that determined by the experiments in hydrochloric acid. At the higher concentrations these mixtures may be regarded as practically pure solutions of perchloric acid or of sodium chloride, and therefore we should expect the straight line relation to hold. Unfortunately the experiments were not planned to illustrate this effect and several of the experiments at low ionic strength were performed in mixtures containing relatively large amounts of hydrochloric acid. The values of the ionic strength given are based upon concentrations expressed in moles per liter rather than in molality.[6]

An additional test of Equation 4 may be made by combining the rate measurements (that is, values of χ) with experimentally determined values of $f_{H_2O_2}$. If the reaction complex has properties similar to those of a stable neutral molecule, we may expect that

$$\log f_x = \log (K/\chi) f_{H_2O_2} = \mu k_x \qquad (5)$$

The Activity of Hydrogen Peroxide in Sodium Chloride and Sodium Sulfate Solutions[7]

The activity of hydrogen peroxide in aqueous salt solutions can be readily determined by "partition" experments with a suitable immiscible solvent. A variety of organic solvents have been investigated;[8] of these iso-amyl alcohol is probably best adapted to the purpose.[9]

The following *experimental procedure* was adopted. The aqueous peroxide solution, containing a known amount of salt (weighed out as anhydrous material), was made up in a glass-stoppered cylinder and placed in a 25° thermostat to attain thermal equilibrium. After an hour or more a definite amount of iso-amyl alcohol (also at 25°) was added to the aqueous solution. The cylinder was then shaken vigorously until the two phases formed a fine emulsion and then returned to the thermostat and allowed to remain for two hours. At the end of this time the two phases had separated into clear, apparently homogeneous layers and samples were withdrawn for analysis.[10]

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[5] See pp. 2072–2073, ref. 1.

[6] Compare footnote 4.

[7] These experiments were performed at the University of California in 1925.

[8] See Walter and Lewis, THIS JOURNAL, **38,** 633 (1916).

[9] (a) H. Calvert, *Z. physik.* Chem., **38,** 512 (1901); **(b)** A. Joyner, Z. *anorg. Chem*, **77,** 103 (1912).

[10] The experiments of Joyner (ref. 9b) indicate that the partition equilibrium is attained very rapidly.

Materials.—The salts were purified by repeated crystallization of the "C. P." materials. The stock hydrogen peroxide solution was made by diluting "perhydrol." The iso-amyl alcohol was purified by twice distilling "C. P." material in an all-glass still, discarding the first and last fractions.

In the presence of *iso*-amyl alcohol, hydrogen peroxide cannot be titrated with permanganate solution.[9a] After a number of preliminary experiments, the following analytical procedure was adopted. To determine the aqueous solution: add the sample (2 cc.) to *a* glass-stoppered flask containing 50 cc. of distilled water, 1 cc. of concentrated sulfuric acid and 4 g. of potassium iodide, allow to stand for thirty minutes and titrate the resulting iodine with thiosulfate to a starch end-point. To determine the alcohol solution: add the sample (10 cc.) to a glass-stoppered flask containing 200 cc. of distilled water, 4 cc. of concentrated sulfuric acid and 4 g. of potassium iodide, allow to stand for thirty minutes and titrate with thiosulfate, shaking frequently, until the yellow color disappears from the floating droplets of alcohol.[11] These methods give results reproducible within 0.5%. The method for the aqueous solution was shown to give results identical with those obtained by direct titration with permanganate in the absence of the alcohol.

Samples of the alcohol (upper) layer were withdrawn and measured with an ordinary pipet. Samples of the aqueous layer were obtained by introducing a sealed glass tube into the solution, breaking the thin glass seal[12] against the bottom of the vessel and forcing a sample of the lower layer out by air pressure.

Results and Calculations.—The experiments of Joyner[9b] at 0° and of Calvert[9a] at 25° demonstrate that the activity of hydrogen peroxide in aqueous solution is practically independent of its concentration for concentrations between 0.10 and 2.0 M. In light of these results, all of our experiments were performed with hydrogen peroxide solutions of about 1.5 M. The results of the partition experiments are summarized in Table I. The concentration of the added salt, in moles per liter, is given in the second column; the mean value of the distribution constant, D, in the third; and the number of separate experiments, upon which the mean value was based, in the fourth column.

TABLE I

THE ACTIVITY OR HYDROGEN PEROXIDE IN AQUEOUS SALT SOLUTIONS AT 25°

No.	Added salt	$D = m_{\text{aq.}}/m_{\text{alc.}}$	No. of expts.	$f_{H_2O_2}$	$-\log f_{H_2O_2}/\mu$
1[9a]	None	7.03 ± 0.05	8	1.00	
2	None	6.87 ± 0.07	11		
3	0.25 m, NaCl	7.21 ± 0.01	2	0.96	0.064
4	0.50 m, NaCl	7.33 ± 0.05	4	.95	.045
5	1.00 m, NaCl	7.52 ± 0.07	4	.92	.034
6	2.00 m, NaCl	8.16 ± 0.01	2	.85	.035
7	4.00 m, NaCl	9.21 ± 0.04	2	.76	.031
8	0.25 m, Na_2SO_4	7.62 ± 0.04	2	.91	.054
9	0.50 m, Na_2SO_4	7.96 ± 0.05	2	.87	.039
10	1.00 m, Na_2SO_4	8.65 ± 0.10	3	.80	.032

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[11] As was pointed out by Calvert (ref. 9a), it is impossible to obtain a starch iodine color in the presence of the alcohol phase. He overcame this difficulty by adding sufficient water at 55" to render the titration mixture homogeneous.

[12] Compare Abbott and Bray, THIS JOURNAL, 31, 738 (1909).

The values of $f_{H_2O_2}$ listed in the fifth column are based upon the assumption that the value for pure aqueous solution is unity.[13] In these computations we have used a value of 6.95 for the distribution coefficient between alcohol and pure water; this is an average of the value presented here (6.87) and that given by Calvert (7.03).

We would predict from Equation 3 that $\log f_{H_2O_2}/\mu$,[14] given in the last column, should have a constant value. While the observed trend may be real,[15] it is also possible that it is due to an error in the average value chosen for the distribution coefficient with pure aqueous solutions. The trend could be eliminated by choosing a value 2% higher.

The Measured Velocity and the Activity of Hydrogen Peroxide.—By combining values of $f_{H_2O_2}$ with velocity measurements which were performed in sodium chloride solution, we may test the validity of Equation 5. The results of such a comparison are summarized in Table II. The first five columns are taken from Table I, ref. 1. The values of $f_{H_2O_2}$, Col. 6, were interpolated from Table I. In computing k_x, Col. 7, K was obtained by extrapolating χ to infinite dilution (Fig. 1) and has a value of 11.7×10^{-9}

TABLE II

INTERPRETATION OF THE REACTION VELOCITY IN SODIUM CHLORIDE SOLUTIONS

No.	(HCl)	(NaCl)	μ	$\chi \times 10^5$	$f_{H_2O_2}$	$\frac{\chi}{f_{H_2O_2}} \times 10^5$	k_x	a_{H_2O}	$K'_a \times 10^5$
1	0.444	0.50	0.94	9 5	0.92	10.3	0.059	0.97	11.3
2	.444	1.00	1.44	9.3	.89	10.5	.033	.95	12.2
3	.098	2.00	2.10	7.3	.85	8.6	.064	.93	10.7
4	.222	1.89	2.11	8.0	.85	9.4	.045	.93	11.7
5	.098	3.00	3.10	6.6	.80	8.25	.049	.89	11.7
6	.098	4.00	4.10	4.9	.75	6.55	.062	.85	10.8

While there is considerable erratic variation in the values of k_x, there is no apparent trend. This may be considered as definite evidence in support of Equation 5. It follows from this that when due allowance is made for the variation of the activity coefficients of the neutral molecules involved, the rate of decomposition of hydrogen peroxide in acid chlorine-chloride solutions at ionic strengths between 0.1 and 4.0 is accurately represented by the Bronsted formula, and that it is unnecessary in this case to make allowance for any change in the nature of the solvent.[16] It is interesting to note that k_x has a value typical of normal non-electro-

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[13] For a discussion of factors, presumably negligible in this case, which can affect the accuracy of activity determinations based upon distribution measurements, see Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Company, Inc., New York, 1923, p. 262.

[14] Here, as in the rate measurements, the values of the ionic strength are based upon concentrations expressed in moles per liter rather than in moles per 1000 g. of water.

[15] Compare the data recorded by Randall and Failey, ref. 4.

[16] See Bronsted, *Z. physik. Chem.*, 115, 359–363 (1925).

lytes[3] and unlike $k_{H_2O_2}$ is positive in sign; that is, the fugacity of the complex is increased by the addition of salts.

It is also possible to interpret these data in terms of the "activity rate" theory.[17] According to this theory the reaction velocity is proportional to the product of the activities of the components, and the velocity equation is

$$v = K_a a_{H_2O_2} a_{H^+} a_{Cl^-} \qquad (6)$$

However, the data of Col. 7, Table II, demonstrate that K_a $(= \chi / f_{H_2O_2})$ is not a constant. It was suggested by G. N. Lewis[18] that the departure from constancy of K_a might be due to the solvent entering directly into the reaction. As is demonstrated by the data in the last column of Table II, we may obtain an empirical fit if we introduce[19] $a^3_{H_2O}$ into Equation 6. This corresponds to the assumption that three molecules of water take part in the reaction.[20] It is, unfortunately, not possible to determine $a_{H_2O_2}$ in the presence of hydrochloric acid by the distribution method used, both because of the decomposition of hydrogen peroxide in hydrochloric acid and because of the solubility of the acid in *iso*-amyl alcohol. In order to give K' a constant value of about 11.7×10^{-5} for the measurements in concentrated hydrochloric acid, we must assume that hydrochloric acid and sodium chloride have about the same effect on the activity of hydrogen peroxide. However, if this is done, the experiments in dilute solution exhibit a departure which is apparently too great to be attributed entirely to experimental error. Therefore, in spite of the constancy of K' for the measurements in sodium chloride solutions, it seems improbable that the modified form of the "activity rate" theory represents the facts.

A Discussion of Two Analogous Reactions.—The velocity of the decomposition of hydrogen peroxide in a bromine–bromide solution[21] and the velocity of rearrangement of chloro-acetylaminobenzene in an acid chloride solution[22] can be represented by laws analogous to the law determined for the decomposition of hydrogen peroxide in an acid chlorine–chloride solution.

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[17] See for example Harned and Seltz, THIS JOURNAL, 44, 1476 (1922).

[18] Private communication.

[19] The values of a_{H_2O} given in Table II were computed from the values of γ_{NaCl} presented by Lewis and Randall, ref. 13, p. 351.

[20] It is not at all improbable that water does enter into the reaction, although there is, of course, no *a priori* reason for selecting the third or indeed any positive power. It is a suggestive fact that Walton and Jones, THIS JOURNAL, 38, 1955 (1916), find that certain hydrogen peroxide decomposition reactions occurring in non-aqueous solvents are of second order.

[21] (a) Bray and Livingston, THIS JOURNAL, 45, 1251 (1923); (b) Livingston and Bray, *ibid.*, 45, 2048 (1923); (c) Livingston, *ibid.*, 48, 53 (1926).

[22] (a) Rivett, *Z. physik. Chem.*, 82, 201; 85, 113 (1913); (b) Harned and Seltz, THIS JOURNAL, 44, 1480 (1922); (c) Åkerlöf, Medd. K. Vetenskafisakad. *Nobelinstitut*, 6, No. 2 (1922); (d) Soper, J. Phys. *Chem.*, 31, 1192 (1927).

The decomposition of hydrogen peroxide in acid bromine–bromide solutions has been studied chiefly at ionic strengths less than unity. Under these conditions its velocity may be represented with fair accuracy by the following equation.

$$v = \chi_{\mathrm{HBr}}(\mathrm{H_2O_2})(\mathrm{H^+})(\mathrm{Br^-})f^2_{\mathrm{HBr}} \qquad (7)$$

However, an examination of the data shows that there is apparently a systematic decrease in the value of χ_{HBr} with increasing ionic strength. A plot of log χ against μ shows that the data are consistent with an equation analogous to Equation 4. The measurements performed in hydrobromic acid solutions (at ionic strengths between 0.01 and 0.4) indicate a value of about -0.07 for k'. The experiments performed in solutions containing potassium bromide and sulfuric acid (at ionic strengths[23] between 0.05 and **4.3)** exhibit considerable erratic variation but are consistent with a value of about -0.04 for k'.

The velocity of rearrangement of chloro-acetylaminobenzene was measured by Rivett[22a] in solutions of hydrochloric acid up to one molal and in solutions containing 0.25 M hydrochloric acid and one of a number of different chlorides (as well as sulfuric acid) at a variety of concentrations up to an ionic strength of about 4. More recently Harned[22b] has repeated Rivett's measurements in hydrochloric acid solutions. Åkerlöf[22c] measured the rate in solutions containing 0.25 M hydrochloric acid and aluminum chloride at concentrations up to 2 N. It has been demonstrated that the rate-determining step in the reaction is $\mathrm{C_6H_5{\cdot}NHClAc + H^+ + Cl^- \longrightarrow X}$. This mechanism should lead to a rate equation similar to Equation 4, and therefore the plot of log $[k/(\mathrm{H^+})(\mathrm{Cl^-})f^2_{\mathrm{HCl}}]$ (where k is the first order constant) against μ should be a straight line. We may use the measurements of Harned[24] to obtain approximate values of f_{HCl} in alkali chloride solutions. The experimental values for alkali chloride solutions fall approximately on straight lines with slopes of about -0.09; but these lines do not appear to extrapolate to the same point in dilute solution. Rivett's experiments in pure hydrochloric acid give a straight line with a slope of 0.06; the values of Harned and Seltz are practically constant, but show a slope of about -0.01 if recent values[25] of f_{HCl} are used. These apparent inconsistencies are probably due to a factor which has been discussed by

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[23] Based upon concentrations expressed in moles per liter rather than in molality. This probably introduces a considerable error in the more concentrated solutions. See note b, Table II, ref. 20. As has already been stated (ref. 21c, p. 55), the values of χ_{HBr} measured in KBr–sulfuric acid solutions are consistently 10% higher than those measured in hydrobromic acid solutions, or in solutions containing HBr and metallic bromides. This difference must be due to some unknown difference in experimental conditions.

[24] Harned, THIS JOURNAL, 42, 1808 (1920); also Harned and Brumbaugh, *ibid.*, 44, 2729 (1922).

[25] Randall and Young, *ibid.*, 50, 989 (1928).

Soper.[22d] He has shown that there are two possible products of the reaction, one of which is an oxidizing agent, and that, therefore, the iodimetrically measured rate is always less than the actual rate. This effect is greatest when $a_{H^+} \times a_{Cl^-}$ is small. A correction for this factor would raise all of the values of k for dilute solution experiments, especially those performed in dilute hydrochloric acid solutions. If proper allowance were made for this factor and the correct values of f_{HCl} were employed, it is very probable that the velocity could be accurately expressed in terms of an equation similar to Equation 4.

In conclusion we may state that for the type of reaction considered here,[26] Bronsted's equation is sufficient to represent the reaction velocity measurements at all concentrations investigated. Taken in conjunction with the success of the theory in interpreting the results of velocity measurements for widely different types of reactions in dilute solutions,[27] this constitutes strong empirical evidence for the general validity of the Bronsted hypothesis as applied to reactions in aqueous solution. The application of the theory to other types of reactions in concentrated solutions will be considered in another paper.

Acknowledgment should be made to Professor W. C. Bray and to Professor F. H. MacDougall for their kind interest and criticism.

Summary

1. The Bronsted reaction velocity equation has been combined with the Debye and McAuley equation for the activity of non-electrolytes to obtain an expression for the rate of decomposition of hydrogen peroxide in acid chlorine–chloride solutions

$$v = K\,(H_2O_2)(H^+)(Cl^-)f^2_{HCl} \cdot 10^{\mu k}$$

It has been shown that this expression is in agreement with the experimental material.

2. The activity of hydrogen peroxide in sodium chloride and sodium sulfate solutions has been determined by distribution measurements. These results have been used to test a prediction based upon the reaction velocity theory.

3. Some discussion of the velocity measurements of two analogous reactions has been presented.

MINNEAPOLIS, MINNESOTA

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[26] A reaction between two ions having charges of similar magnitude but of unlike sign, and a neutral molecule. This is practically the same as Bronsted's reactions type VI (compare reference 2a, p. 177).

[27] (a) Bronsted, ref. 2a and b; (b) Bronsted and Delbanco, *Z. anorg. Chem.*, **144**, 248 (1925); (c) Livingston, ref. 21c; (d) Bronsted and Livingston, THIS JOURNAL, 49, **435** (1927).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CINCINNATI]

THE ETHYL ACETATE EQUILIBRIUM

BY R. C. CANTELO AND R. D. BILLINGER

RECEIVED JUNE 30,1928 PUBLISHED DECEMBER 10, 1928

When the system ethyl alcohol, acetic acid, ethyl acetate and water has reached a state of equilibrium for a given temperature and pressure, this equilibrium state is expressed by the chemical equation $C_2H_5OH + HAc \quad C_2H_5Ac + H_2O$.

For a virtual change from equilibrium $dZ = 0$, where Z is the thermodynamic potential, and since $dZ = \Sigma\mu dm$, where μ = specific chemical potential and m = mass of component, we may write: $\bar{\mu}_1 + \bar{\mu}_2 = \bar{\mu}_3 + \bar{\mu}_4$, where $\bar{\mu}_1$, $\bar{\mu}_2$, - - - are the molecular chemical potentials respectively of ethyl alcohol, acetic acid, - - -.

Now for each of the four substances constituting the system we have an equation of the form $\bar{\mu}_1 - \bar{\mu}_{1,0} = RT \ln a_1$, where a_1 is the thermodynamic concentration or activity of the component in the system, $a_{1,0}$ for the standard state being arbitrarily placed equal to 1. It is then a simple matter to derive the mass action expression for equilibrium, namely, $K_a = a_3a_4/a_1a_2$. Now it is quite possible that a change in the thermodynamic environment may change the value of one or more of the chemical potentials of the substances involved, and such changes in chemical potential will result in a change in the value of K_a, the equilibrium constant.

In the present investigation we have sought to change the thermodynamic environment by using in place of water alone solutions of the salts sodium chloride, sodium thiocyanate and sodium iodide. These salts form a Hofmeister series as follows: $\overline{CNS}$ $\overline{I}$ $\overline{Cl}$, as regards their relative effects in retarding gelation, that is, in lowering the temperature of gelation. The relative effects of these salts are of interest, therefore, with respect to the water equilibrium. Bancroft[1] considers liquid water to be an equilibrium mixture of hydrol and polyhydrol, the latter being a polymerized form of the former. He ascribes the greater peptizing action of potassium iodide over potassium chloride on gelation in water to the water equilibrium being shifted in the direction of more hydrol, the peptizing agent.

Schlesinger[2] investigated the influence of $LiCl$, $NaCl$, KCl and $CaCl_2$ on the ethyl acetate equilibrium at 100°, and found that the equilibrium was shifted, owing to the presence of these salts. He found that with $NaCl$, $LiCl$ and $CaCl_2$, his equilibrium constant could be calculated from the linear equation, $K = 3045 - 21.217\,C$, C being the salt concentration in milliequivalents per mole of water.

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[1] Bancroft, *J. Phys. Chem.*, 30, 1194 (1926).

[2] Schlesinger, *Ber.*, 59B, 1965 (1926).

Experimental Method

Weighed quantities of acetic acid, ethyl alcohol and water or salt solution were mixed together in a weighed flask. From this mixture small glass tubes were filled and sealed by means of a blast lamp. The tubes were weighed before and after filling to obtain the weight of sample taken.

The method of filling the tubes was to fit up the weighed flask as a wash bottle with a capillary jet; then by means of a current of air, dried by passing through calcium chloride, it was possible to force the liquid into the small tubes.

The acetic acid, ethyl alcohol and neutral salts used were all c. p. chemicals which were tested for impurities. The acid contained 99.39% of acetic acid by weight and the alcohol 95.75% by weight. The salts were all thoroughly dried before using.

The sealed tubes were placed in a bath of carbon tetrachloride which was kept refluxing by a simple heater. The heater consisted of a 100-watt incandescent lamp in a can insulated with sheet asbestos. By this arrangement it was possible to keep the tubes containing the esterification mixture at a temperature of 78°.

Esterification in the absence of a mineral acid catalyst is slow, even at this temperature, and it was necessary to continue the heating for from thirty to forty days. Then from time to time a tube was taken from the bath, cooled in ice, the capillary end broken and the contents placed in ice cold, freshly boiled water. The mixture was transferred to a volumetric flask and an aliquot portion taken for titration against standard barium hydroxide solution. By means of the titration value the concentration of acetic acid was known in the resulting mixture, and from the known initial concentrations it was possible to calculate the concentration of all four constituents in the equilibrium mixture. Concentrations were figured in terms of millimoles of the constituents and the equilibrium constant K_E was then expressed as

$$K_E = \frac{\text{Millimoles of } CH_3COOC_2H_5 \text{ X Millimoles of } H_2O}{\text{Millimoles of } CH_3COOH \text{ X Millimoles of } C_2H_5OH}$$

When several successive samples gave approximately equal values of K_E, the equilibrium was assumed to have been reached.

TABLE I

ESTERIFICATION WITH NO ADDED SALT

Run	Sample	K_E	Av. K_E	Concn., init.	CH_3-COOH final	Concn. init.	C_2H_5OH, final	Concn. init.	H_2O, final	Concn. CH_3-$COOC_2H_5$, final
1st	A	3.686	3.705	866.9	459.8	848.4	441.3	1430.4	1837.5	407.1
	B	3.723		866.9	458.6	848.4	439.7	1430.4	1838.7	408.3
2nd	A	3.755	3.708	867.8	458.4	847.6	438.2	1433.0	1842.4	409.4
	B	3.661		861.8	461.5	847.6	441.3	1433.0	1839.3	408.3

The initial concentration refers to the concentration, expressed in millimoles, in the original mixture before reaction occurs. The final concentration refers to the concentration after equilibrium is established.

Table II

Esterification in the Presence of Sodium Chloride

Neutral salt, N	Sample	K_E	Av. K_E	Concn. init.	CH_3-COOH final	Concn. init.	C_2H_5OH, final	Concn., init.	H_2O, final	Concn. CH_3-$COOC_2H_5$, final
0.481	A	3.872	3.902	170.9	91.55	163.4	84.0	296.2	375.5	79.3
	B	3.931		170.9	91.06	163.4	83.5	296.2	376.0	79.8
1.000	A	4.089	4.082	865.3	444.7	848.4	427.8	1429.2	1849.8	420.6
	B	4.074		865.3	445.2	848.4	428.3	1429.2	1849.3	420.1
1.426	A	4.221	4.235	866.7	443.5	857.7	434.5	1499.0	1922.2	423.2
	B	4.249		866.7	442.6	857.7	433.6	1499.0	1923.1	424.1
2.000	A	4.413	4.438	866.8	435.4	848.8	417.5	1428.7	1860.0	431.3
	B	4.463		866.8	433.9	848.8	416.0	1428.7	1861.5	432.8

Table III

Esterification in the Presence of Sodium iodide

Neutral salt, N	Sample	K_E	Av. K_E	Concn. init.	CH_3-COOH final	Concn. init.	C_2H_5OH, final	Concn., init.	H_2O, final	Concn. CH_3-$COOC_2H_5$, final
0.477	A	3.839	3.848	170.9	91.29	163.6	83.99	290.2	369.81	79.61
	B	3.857		170.9	91.16	163.6	83.86	290.2	369.94	79.74
0.946	A	4.053	4.056	170.9	90.31	163.6	83.01	296.5	377.09	80.59
	B	4.059		170.9	90.27	163.6	82.97	296.5	377.13	80.63
1.448	A	4.128	4.143	170.8	89.39	163.2	81.79	289.3	370.71	81.41
	B	4.159		170.8	89.25	163.2	81.65	289.3	370.85	81.55
1.902	A	4.192	4.186	170.5	89.09	162.8	81.39	292.0	373.41	81.41
	B	4.179		170.5	89.17	162.8	81.47	292.0	373.33	81.33

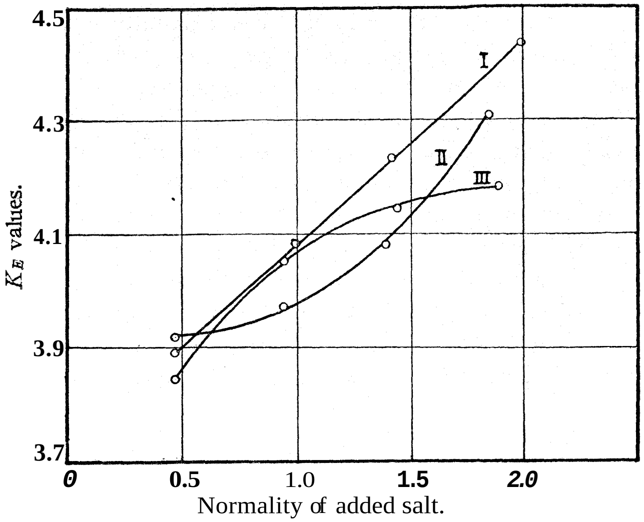
Table IV

Esterification in the Presence of Sodium Thiocyanate

Neutral salt, N	Sample	K_E	Av. K_E	Concn. init.	CH_3-COOH, final	Concn., init.	C_2H_5OH, final	Concn., init.	H_2O, final	Concn. CH_3-$COOC_2H_5$, final
0.473	A	3.893	3.916	170.9	91.49	163.1	83.69	295.7	375.11	79.41
	B	3.939		170.9	91.15	163.1	83.35	295.7	375.45	79.75
0.938	A	3.927	3.973	171.8	91.54	163.3	83.04	291.7	371.96	80.26
	B	4.018		171.8	90.94	163.3	82.44	291.7	372.56	80.86
1.407	A	4.114	4.080	171.3	90.24	163.2	82.14	295.2	376.26	81.06
	B	4.046		171.3	90.68	163.2	82.58	295.2	375.82	80.62
1.840	A	4.319	4.313	170.6	88.33	163.8	81.53	295.8	378.07	82.27
	B	4.307		170.6	88.40	163.8	81.60	295.8	378.00	82.20

Discussion of Results

Tables II, III and IV, and Fig. 1 show that K_E increases with increasing salt concentrations. When sodium chloride is the added salt, the equilibrium constant is a linear function of the concentration of the salt, but the effect of sodium iodide and sodium thiocyanate is more complicated. Each salt appears to have its own specific effect and work at present in progress in this Laboratory seems to indicate that one salt at least depresses the equilibrium constant below the value 3.7. Further work is evidently necessary before our values may be explained, and work is now in progress with a view to determining the relative chemical potentials of the components in the system with and without the addition of salts. It may be pointed out, however, that the Hofmeister series does not appear to hold for the order of the effects upon the equilibrium constant at 78°.



I, Curve for K_E values with NaCl; II, curve for K_E **values with** NaCNS; III, curve for K_E values with NaI.

Fig. 1.

Summary

The ethyl acetate equilibrium depends upon the equality of the sum of the chemical potentials of the ethyl alcohol and acetic acid to the sum of the chemical potentials of the ethyl acetate and water. Any change in thermodynamic environment may change the value of one or more of these potentials, thereby giving a new value for the equilibrium constant.

The equilibrium constant in the absence of salts for this system has been measured and found to be equal to 3.7.

The equilibrium constant in the presence of salts has been measured and found to increase with the concentration of the salt in the water solution used in place of water alone. With sodium chloride as added salt, the equilibrium constant increases linearly with the concentration of sodium chloride. With sodium thiocyanate and sodium iodide, the effect is more complicated.

The order of the effects of the anions upon the equilibrium constant is not that of a Hofmeister series.

Cincinnati, Ohio

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

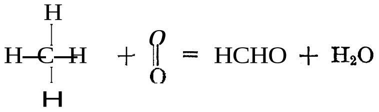
OXIDATION OF METHANE WITH NITROGEN PEROXIDE

BY PER K. FROLICH, P. J. HARRINGTON AND ALDEN H. WAITT

RECEIVED JULY 2, 1928 PUBLISHED DECEMBER 10, 1928

The products ordinarily formed in the direct oxidation of methane are carbon dioxide, carbon monoxide and water. According to Bone's hydroxylation theory, however, the reaction proceeds stepwise with methanol, formaldehyde and formic acid as the intermediate products of oxidation.[1] Although it has been possible to isolate formaldehyde by carefully controlled partial oxidation of methane, nevertheless, no success has been met with in trying to produce methanol by the same procedure. This is supposedly due to the fact that the alcohol is so much more readily oxidized than the hydrocarbon, thus making successive quantities of oxygen attack the initially formed methanol molecules in preference to the remaining methane. Hence methanol is never permitted to build up to concentrations sufficient for its detection. The same reasoning holds for formaldehyde, which, however, represents a further step in the oxidation and therefore is less difficult to isolate when the oxygen concentration is kept low. In normal combustion, however, with a high concentration of oxygen and high temperature, reaction proceeds beyond the formaldehyde stage, with the resulting formation of the ultimate products, carbon monoxide and dioxide.

If this line of reasoning be correct, it should be possible to isolate the intermediately formed alcohol if the process could be carried out under such conditions that the available oxygen, present in only limited concentration, could be consumed by the methane molecules almost instantaneously, avoiding any further reoxidation. It would seem that this could be accomplished by bringing a mixture of nitrogen peroxide with an excess of methane up to reaction temperature, followed by rapid cooling to stabilize the oxidation products against thermal decomposition. Since nitrogen peroxide is capable of liberating 1 atom of oxygen, the tendency for further oxidation of the initially formed methanol would be materially reduced.[2] With elementary oxygen, on the other hand, the conditions seem less favorable in that the consumption of two atoms of oxygen is more probable



$$\mathrm{CH_4} + \mathrm{O{=}O} = \mathrm{HCHO} + \mathrm{H_2O}$$

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[1] Bone, "Coal and its Scientific Uses," p. 176.

[2] There is, of course, a further possibility of direct reaction of nitrogen peroxide with methane, and from such intermediate substances the final oxidation products may result.

Attempts to isolate intermediate products by oxidation of methane with nitrogen peroxide have already been reported on by Bailey,[3] who found that formaldehyde was produced at a minimum reaction temperature of 450° when a mixture of the two gases was passed through a heated porcelain tube. Bibb[4] has claimed the production of valuable oxidation products from methane by a similar procedure, except that he employed the nitrogen peroxide merely as a gas phase catalyst, limiting its concentration to 2%.

In the present investigation a minimum reaction temperature below 450° with production of methanol was sought, using more than 2% of nitrogen peroxide as an oxidizing agent and various surface catalysts.

Experimental Procedure

In the apparatus, which was made entirely of Pyrex glass, nitrogen peroxide was generated from copper and fuming nitric acid, dried and then liquefied in a bulb surrounded by melting ice. Carefully metered and measured natural gas containing 98.3% of methane was slowly bubbled through the peroxide and saturated with it at 0°. Measured methane was then added to adjust the percentage of peroxide in the mixture to that desired and the gases were passed through a reaction chamber 14 cm. long and of 2.8 sq. cm. in free cross section. A central tube extending through the entire length of the reactor held a thermocouple with a movable weld. The chamber was externally heated by a coil of resistance ribbon. Following the chamber, liquid product was removed through a condenser to a cooled bulb, while the gases were scrubbed and discarded. For the recovery of the nitrogen oxides, oxidation and absorption in sulfuric acid worked successfully.

Samples of liquid product were fractionated and the specific gravity, acidity and formaldehyde content found. With the aid of exit gas analyses, material balances were made and minimum reaction temperatures were investigated. Variations in the minimum reaction temperature and in the quantity and quality of product with variation in rates of gas flow (from 8 to 45 liters per hour) and percentage of nitrogen peroxide in the inlet gas mixture (from 8 to 35%) were studied, as well as the effects of pumice, platinized asbestos, vanadium pentoxide, nickel wire and hopcalite as catalysts.

Results

The results of a series of experiments made with an open chamber and with the chamber filled with pumice granules are given in Table I. Despite great difficulties in the measurement of the corrosive gases and in gas and liquid analyses, the material balances were satisfactory.

The minimum temperature was taken as the point above which the gases issued colorless from the reaction chamber, and below which they came out colored brown by nitrogen peroxide, the absence of color being taken as evidence of reduction of the peroxide as a result of reaction with methane. From the data for the open chamber, it will be noted that the minimum reaction temperature varies both with the rate of gas flow and the ratio of nitrogen peroxide. As shown in Fig. 1, the temperature registered by the thermocouple increases linearly with the rate of flow,

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[3] Bailey, U. S. Pat. 1,319,748, Oct. 28, 1919.

[4] Bibb, U. S. Pat. 1,392,886, Oct. 4, 1921.

TABLE I

OXIDATION OF METHANE WITH NITROGEN PEROXIDE

Basis, 1 hour

CH_4+ NO_2 entering, l.	NO_2 in entering gas, %	Minimum reac. temp., °C.	Exit gas analysis, %						Liq. prod. cc.	% Entering carbon going to			
			NO	CO_2	CO	H_2	CH_4	N_2		RCHO	Waste as CO+CO_2	Un-changed	Unacd. for
						Open chamber							
32.3	35.5	538	..	...	...	..	..	...	7.9	...	..	..	...
32.9	35.5	532	25.2	4.1	8.8	24.4	36.3	1.2	7.5	2.0	25.2	70.9	1.9
9.3	35.5	465	24.4	4.3	9.4	27.4	33.6	0.8	1.6	3.4	27.0	67.5	2.1
43.1	35.5	568	29.5	3.1	3.4	8.2	54.3	1.5	9.8	0.9	10.5	88.1	0.5
24.9	22.5	482	16.3	3.7	9.5	22.9	46.5	1.1	4.8	2.0	21.3	75.2	1.5
21.7	12.6	451	12.0	1.0	5.1	6.3	74.4	1.2	2.7	1.8	7.4	89.6	1.2
14.0	8.6	440	7.6	0.0	4.6	10.3	76.2	1.3	0.8	1.5	5.6	91.8	1.1
						Pumice							
20.0	35.5	605	27.3	7.1	6.5	12.5	44.9	1.7	5.0	1.1	22.9	75.6	0.4
38.8	35.5	680	28.9	5.6	3.4	10.6	49.5	2.1	8.5	0.8	15.3	83.8	.1
9.3	6.0	534	6.1	0.0	3.0	0.4	89.5	1.0	0.6	1.0	3.2	95.0	.8

being higher with greater concentrations of nitrogen peroxide. This shows the combined effect of radiation from the electric heating wire, which obviously is at a higher temperature the higher the rate of gas flow through the chamber, and of the heat liberated by the reaction. By extrapolating to zero rate of flow, however, the minimum reaction temperature for the open tube is determined as about 430°.

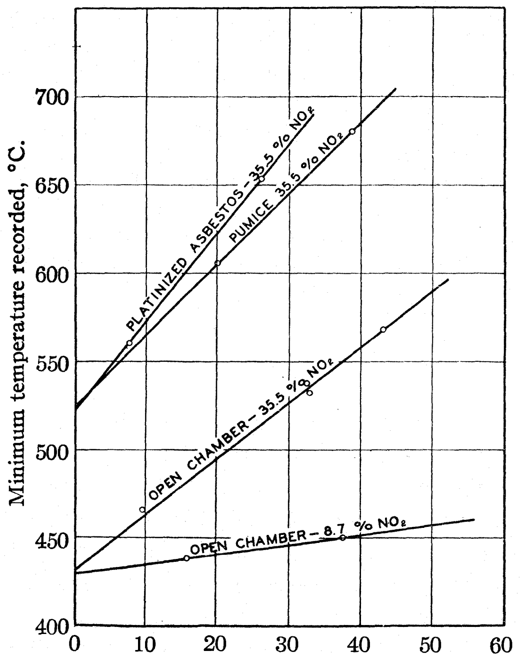

Fig. 1.

The liquid products collected in the condenser contained varying amounts of nitric and, probably, nitrous acid, usually corresponding to a normality of the order of one. Careful fractionations of the liquid products failed to reveal any methanol and only indefinite and small fractions indicating formic acid were obtained. No information could be obtained from the literature in regard to the problem of distinguishing formic acid from mixtures of nitric and nitrous acids, and after many futile attempts the effort to positively identify formic acid was finally abandoned. The conversion of entering methane to formaldehyde varied roughly between 1 and 3.5%, as shown in Table I. In general, the lower the minimum reaction temperature the better the yield of formaldehyde. From a comparison of the data for the various experiments it follows that a low rate of flow with a gas mixture containing a low concentration of nitrogen peroxide results in the highest ratio of formaldehyde to carbon monoxide and dioxide. The formation of these latter compounds, representing further stages of oxidation, is quite considerable. Even in the best experiments the ratio of formaldehyde to carbon monoxide and dioxide, figured on a methane basis, is less than 1:3. Although it might have been possible to improve the formaldehyde yield, such attempts were beyond the scope of this work.

As would be expected, a high yield of formaldehyde on the basis of methane reacting coincides with a low carbon dioxide production, both being characteristic of mild oxidation of the methane molecule.

The loss of nitrogen peroxide by complete decomposition to elementary nitrogen is small, being of the order of magnitude of 1% per passage through the reactor.

In addition to the runs recorded in Table I some fifty experiments were made, mostly with pumice and other contact substances.[6] In the case of catalysts, the reaction temperature was invariably higher than with the open chamber, other conditions being the same, due to localization of the reaction and the formation of a hot spot, as detected by the movable thermocouple. Curves for pumice and platinized asbestos are given in Fig. 1. Vanadium pentoxide gave temperatures in the same region, while a nickel wire introduced into the chamber brought the temperature up by another hundred degrees. The only exception was hopcalite, which gave reaction at approximately the same temperature as the open chamber.

An interesting point is the possibility of reaction between the higher hydrocarbons, present in small amounts, and liquid nitrogen peroxide to form acetic acid. After each run the remainder of the nitrogen peroxide was allowed to evaporate and in almost every case there appeared a residue of several cubic centimeters of a clear, yellow-tinged liquid. This material undoubtedly contained nitric acid and dissolved oxides of nitrogen, but upon careful qualitative analysis it gave a pronounced odor of acetic acid, which apparently was present in considerable quantity.

Conclusions

The fact that methanol is not detected among the products of reaction does not necessarily imply that the alcohol is not formed in methane oxidation. Quite the contrary, methanol seems to be a logical intermediate compound when methane is oxidized with nitrogen peroxide, which splits off only one atom of oxygen per molecule. The failure of the alcohol to appear among the final products can hardly be due solely to further oxidation to formaldehyde, for, as is outlined in the introduction, it is

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[5] Cooper and Fasce, *Ind. Eng. Chem.*, 20, 420 (1928).

[6] A. H. Waitt, M. I. T. "Thesis," 1926; P. J. Harrington, M. I. T. "Thesis," 1927.

improbable that all the initially formed methanol molecules would be brought in contact with a second molecule of nitrogen peroxide. It is far more reasonable to believe that the high temperature of operation is responsible for thermal decomposition of the alcohol. While methanol is perfectly stable with respect to carbon monoxide and hydrogen at room temperature, it has been pointed out by Lewis and Frolich[7] that the equilibrium constant changes rapidly with temperature, leaving less than 2% of methanol in an equilibrium mixture at 300°. At the temperatures in question, 430° and above, it may therefore be expected that the initially formed methanol decomposes quantitatively into carbon monoxide and hydrogen. Furthermore, the heat of reaction undoubtedly raises the temperature of the alcohol molecules formed to a level above that recorded by the thermocouple as the average for the entire gas mixture. The high content of carbon monoxide and hydrogen in the off-gases may well account for such thermal decomposition of intermediately formed methanol.[8] Instead of decreasing the temperature of reaction, catalysts make the conditions less favorable to the stabilization of methanol by causing a temperature increase and hence even the yield of formaldehyde goes down in the presence of catalysts.

Summary

1. The minimum reaction temperature for the oxidation of methane with nitrogen peroxide is about 430° in an open Pyrex tube. The presence of catalysts results in higher temperatures due to the formation of a hot spot.

2. Methanol cannot be detected among the products of reaction. It is surmised that the alcohol is formed intermediately but decomposes into carbon monoxide and hydrogen, rather than being quantitatively reoxidized.

3. Formaldehyde is formed in good quantities, the maximum yield observed corresponding to somewhat less than one-quarter of the methane reacting. Formaldehyde production is favored by conditions which tend to lower the reaction temperature. These conditions are: low nitrogen peroxide concentration, slow rate of flow and absence of contact surfaces. The accompanying losses of nitrogen peroxide by decomposition to elementary nitrogen are small.

4. The presence of formic acid, as indicated by fractionation of the liquid condensate, could not be verified by direct analysis, due to the disturbing influence of the relatively high concentrations of nitric and nitrous acids.

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[7] Lewis and Frolich, Ind. Eng. *Chem.,* **20,285** (1928).

[8] It is assumed that the low hydrogen concentration in the last experiment in Table I is due to an analytical error.

5. Attention is called to the possible formation of acetic acid by reaction in the cold of liquid nitrogen peroxide with small amounts of higher hydrocarbons present in the methane.

CAMBRIDGE, MASSACHUSETTS

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

SYMMETRICAL AND ANTISYMMETRICAL HYDROGEN AND THE THIRD LAW OF THERMODYNAMICS. THERMAL EQUILIBRIUM AND THE TRIPLE POINT PRESSURE

BY W. F. GIAUQUE AND H. L. JOHNSTON

RECEIVED JULY 10, 1928 PUBLISHED DECEMBER 10, 1928

The suggestion of Heisenberg[1] that hydrogen and other homopolar molecules exist in two forms, symmetrical and antisymmetrical, offers the most satisfactory explanation for the alternating intensity observed in the band spectra of these substances. This suggestion has been used by Dennison[2] to explain the heat capacity of hydrogen gas over the low temperature range in which it is taking up its rotational degrees of freedom. Dennison's theoretical curve is the first one of a large number offered by various authors which has agreed with the experimental heat capacity data within the limit of error.

A physical conception of symmetry and antisymmetry in the hydrogen molecule arises from the assumption of nuclei which may spin on their own axes. When the two spinning protons oppose each other, the molecule is symmetrical; when their angular momentum is additive, it is antisymmetrical. The statistical weight of the latter variety is increased by the factor three, since a total spin of $j = 1$, one-half unit for each proton, is assumed, and the *a priori* probability p is as usual taken equal to $(2j + 1)$. The symmetrical form takes up only the even rotation states $j = 0, 2, 4, 6, \ldots\ldots,$ while the antisymmetrical assumes the rotation states $j = 1, 3, 5 \ldots\ldots$

In order to explain the heat capacity of hydrogen, Dennison found it necessary to assume that the transitions between symmetrical and antisymmetrical states are so rare that they do not occur appreciably during the experimental determination of heat capacity. Dennison's assumptions are supported by the band spectra data and interpretation of Hori.[3] Birge[4] has shown that Hori's data lead to a value of 0.480×10^{-40} g. cm.^{2} for the moment of inertia of the hydrogen molecule in its normal state. Hori gave 0.467×10^{-40} as the value which the molecule would have if it lost its last half unit of vibration. This latter value should not be used

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[1] Heisenberg, *Z. Physik*, 41, 239 (1927).

[2] Dennison, *Proc. Roy. Soc.*, 115A, 483 (1927).

[3] Hori, Z. *Physik*, 44, 834 (1927).

[4] Birge, *Proc. Nat. Acad. Sci.*, 14, 12 (1928); *Nature*, Jan. 28, 1928.

for heat capacity calculations. Dennison found 0.464×10^{-40} from the heat capacity data available to him. Cornish and Eastman[5] found 0.475×10^{-40} from their own heat capacity measurements previously to the calculation of Birge. Condon[6] has found from a purely theoretical calculation of the hydrogen molecule problem that 0.426×10^{-40} is a rough value of the moment of inertia and is definitely a lower limit. This would be increased to 0.44×10^{-40} g. cm.^{2} when one-half unit of vibration in the normal state is considered.

Shortly after the publication of Dennison's paper, Dr. E. U. Condon communicated with this Laboratory in the hope that experimental work on the heat capacity of hydrogen gas carried out by Cornish and Eastman[5] might be extended to include a very direct test of Dennison's idea. Condon's suggestion was based on the assumption that hydrogen gas, kept at the temperature of liquid air for sufficient time, might be expected to change from about one-fourth symmetrical to nearly all symmetrical. Subsequent determination of the heat capacity would, if the transition occurred, show a markedly different heat capacity, as may be seen from the computations in Dennison's paper. Unfortunately, the apparatus of Cornish and Eastman had been completely dismantled shortly before the arrival of Condon's letter. However, in connection with the study of the entropies of gases being carried out in this Laboratory, we have apparatus in which it is a comparatively easy matter to measure the vapor pressure of hydrogen. Also, the problem of keeping a considerable quantity of hydrogen gas at the temperature of liquid air for a long period presented little difficulty since large quantities of liquid air are always kept on hand. It seemed worth while to measure the vapor pressure of hydrogen which had been kept at a low temperature for a considerable period of time. The mean life of the transition has been estimated by Heisenberg at about three weeks. Condon suggested that two or three months at liquid air temperature might be expected to produce a considerable change.

Apparatus.—A steel container holding about ten moles of gas at a pressure of seventy-five atmospheres and a temperature of about 85°K. was filled with pure hydrogen, prepared by electrolysis and purified by means of a nickel catalyst until the oxygen present by diffusion was reduced to about 0.01%. The container was suspended in a Pyrex glass Dewar tube by means of a steel capillary tubing of very small bore and 45 cm. long which served as an inlet and outlet for the gas. The Dewar tube was approximately 90 cm. long and 11 cm. inside diameter. The liquid air required was about four liters every two days.

The vapor pressure measurements were carried out in the apparatus previously used by Giauque, Johnston and Kelley[7] for measurements of the vapor pressure of hydrogen and of oxygen. The description of this apparatus has been given by Giauque and

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[5] Cornish and Eastman, THIS JOURNAL, 50,627 (1928).

[6] Condon, Proc. *Nat. Acad. Sci., 13,* 466 *(1927).*

[7] Giauque, Johnston and Kelley, THIS JOURNAL, **49,2367** (1927).

Wiebe.[8] The hydrogen was withdrawn from the container through a sensitive needle valve.

Vapor Pressure of Hydrogen.—It was thought desirable to measure the vapor pressure of ordinary hydrogen shortly before making the measurements on the material which had been kept cold, so this was done. While it seemed improbable that the process of crystallization would in any way affect the relative amounts of symmetrical and antisymmetrical molecules, this was investigated by measuring the vapor pressure of the liquid both before and after solidification. The measurements, made at 53.7 cm. pressure, agreed to better than 0.01". The triple point pressure of the ordinary hydrogen measured on May 1, 1928, was 5.383 international cm., while the reading on the gold resistance thermometer was 83.417 ohms.

The special hydrogen was kept at the temperature of liquid air from October 19,1927, to May 3, 1928, a total of 197 days. In order to introduce the hydrogen into the apparatus, it was necessary to pass through a section of tubing at room temperature. The rate of transfer of the gas was such that it was kept at room temperature for approximately fifteen seconds. It was immediately obvious during the course of the observations that any difference which might exist was extremely small, so further efforts were concentrated on the triple point pressure.

The measurements on the special hydrogen are given in Table I. In the first column, the approximate percentage of the material melted is given. It will be noticed that the pressure was higher when a large amount of liquid was present. The reason appeared to be superheating of the liquid

TABLE I

TRIPLE POINT PRESSURE OF SPECIAL HYDROGEN

May 3, 1928

Percentage melted	Pressure, international cm. of Hg	Resistance thermometer, ohms
15	5.338	83.411
50	5.334	83.411
70	5.360	83.412
95	5.392	83.414
Melted, then cooled below triple paint. Heated		
15	5.344	83.413
50	5.344	83.413
85	5.380	83.412
Melted, then cooled below triple point. Heated		
90	5.364	83.411
Increased heat leak by 150%		
90	5.408	83.412
Accepted values	5.34	83.412

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[8] Giauque and Wiebe, THIS JOURNAL, 50,101 (1928).

near the surface, due to heat leak from above. The last two observations listed in Table I were designed to decide this question. With most of the material melted, a measurement was made; then with no other change the heat leak was increased about 150% by raising the temperature of the surroundings a few degrees. The next measurement showed the expected increase in pressure. It appears to be very difficult to avoid a slight superheating of the hydrogen and we suspect that the deviations of various previous observers may be due largely to this effect. The heavy gold walls of the container with the interior gold vanes were apparently unable to prevent a surface heating effect of the order of one-hundredth of a degree necessary to explain the increase in pressure. For this reason we have not considered any measurements where more than half of the hydrogen was melted and take the triple point pressure of the special hydrogen as 5.34 cm.

The surface heating effect made it desirable to repeat the measurements on ordinary hydrogen with greater care, especially since we had not recorded the percentage melted in that case. The results of these measurements are given in Table II. The third and fourth measurements were designed to demonstrate the surface heating in a second manner. With about 85% of the material melted, some of the hydrogen was evaporated from the surface by means of a pump. A reading taken immediately after this agreed with the previous results, but on standing for fifteen minutes the pressure had risen to a considerably higher value.

TABLE II

TRIPLE POINT PRESSURE OF ORDINARY HYDROGEN

May 30, 1928

Percentage melted	Pressure, international cm. of Hg	Resistance thermometer, ohms
<1	5.391	83 417
15	5.394	....
Melted 85% and evaporated some by reduced pressure		
85	5.390	83.417
Fifteen minutes after the surface evaporation		
85	5.440	....
Accepted values	5.39	83.417

The value previously obtained by Giauque, Johnston and Kelley[7] was 5.37 cm. The present determinations of 5.38 and 5.39 cm. seem to indicate that the triple point pressure of ordinary hydrogen is 5.38 ± 0.01 cm. This is in good agreement with the 5.382 cm. value of Onnes and Braak[9] and the 5.38 cm. value of Simon and Lange.[10] Henning[11] has recently ob-

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[9] Onnes and Braak, *Comm. Phys. Lab. Univ. Leiden*, 1926, 184.

[10] Simon and Lange, *Z. Physik*, 15,312 (1923).

[11] Henning, *ibid.*, 40, 775 (1926).

tained a value of 5.486 cm. as a result of four experiments varying from 5.480 to 5.495 cm. The 5.34 cm. value of the triple point pressure of the special hydrogen is lower than any value obtained for ordinary hydrogen. The 0.005-ohm difference on the resistance thermometer, which is not very sensitive at this temperature, indicates that the triple point temperature of the special hydrogen was 0.04" lower than that of ordinary hydrogen. We do not feel that we can claim with certainty that a difference exists but the apparent difference is beyond the limit of any error of which we are aware. The greater part of the hydrogen remains and is being kept cold. We hope to make further observations on its properties at a considerably later date.

The Entropy Effect Due to Symmetrical and Antisymmetrical Hydrogen

Heisenberg[1] in suggesting the presence of more than one kind of hydrogen mentioned an effect on the entropy as a consequence. Fowler[12] has recently considered the manner in which the statistical calculation of the entropy of hydrogen gas must be modified by the recognition of the two forms. However, in making this same calculation we are unable to arrive at the same result. It appears that Fowler's calculation amounts to having considered the entropy of symmetrical and of antisymmetrical hydrogen individually, but has omitted the entropy of mixing of the two. We cannot be sure from his statements that this has not been done intentionally, but, if so, we can see no reason for it.

We consider the matter as follows. Let us assume that the ratio of symmetrical to antisymmetrical molecules is one to three and that the gas has been cooled to a temperature at which it is acting in the manner of a monatomic gas. The statistical weight-of the symmetrical variety is unity while the weight of the antisymmetrical molecules is nine; that is, one-quarter of the gas consists of one kind of molecules and the other three-quarters is divided between nine varieties which arise from the consideration that the unit of momentum of the combined nuclei gives rise to three orientations which are themselves distributed between the three additional orientations arising from the molecular rotation which the antisymmetrical variety retains in its lowest rotation state. The entropy of such a mixture should exceed the entropy of a monatomic gas merely by the entropy of mixing of the ten varieties. Therefore, $AS = -{}^1/_4\, R \ln {}^1/_4 - {}^3/_4\, R \ln {}^1/_{12} = 4.39$ cal./deg. per mole. Thus 4.39 E. U. must be added to the value obtained from the Sackur equation. Fowler found ${}^3/_2\, R \ln 3 = 3.27$ E. U.

The assumption of an exact one-to-three ratio between the two forms of hydrogen is open to question on two grounds: first, the true equilibrium at room temperature would favor the symmetrical form by several per

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[12] **Fowler,** *Proc. Roy. Soc.*, 118A, *52 (1928).*

cent. if the various rotational energy levels represent the only energy differences between the two forms; second, it is not known that there is not an energy difference between the two forms in addition to that accompanying the rotation change. The alternating lines of the band spectra fall in a smooth series, showing as would be expected that the molecular dimensions are not appreciably different; however, this does not, in itself, eliminate the possibility of a sufficient energy of transition to modify the one-to-three ratio considerably. The band spectra intensity determinations are not very accurate. Dennison's[2] limits of 1:3.5 and 1:2.7 obtained from the heat capacity data are the best experimental indication that the coupling energy is small. The entropy effect corresponding to the above limits is 4.45 E. U. and 4.34 E. U., respectively. Therefore, if Dennison's interpretation of the behavior of hydrogen is correct, we must add 4.38 ± 0.06 cal./deg. per mole to the entropy as given by the Sackur equation or by the ordinary application of the third law.

It has long been generally recognized that the entropy of hydrogen, as given by the direct application of the third law of thermodynamics in the ordinary manner, is lower than the value obtained indirectly from this law. Fowler notes that his 3.27 E. U. increase is rather too large an addition. We agree with this and our calculated amount of 4.39 E. U. is no improvement from this point of view. The only apparent alternative to assuming the non-existence of antisymmetrical hydrogen is to adopt the suggestion of Fowler that the products of reactions in which hydrogen is consumed must also have the antisymmetrical property.

Fowler calls attention to the failure of the Nernst heat theorem for such a substance as hydrogen, but states that the theorem would be true in this case if true equilibrium were attained since there is but one form of the symmetrical state. This question of true equilibrium between the various molecular species of a pure substance was the principal point which led Lewis and Gibson[13] to question the Nernst heat theorem and to make a restatement of the entropy principle which they have called the third law of thermodynamics. We believe that true equilibrium in any system must lead to an ordered crystalline state at the absolute zero of temperature and it is only to this perfect crystalline state, "lacking any sort of randomness," that Lewis and Gibson have assigned zero entropy.

We should like to call attention to a point that has apparently not previously been recognized, namely, that true equilibrium, even in a solution of isotopes, would, in the absence of any specific effect due to nuclear differences, lead to complete separation of the various components at the absolute zero, as may be shown by the thermodynamic equation[14]

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

[14] **Ref. 13,** page 244.

$$\frac{dN_1}{dh} = \left(\frac{W\overline{V}_1}{V}\right) - W_1\frac{N_1g}{RT}$$

obtained for a perfect solution. h is the height, g the acceleration of gravity; W and V the molal mass and volume, respectively, of the solution, and N_1, W_1 and $\overline{V}_1$ the mole fraction, molal mass and partial molal volume, respectively, of component one. The existence of some specific force due to nuclear differences would, of course, in itself, suffice to eliminate randomness either by separation into phases or specific combination as the temperature approached the absolute zero. The above-described processes are, of course, experimentally unrealizable, but we wish to clearly distinguish between the truth of the third law of thermodynamics and our experimental difficulties in using it directly.

It is becoming apparent that there are, perhaps, many substances in which the attainment of equilibrium is so slow as to interfere with the practical application of the third law without recognition of sources of entropy which do not appear from the measurement of heat capacity alone.

The entropy effect due to orientations arising from unbalanced angular momentum of electronic systems has been discussed by Schottky,[15] and by one of us.[16]

In the case of this large group of substances, the practical difficulty in obtaining the entropy from heat capacity measurements alone may be due not only to lack of equilibrium but to the fact that transformation to a single orientation by existing magnetic and electrical fields would occur at temperatures below those experimentally practicable. The behavior of pure antisymmetrical hydrogen, could it be obtained, would be analogous to the above case.

Summary

The triple point pressure of ordinary hydrogen has been found to be 5.38 ± 0.01 cm.

The triple point pressure of hydrogen which had been kept at the temperature of liquid air for 197 days was 5.34 cm. The difference between the two values is small, but we know of no source of experimental error that would account for it.

The experiment was carried out to obtain information concerning the existence of symmetrical and antisymmetrical hydrogen and the extremely slow transition rate believed to exist between the two forms. No large difference in pressure was anticipated. We have regarded the experiment as one that could give evidence for but not against the existence of the two forms.

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[15] Schottky, *Physik. Z.*, 22, 1 (1921); 23, 9 (1922).

[16] Giauque, This Journal, 49, 1870 (1927).

It has been calculated that the entropy effect due to the existence of the two forms of hydrogen would be 4.39 ± 0.06 cal./deg. per mole. This amount must be added to that given by the Sackur equation or to that given by the ordinary application of the third law of thermodynamics. It does not appear possible to reconcile this addition with third law data unless a similar consideration, not necessarily leading to the same amount, is applied to molecules containing hydrogen. These effects may be expected in many, if not most, of the other elements.

We believe that any system approaches zero entropy as the absolute zero of temperature is approached when true equilibrium exists in the distribution of energy between such energy states as are actually occupied by the system. As a particular example, the cooling of a solution of isotopes is considered. Our conclusions are in complete agreement with the third law of thermodynamics as stated by Lewis and Gibson, although we recognize additional difficulties in the application of this law.

We wish to emphasize the distinction between the exactness of the third law of thermodynamics and our experimental inadequacy in using it directly.

BERKELEY, CALIRORNIA

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 182]

EQUILIBRIUM BETWEEN ALUMINUM CARBIDE AND NITROGEN AT HIGH TEMPERATURES

BY C. H. PRESCOTT, JR.[1] AND W. B. HINCKE

RECEIVED JULY 17,1928 PUBLISHED DECEMBER 10, 1928

Plan of the Investigation

The present work is a continuation of a program of research in the field of high-temperature equilibria involving the extension of our previous methods to cover a region of very low pressures. Measurements have been made of equilibrium pressures from 0.0016 mm. to 0.017 mm. at temperatures from 1774°K. to 1909°K. The McLeod gages now in use would cover the range up to 5 mm. The manometer technique previously devised has been used at pressures from 3 cm. to 2.3 atmospheres and at temperatures up to 2500°K. So the combined methods seem applicable to pressures differing by a factor of a million and at temperatures from 1000°K. to 2500°K. The most significant region probably lies above 1500°K. where more conventional technique is inapplicable.

The subject of the present work is the equilibrium of the system aluminum carbide, nitrogen, aluminum nitride and carbon. The equilibrium pressure of nitrogen may be approximately predicted by combining the

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[1] National Research Fellow in Chemistry.

results of Fraenkel[2] on the system aluminum oxide, carbon, nitrogen, aluminum nitride, with those of our own experiments on the system aluminum oxide, carbon, aluminum carbide and carbon monoxide.[3] These values have been verified by the present experiments. According to Fichter and Oesterheld[4] the sublimation of aluminum nitride accompanied by decomposition begins at 1870° under about 14 mm. of nitrogen. The chemistry of aluminum nitride has been thoroughly reviewed by Krase, Thompson and Yee.[5]

This investigation was aided financially from a grant made to Professor A. A. Noyes by the Carnegie Institution of Washington.

Apparatus and Procedure

The temperature measurements were made with an optical pyrometer. The details and corrections have already been described.[6]

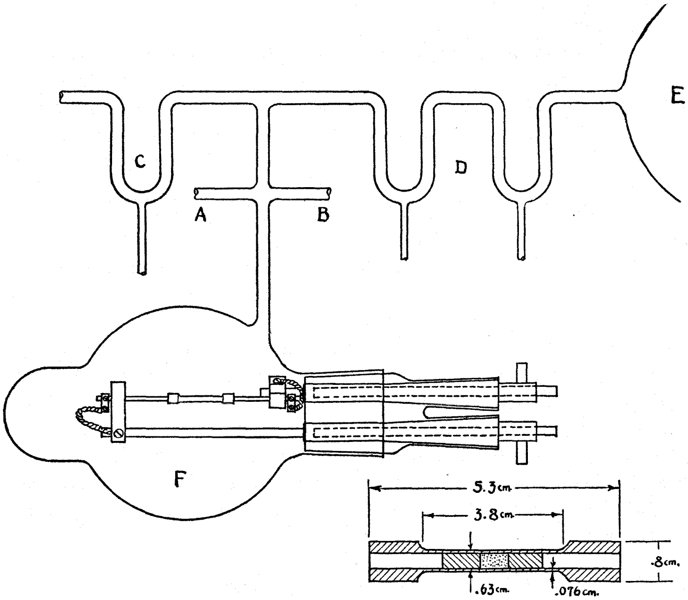

Fig. 1.—Apparatus for low pressure equilibria.

The furnace, shown in Fig. 1, was a tube of Acheson graphite 5.3 cm. long, 0.8 cm. in diameter at the ends, and 0.53 cm. in the central section for a length of 3.8 cm., with a 0.076 cm. wall. In the preliminary experiments a smaller furnace was used whose center was 0.032 cm. in diameter with a 0.04 cm. wall. A pellet of compressed aluminum and graphite powder about 0.4 cm. long was held in the center of the furnace by graphite

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[2] Fraenkel, *Z. Elektrochem.*, 19, 362 (1913).

[3] Prescott and Hincke, THIS JOURNAL, 49, 2753 (1927).

[4] Fichter and Oesterheld, *Z. Elektrochem.*, 21, 50 (1915).

[5] Krase, Thompson and Yee, *Ind. Eng. Chem.*, 18, 1287 (1926).

[6] Prescott and Hincke, THIS JOURNAL, 49, 2744 (1927); *Phys. Rev.*, 31, 130 (1928).

plugs. In the later experiments a groove was cut on either side of the center centimeter of the furnace to equalize the temperature gradient.

This furnace was supported horizontally on tungsten rods pressed into its ends, which rested on steel guides clamped to water-cooled copper leads. Electrical connection was made by flexible copper wire fastened to steel clamps on the ends of the tungsten rods. The outer ends of the water-cooled leads were tapered to fit ground-glass seals in a Pyrex plug which in turn was ground to fit a 1-liter Pyrex flask. Seals were made with Dennison's banker's specie sealing wax. A plane glass window was waxed to the end of a **2.5-cm.** tube which projected 16 cm. from the side of the flask, as the flask itself became clouded with a mirror of metallic aluminum. This was developed from apparatus used in preliminary studies on zirconium oxide and carbon.[7]

The flask (F) was connected through a mercury cut-off (C) to a single-stage mercury diffusion pump backed by a Hyvac oil pump. Two mercury cut-offs (D) connected to a 3-liter flask (E) which served as a nitrogen reservoir. Small amounts of nitrogen were introduced by alternately opening the two cut-offs. Tube A led to a Toepler pump which withdrew samples of gas for analysis.[8] Tube B led to two McLeod gages with a combined range from 10^{-4} to 5 mm. Their volumes were as small as possible, 50 and 7 cc., to minimize dead space.

In the procedure finally adopted the whole apparatus was evacuated and the furnace run for a moment at 1500°K. to drive off a part of the adsorbed gases. Hydrogen was next introduced to one atmosphere and the furnace run at 1880°K. for one hour. This baked off the remaining gases, formed the aluminum carbide and partially sintered it, reducing the amount of metallic aluminum which vaporized later. It also helped bake out the Pyrex flask. The apparatus was next evacuated and filled to 6 cm. of nitrogen and the furnace run at 1880°K. for from thirty minutes to three hours to change some of the carbide to nitride. It was again evacuated and a stream of tap water turned on at the top of the flask which completely enveloped it and kept it cold while equilibrium measurements were taken. After this treatment the evolved gases were from 97 to 101% nitrogen as compared to 10% without the stream of water. The gases evolved from the walls were chiefly hydrogen and carbon monoxide. The carbon monoxide probably came from water vapor which reacted with the carbon furnace. The hydrogen was too much in proportion to be accounted for in this way unless the water vapor also reacted with the aluminum on the walls.

For the preliminary baking the current was drawn from a 1-kw. transformer. During the measurements it was drawn from a storage battery. To maintain the larger size of furnace at 1880°K. required 100 amps. at 10 volts, though most of the power was lost in the leads.

The Equilibrium Measurements

The reacting material was in each case a pellet of Baker's analyzed metallic aluminum and Acheson graphite, each ground to pass 200 mesh, and mixed in proportions to form Al_4C_3 with a 10% excess of carbon to reduce any oxide which might be in the finely divided aluminum.

In the first significant experiment such a pellet was run for an hour at 1880°K. in one atmosphere of nitrogen. It was then removed and tested for combined nitrogen. A sample was digested in sodium hydroxide and vapors caught in 0.02 N hydrochloric acid as in a standard

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[7] Prescott, THIS JOURNAL, 48, **2534** (1926).

[8] Prescott, *ibid.*, **50**, **3237** (1928).

Kjeldahl determination. Further samples were run under reduced pressures of nitrogen down to 1 mm. All showed a considerable proportion of combined nitrogen.

The first equilibrium measurements were made on small furnaces with no cooling water on the flask. Ten times as much interfering gases were evolved as of the nitrogen under consideration. At each temperature several runs were made of an hour's duration, starting each at a different pressure of nitrogen. The final nitrogen pressure was obtained by an analysis of the gases. From the several values of the change of pressure it was possible roughly to interpolate for the equilibrium pressure. The values obtained with two different furnaces are plotted as points in triangles in Fig. 2, a graph where one scale is proportional to the logarithm of the equilibrium pressure in millimeters, and the other is proportional to the reciprocal temperature. A blank run, however, indicated that some nitrogen was also evolved from an empty furnace, of the same order of magnitude as the former pressure changes, so the results are rather dubious. To get sufficient material the pellets were made about 0.6 cm. long and at the conclusion of each series little aluminum remained except at the ends of the original pellet, a region probably at lower temperature than the maximum temperature where the pyrometer was sighted. In view of such uncertainties these measurements are of little weight in comparison with later determinations under better conditions.

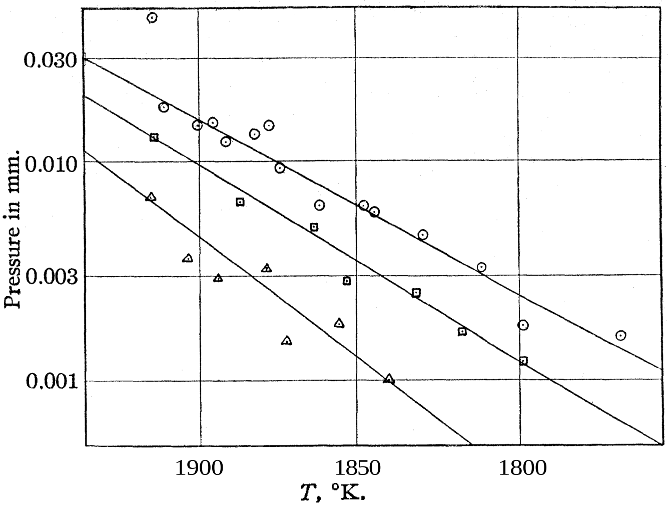
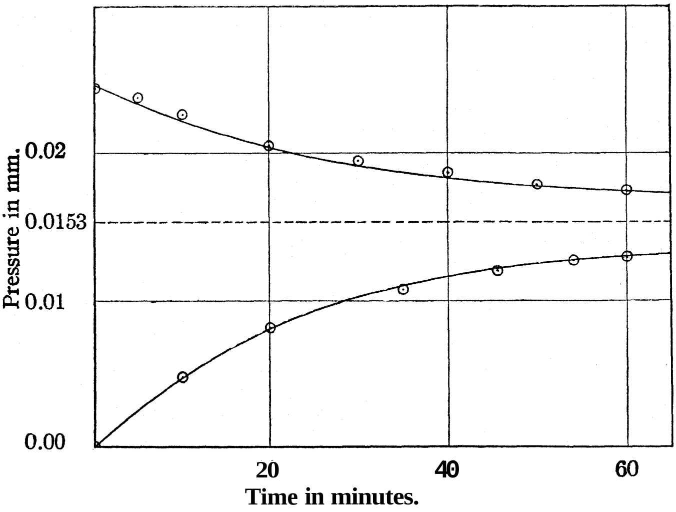


Fig. 2.—Preliminary and final results. Log P, $= 12.772 - 27697/T$.

The next measurements were a series of runs on a single large furnace after preliminary baking in hydrogen and with cooling water on the flask.

The interfering gases dropped to a few per cent. and it was possible at once to follow the changes in nitrogen pressure on the McLeod gages, so that two runs of one hour each were sufficient to determine an equilibrium pressure. The results are plotted as points in squares in Fig. 2. It was noticed in assembling that the contact between one tungsten rod and the furnace was quite loose. It was also noticed that this contact ran rather hotter than the other. Unfortunately the pyrometer was still sighted at the maximum of temperature, which, due to the unsymmetrical heating, probably did not coincide with the geometrical center of the furnace where the charge was located. The discrepancy between these and the later results would be equivalent to a temperature error of 36°.



Pig. 3.

With the next furnace the loose contact was eliminated and in two later furnaces grooves were cut to equalize the temperature gradient along the middle portion of the furnace. The pyrometer was sighted at the geometrical center where the charge was definitely located. Fig. 3 is a typical example of two runs which determined an equilibrium pressure. The furnace was run for ten minutes on the pumps. The mercury cut-off C was then released and the pressure rose as shown in the lower curve of the figure. After an hour the current was turned off and the gas pumped off for analysis.[8] Cut-off C was (Fig. 1) lowered and the flask evacuated. It was again raised and nitrogen introduced from the reservoir E to twice the final pressure of the previous run. The furnace was then run for an hour, the pressure falling as shown in the upper curve of the figure. This gas was also pumped off for analysis. In this case both contained 98.5% nitrogen. The two final pressures were corrected and their average taken as the equilibrium pressure: 0.0150 mm. at 1895°K. The broken line on the figure is the average of the uncorrected pressures. The equilibrium values obtained from these three furnaces are plotted as points in circles in Fig. 2 and also in Fig. 4 by themselves.

Anomalous results were obtained from two furnaces in cases where mercury was spilled into the furnace flask before the baking in nitrogen. Nitrogen was evolved at pressures up to one-half millimeter. In the one case which was thoroughly studied reverse rates were at first obtained above this pressure, but later no absorption of nitrogen occurred. Upon removal and analysis of the pellet the nitrogen content was found to be just slightly less than that corresponding to the formation of AlN. This indicated the absence of any aluminum compound higher in nitrogen content. On keeping mercury out of the furnace flask no further trouble resulted. The formation of a nitride of mercury is improbable, so the effect is probably due to adsorption on the finely divided material which distilled around. This gave off gas during the runs, the absorption of nitrogen going on until all of the aluminum carbide present was converted to nitride. It should be noted that mercury vapor was always present at about 10^{-3} mm. from the various traps and gages but never figured in any of the McLeod gage readings of gas pressure.

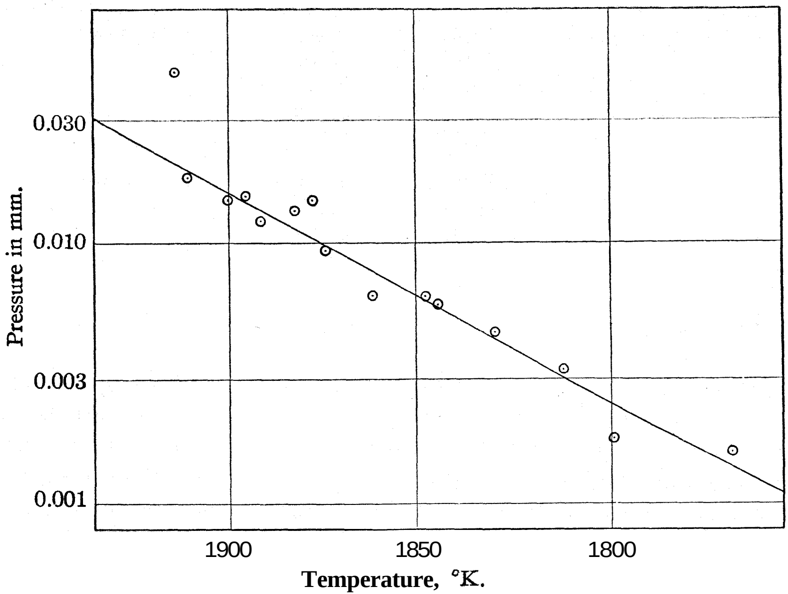


Fig. 4.—$4AlN + 3C = Al_4C_3 + 2N_2$. $\log P_{mm.} = 12.772 - 27697/T$.

Results of the Measurements

The most certain and reproducible results are those plotted in Fig. 4.

The same data are recorded in Table I, together with the duration of the initial baking in nitrogen.

TABLE I

EQUILIBRIUM PRESSURES AND TEMPERATURES

Furnace	Detn.	Temp., °K.	Press., mm.	Time of nitrification
A	1	1895	0.01503	145 minutes
	2	1874	.00954	
	3	1850	.00622	
	4	1829	.00458	
	5	1877	.01453	
B	1	1884	.01334	60 minutes
	2	1845	.00582	
	3	1813	.00325	
	4	1774	.00158	
	5[a]	1915	.0455	
C	1	1891	.01215	30 minutes
	2	1901	.01461	
	3	1909	.01732	
	4	1799	.00176	
	5	1862	.00612	

[a] Discarded.

According to the times of nitrification furnace A should have had the highest nitrogen content and C the lowest. This accords with the fact that the final determinations on furnaces A and B fell high, and on furnace C low, although the initial determinations are in very excellent agreement. As material volatilized from the pellet, either carbide or nitride would tend to be exhausted as both were appreciably volatile. The trend of the equilibrium pressures might indicate a slight dependence on concentration effects due to mutual solubility of the solid phases, but is more probably a dynamic effect depending on the methods of measurement. In a true equilibrium state forward and reverse reaction velocities must be equal, and both will occur simultaneously at the same solid interface. When an observable reaction occurs, however, the interface will spread into the reacting material, so the area of the interface and the net over-all velocity of reaction will depend to some extent on the mass of the reacting material. This dependence will decrease the closer approach is made to equilibrium conditions, but will always influence equilibrium measurements derived from the interpolation of finite velocities of reaction, particularly when materials become exhausted.

This might be a valid reason for rejecting such a determination as B 5, the last of its series. A least-square solution of the data in Table I gave a probable error corresponding to an 18% deviation in the pressure. On account of its large deviation the point B 5 could be rejected in accordance with established principles from the laws of probability.[9] A least square solution of the remaining data for the constants of the linear relation shown in Fig. 4 gave the result where log p is the common logarithm of the pressure in millimeters and T the absolute temperature

$$\text{Log } p_{\text{mm.}} = 12.772 - 27697/T$$

Or for the pressure in atmospheres

$$\text{Log } p_{\text{atm.}} = 9.891 - 27697/T$$

with a probable error corresponding to an 11% deviation in the pressure, which is equivalent to 5.8° in the temperature measurements.

In reading pressures, particularly with a McLeod gage, the errors to be expected will be roughly proportional to the pressure, so the weights of observations will be most nearly equal when expressed on a logarithmic scale. Also, in matching light intensities, by Weber's law a difference in visual sensation corresponds to a change in the logarithm of the energy intensity. By the Wien radiation law

$$\frac{1}{T} - \frac{1}{T'} = \frac{\lambda \ln \epsilon}{c_2}$$

Here ϵ would correspond to the ratio of intensities, the logarithm of the ratio of intensities being proportional to the difference in the reciprocal temperature. So the weights of observations should be most nearly equal in the scale adopted, that of the logarithm of the pressure against the reciprocal temperature. Also, since the van't Hoff equation predicts a linear relation for small changes of the heat of reaction, this is the most convenient scale for the adjustment of observations.

$$2.303 \log K = -\frac{AH}{RT} + \text{const.}$$

Thermodynamic Calculations

The equation expressing the chemical reaction involved is

$$4AlN + 3C = Al_4C_3 + 2N2$$

We may now proceed to calculate the free-energy increase (AF) and the heat-content increase (ΔH) attending this reaction when the nitrogen pressure is one atmosphere.

The value of AF may be derived from the equilibrium pressure p by the familiar thermodynamic equation $AFo = -RT$ In K, where $K = p^2$. From the determination of the equilibrium pressure p tabulated in Table I, we thus obtained the values given in Table II.

From the expressions for $\log_{10} p$ derived in the same section we similarly obtain the relations, AFo = 253,630 − 90.58 T, and ΔH = 253,630 calories. At 1875°K. the equilibrium pressure is 0.0100 mm. and the free-energy change is 83,800 calories.

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[9] Meniman, "Method of Least Squares," John Wiley and Sons, Inc., New York, 1911, p. 166.

TABLE II

FREE-ENERGY INCREASE ATTENDING THE REACTION

Temp., T, °K.	1909	1901	1895	1891	1884	1877	1874
AF°, cal.	81150	82150	81700	83100	82100	81200	84100
Temp., T, °K.	1862	1850	1845	1829	1813	1799	1774
$\Delta F°$, cal.	86900	86300	86500	87500	89100	92800	92400

The molal heat capacities, (C_p), of graphite and nitrogen were taken from Lewis and Randall,[10] and those for aluminum carbide and nitride estimated from Kopp's law according to the scheme given in Noyes and Sherrill,[11] taking the atomic heat of nitrogen as 2.9, the mean of carbon and oxygen.

For C $C_p = 1.1 + 0.0048T - 0.0000012T^2$
For N_2 $C_p = 6.50 + 0.0010T$
For Al_4C_3 $C_p = 30.2$
Por AlN $C_p = 9.1$

From the above-mentioned heat of reaction and the value of the free-energy change at 1875°K., the following equations are obtained and from them by extrapolation the following values at room temperature

$$AH = 260{,}954 + 3.5T - 0.0062T^2 + 0.0000012T^3$$
$$\Delta F° = 260{,}954 - 3.5T \ln T + 0.0062T^2 - 0.0000006T^3 - 77.621T$$
$$\Delta H_{298} = 261{,}478 \text{ cal.} \qquad \Delta F°_{298} = 232{,}406 \text{ cal.}$$

From these values and the values for the formation of aluminum carbide given by Prescott and Hincke[12] values may be calculated for the formation of aluminum nitride from its elements.

$$2N_2 + Al_4C_3 = 4AlN + 3C \qquad \Delta H_{298} = -261{,}478 \qquad \Delta F°_{298} = -232{,}406$$
$$4Al + 3C = Al_4C_3 \qquad = -60{,}260 \qquad = -53{,}240$$
$$Al + {}^1/_2N_2 = AlN \qquad = -80{,}434 \qquad = -71{,}411$$

By combining equations for the oxide–carbide equilibrium[i2] with those for the carbide–nitride equilibrium given above, the following relations are obtained for the reaction involving the simultaneous reduction and nitrification of aluminum oxide

$$Al_2O_3 + 3C + N_2 = 2AlN + 3CO$$
$$\log K = 14.74 - 27743T \qquad K = p^3_{CO}/p_{N_2}$$
$$AF° = 127{,}065 - 67.5T \qquad AH = 127{,}065 \text{ cal.}$$
$$AH = 138{,}178 + 3.5T - 0.0062T^2 + 0.0000012T^3$$
$$AF° = 138{,}178 - 3.5T \ln T + 0.0062T^2 - 0.0000006T^3 - 56.385T$$
$$\Delta H_{298} = 138{,}711 \text{ cal.} \qquad \Delta F°_{298} = 115{,}947 \text{ cal.}$$

From the above equation the values of the equilibrium constant at 1500 and 1600° are, respectively, 0.123 and 0.851. For a total pressure of one

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[10] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, **1923**, pp. 80, 569, 576.

[11] Noyes and Sherrill, "Chemical Principles," Macmillan Co., New York, **1922**, p. 93.

[12] Prescott and Hincke, THIS JOURNAL, **49**, 2753 (1927).

atmosphere the fraction of carbon monoxide in an equilibrium mixture would be 41.6 and 66.0%. These values are on the upper limits which Fraenkel[2] assigned from his study of this reaction: 25 – 40% at 1500° and 50 – 65% at 1600°.

Summary

Apparatus has been devised and methods have been extended for the study of chemical equilibria at incandescent temperatures at pressures of 0.01 mm. Determinations were made for the reaction $4A1N + 3C = Al_4C_3 + 2N_2$. The increases in free energy and heat content that would attend this reaction between 1775°K. and 1910°K. at one atmosphere pressure were found to be those given by the equations $AF^o = 253,630 - 90.58T$, and $\Delta H =$ 253,630 cal. At 1875°K. the equilibrium pressure is 0.0100 mm. and the free-energy change is 83,800 calories.

Calculations have been made for the reaction $Al_2O_3 + 3C + N_2 = 2A1N + 3CO$. The corresponding equations are $AF^o = 127,065 - 67.51"$ and A H = 127,065 cal, These values are in agreement with the observations of Fraenkel on this reaction.

PASADENA, CALIFORNIA

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 183]

APPARATUS FOR MICRO GAS ANALYSIS

BY C. H. PRESCOTT, JR.[1]

RECEIVED JULY 17, 1928 PUBLISHED DECEMBER 10, 1928

In connection with measurements on the equilibrium between aluminum carbide and nitrogen[2] it was necessary to analyze quite small quantities of gas to determine the partial pressure of nitrogen. Langmuir[3] has briefly described methods by which quantities of gas as small as one cubic millimeter at atmospheric pressure may be subjected to quantitative analysis. The author has seen this apparatus through the courtesy of Dr. Langmuir and recalls that the methods consisted in treating very small volumes of gas with aqueous reagents at atmospheric pressure.

In the present technique the gases are handled at low pressure over mercury using solid reagents. The volumes are of reasonable size and no gases need be introduced but those actually undergoing analysis. The methods would seem capable of a sensitivity at least as great as that indicated by Langmuir, though this has not been necessary for our present work. The apparatus was developed during one phase of the work on

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[1] National Research Fellow in Chemistry.

[2] Prescott and Hincke, THIS JOURNAL, 50,3228 (1928).

[3] Langmuir, *ibid.*, 40, 1378 (1918); *Ind.* Eng. *Chem.*, 20, 333 (1928).

zirconium oxide and carbon,[4] but was not used till recently for quantitative measurements.

The apparatus was designed to operate on samples whose volumes would be a third of a cubic centimeter or less at one atmosphere, and to determine carbon dioxide, carbon monoxide, hydrogen and nitrogen. The pressure in the absorption tubes usually started at less than two millimeters. The carbon dioxide was absorbed in soda lime; the carbon monoxide and hydrogen were oxidized by copper oxide at 250° and the water absorbed in phosphorus pentoxide; the carbon monoxide, now dioxide, was absorbed in soda lime, leaving the nitrogen. After each absorption the gas was collected and compressed to one of a series of graduations in a capillary pipet and the pressure measured on a comparison tube as in a pressure reading on a McLeod gage. The time necessary for each absorption and collection for measurement was about an hour. As only nitrogen was significant for our purposes and the soda lime absorbed both carbon dioxide and water, only one absorption was necessary in a routine analysis.

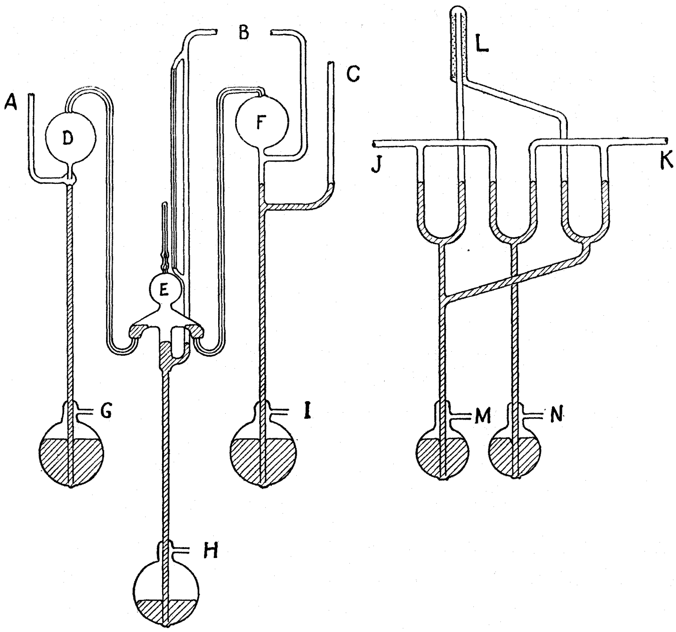

Fig. 1.—Gas analysis apparatus.

The arrangement of apparatus is shown in Fig. 1. The tube A is connected to the apparatus containing at low pressure the gas to be analyzed. A mercury diffusion pump is connected to C. The absorption train is inserted at B, one element of which is shown at the side. Suction is applied

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[4] Prescott, THIS JOURNAL, 48, 2534 (1926).

to H, I, M, N, etc., withdrawing the mercury from all the cut-offs, and the pipet and absorption train are evacuated to 10^{-4} mm. through the tube C. The suction is then released and by applying compressed air at G the Toepler pump D drives a sample of gas into the pipet E. The sample is compressed into the capillary by applying pressure at H, and its pressure–volume product measured. Suction is next applied at H, allowing the gas to flow up the comparison tube and through the absorption train to the pump F. The pump is operated by applying pressure at I and the gas circulated by pumping back into E. The contraction and expansion of volume resulting helps to clear the dead space in E. The suction at H is then released and the gas pumped back into the pipet and measured. The absorption tubes are each located as at I, and connected in series by the tubes J and K, etc. To pass the gas through a tube, suction is applied at M, withdrawing the mercury below the two cut-offs. To by-pass the gas around a tube suction is applied at N, releasing the suction at M. To clear the apparatus all the cut-offs are lowered as before and the gas escapes through C.

One absorption tube (L) contained $^1/_3$ g. of copper oxide, which was calculated to be sufficient for several thousand analyses. The next contained 1.2 g. of soda lime and the last about 0.6 g. of phosphorus pentoxide mixed with powdered pumice stone. These were baked in *vacuo* to the softening point of the Pyrex glass to drive off adsorbed gases. No gas could then be pumped off the copper oxide or soda-lime when they were cold. A little could be obtained from the phosphorus pentoxide and pumice stone. By circulating until there was no further absorption, it was determined that twenty cycles of the pump was sufficient. Fifteen cycles sufficed to recover the unabsorbed gas.

On several samples of pure nitrogen initial and final readings checked to the same scale division (0.3%). Absorption of hydrogen and carbon monoxide were practically complete. Analyses were made on two known mixtures of carbon monoxide and nitrogen. The composition was initially determined from pressures measured in the rest of the apparatus with a McLeod gage. A small correction was made for 0.23% nitrogen in the carbon monoxide. The results of the analyses are shown in Table I. The

TABLE I

RESULTS OF GAS ANALYSES

PV, cc. mm		Composition by analysis		Composition by synthesis	
Initial	Final	N_2, %	CO, %	N_2, %	CO, %
91.5	27.05	29.6	70.4	29.7	70.3
21.98	6.56	29.8	70.2	29.7	70.3
7.59	2.41	31.7	68.3	29.7	70.3
130.0	11.99	9.23	90.77	9.16	90.84
383.0	35.1	9.18	90.82	9.16	90.84
10.63	0.986	9.27	90.73	9.16	90.84

quantities are expressed in cubic centimeters at a pressure of one millimeter of mercury.

The author desires to express his appreciation of the assistance of Mr. W. B. Hincke in making the measurements involved in these experiments. The work was aided financially by a grant from the Carnegie Institution of Washington made to Professor A. A. Noyes.

PASADENA, CALIFORNIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OR THE UNIVERSITY OF WYOMING]

THE DECOMPOSITION OF FORMIC ACID BY SULFURIC ACID. II[1]

BY ERNEST R. SCHIERZ AND HENRY T. WARD

RECEIVED JULY 23, 1928 PUBLISHED DECEMBER 10, 1928

Introduction

In a previous paper by one of the authors[2] it was found that the velocity of decomposition of formic acid in sulfuric acid showed some irregularities when the concentration of sulfuric acid was 91.8%. Knietsch[3] found that specific conductance, melting point and viscosity do not increase continuously on progressive dilution of sulfuric acid. Abnormal values for these properties occur in the range of concentration 92–93.5%.

The present investigation was undertaken to determine the velocity constants for the rate of decomposition of formic acid for various concentrations of sulfuric acid from 85–97% at temperatures of 15, 25, 35 and 45° and to observe whether the irregularity referred to above existed at other concentrations.

Experimental Part

Preparation and Purification of Materials.—The formic acid and the sulfuric acid were prepared by the same methods as those previously used. The formic acid distilled at 25.0–25.5° at 37-38 mm.; $d^{20} = 1.220$; refractive index (Abbé) $n_D^{20} = 1.3708$ and melted at 8°.

Apparatus.—The apparatus used was modified to a slight extent only. The measuring burets were of 100-cc. capacity so that it would not be necessary to use a smaller amount of formic acid. The volume of carbon monoxide evolved from 0.07 cc. of formic acid was about 63 cc. at 45° and the prevailing average pressure 585 mm.

The Effect of Water on the Decomposition of Formic Acid by Sulfuric Acid.—The effect of water on the velocity of the reaction was determined by proceeding in the same manner as in the previous investigation, using like amounts of reagents. The results are summarized in Table I. In

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[1] The work included in this paper is from the thesis presented by Henry T. Ward in partial fulfilment of the requirements for the degree of Master of Science at the University of Wyoming.

[2] Schierz, THIS JOURNAL, 45, 447 (1923).

[3] Knietsch, Ber., 34, 4089 (1901).

order to conserve space, the values of 0.4343 K, the velocity constants calculated from the equation for unimolecular reaction, were each multiplied by SO^3 and entered in the table as K_s. The table contains some

TABLE I

DECOMPOSITION OF FORMIC ACID BY SULFURIC ACID WITH VARIOUS CONCENTRATIONS OF SULFURIC ACID AT SEVERAL TEMPERATURES

	K_s			
H_2SO_4, %	15°	25°	35°	45°
96.69	28.5	91.5	312 (300)*	810 (975)*
94.40	10.4	33.5	106	280 (330)*
92.78	5.1	16.6	53.5	159
91.49	2.7	8.9	28.7	86.2
89.53	1.2*	4.0	13.1	41.4
85.52	0.24*	0.78*	2.5	7.8

values which have been obtained by graphical extrapolation. According to Rice[4] the graphical representation of the logarithm of velocity constants plotted against reciprocal of absolute temperature, for each concentration of sulfuric acid, should be a straight line or nearly so. In cases where the reaction was too slow to measure, extrapolated values, indicated by an asterisk, are inserted in the table; where the velocity was very great (more than half of the total volume of carbon monoxide, 51 cc., being evolved in the first fifteen seconds), both determined and extrapolated values are given.

The values from Table I are shown graphically in Fig. 1. It will be seen that for like concentrations of sulfuric acid the effect of small amounts of water becomes more marked as the temperature at which decomposition occurs increases. For the addition of 1% of water to the sulfuric acid (diluting from 93 to 92%) in the decomposition of formic acid, the constant changes from 19 to 12 (obtained from interpolation on Fig. 1) at 25" and from 175 to 113 at 45°.

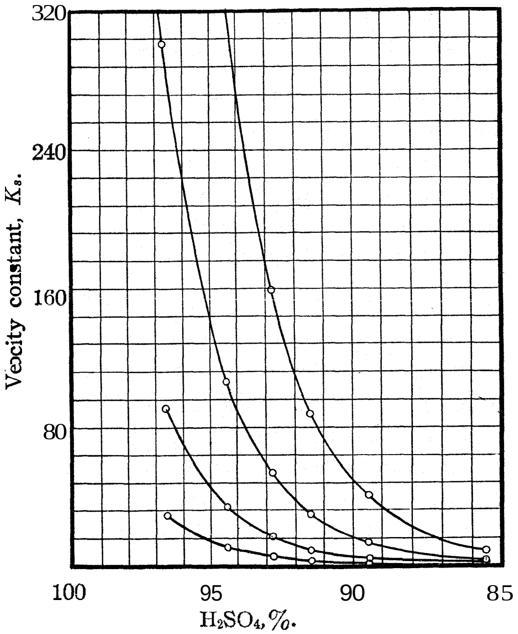

Fig. 1.

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[4] Rice in Taylor, "A Treatise on Physical Chemistry," D. Van Nostrand Co., Inc., New York, 1924, p. 885.

The Effect of Temperature on the Reaction.—The temperature coefficients for 10° intervals have been calculated from the velocity constants at the various temperatures for all of the concentrations of sulfuric acid used. The effect of temperature is summarized in Table II. It will be seen that in general these values decrease as the velocity of reaction increases and that the irregularity found by Schierz[2] has not been found at these concentrations.

The values for E (critical increment) calculated from the integrated form of the simple Arrhenius[5] equation for various temperature intervals are shown in Table II.

TABLE II

TEMPERATURE COEFFICIENTS AND VALUES OR E FOR THE DECOMPOSITION OR FORMIC ACID BY VARIOUS CONCENTRATIONS OF SULFURIC ACID

H_2SO_4, %	K_{25}/K_{15}	E (calcd.)	K_{35}/K_{25}	E (calcd.)	K_{45}/K_{35}	E (calcd.)
96.69	322	19,920	3.27	21,600	325	22,900
94.40	3.22	19,920	3.17	21,420	3.12	22,200
92.78	3.25	20,080	3.22	21,350	2.98	21,300
91.49	3.29	20,310	3.23	21,400	3.10	22,080
89.53	3.33	20,500	3.28	21,650	3.16	22,410
85.52	3.3	20,900	3.2	21,210	3.12	22,200

An examination of these values shows that they are all very nearly the same for any one temperature interval and that there is a general tendency to increase but slightly with increase in temperature. This constancy is in agreement with the work of Essex and Gelormini[6] and Daniels and Johnston,' who conclude that for isolated reactions the critical increment is independent of the temperature.

Conclusions

The results of this investigation, in which the reaction was allowed to proceed at higher temperatures for the more concentrated sulfuric acid, indicate that under these conditions also the role of sulfuric acid is primarily that of a dehydrating agent.

The curves (Fig. 1) show that the change in velocity constant as a function of the percentage composition of sulfuric acid is continuous.

Lichty[8] found the same relation to obtain in his study of the decomposition of oxalic acid by sulfuric acid.

The value of the velocity constant obtained by Schierz for concentration 91.8% (at which the irregularity was noticed) falls on the curve for 25°.

Summary

1. The velocity of decomposition of formic acid by sulfuric acid has

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

[6] Essex and Gelormini, THIS JOURNAL, 48,882 (1926).

[7] Daniels and Johnston, *ibid.*, 43, 53 (1921).

[8] Lichty, J. Phys. Chem., 11,225 (1914).

been measured using the following concentrations of sulfuric acid: 85.52, 89.53, 91.49, 92.78, 94.40 and 96.69% at 15, 25, 35 and 45°.

2, The temperature coefficients have been given. They decrease in magnitude as the velocity constant increases.

3. The values for E (critical increment) have been calculated and found to be nearly equal for all concentrations at the temperature intervals 25°/15°, 35°/25° and 45°/35°.

4. For equal concentrations of sulfuric acid, the effect of small quantities of water becomes more marked with increase in temperature.

5. No irregularities in velocity constants or temperature coefficients were observed in the temperatures and concentrations studied.

LARAMIE, WYOMING

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

THE USE OF POTASSIUM IODATE IN BACK TITRATION FOR THE DETERMINATION OF THE HYPOCHLORITE CONTENT OF SOLUTIONS

BY JOHN R. LEWIS AND R. F. KLOCKOW

RECEIVED AUGUST 2, 1928 PUBLISHED DECEMBER 10, 1928

Volumetric iodate methods for the analysis of a variety of substances have been collected and published by Jamieson.[1] While searching the literature for methods of analyzing sodium hypochlorite solutions, it occurred to the authors that potassium iodate may also be used here. When a standard arsenite, thiosulfate or iodide solution was used in excess to reduce the hypochlorite, it was found that the excess could be determined by titration with potassium iodate according to the method described by Jamieson for the determination of hydrogen peroxide.

Method I (Sodium Arsenite Method).—To a known excess of standard arsenite is added a measured volume of hypochlorite. The unoxidized excess is then titrated with 0.1 N iodate in the presence of at least 12% hydrochloric acid. The results are accurate in the presence of small amounts of nitrate or chlorate.

Method **II** (Sodium Thiosulfate Method).—This method is based upon the fact that sodium hypochlorite oxidizes sodium thiosulfate to sulfate in an acid solution.[2] The titration mixture should be cooled in an ice-bath before adding the iodate. It makes no difference whether the hypochlorite is added to the acid or neutral solution of the thiosulfate. Results are not concordant in the presence of chlorate.

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[1] George S. Jamieson, "Volumetric Iodate Methods," The Chemical Catalog Co., Inc., New York, 1926.

[2] Dienert and Wandenbulcke, *Ann. chim. anal. chim. appl.*, 2, 106 (1920).

Method III (Iodide Method).—In this method the hypochlorite is reduced with potassium iodide. The mixture should be cooled in ice water before titrating with iodate. Chlorate interferes.

TABLE I

RESULTS

No.	NaClO by $Na_2S_2O_3$–I method, g.	NaClO by Method I, g.	NaClO by Method II, g.	NaClO by Method III, g.
1	0.0549	0.0545	0.0546	...
2	.0397	.0396	.0394	...
3	.0134	.0132	.0836	...
4	.0286	.0285	.0285	...
5	.0687	.0689	.0686	...
6	.0667		...	0.0664
7	.0694		...	.0693
8	.0675		...	.0672

Summary

Hypochlorite was determined by reducing with an excess of arsenite, thiosulfate or iodide and titrating the excess with iodate.

MADISON, WISCONSIN

THE GASEOUS EXPLOSIVE REACTION AT CONSTANT PRESSURE. THE EFFECT OF INERT GASES[1]

BY F. W. STEVENS

RECEIVED AUGUST 3, 1928 PUBLISHED DECEMBER 10, 1928

Thermodynamics

The effect of inert gases upon the thermodynamic equilibrium of gaseous explosive reactions has received extended consideration from Nernst and his pupils,[2] who employed in their investigations a spherical bomb of constant volume with central ignition. This series of studies extended to temperatures of over 3000" Abs. and formed part of the most extensive investigation of gaseous reactions involving the equilibrium products of combustion, carbon dioxide and water vapor that has yet been carried out. "No other chemical equilibrium has so far been investigated by so many methods which can also be controlled at the same time by thermodynamic calculations. . . . A specially high value must be attached to explosion methods since by suitable variations of the experimental conditions it enables both the specific heats and the equilibrium to be determined."[3]

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[1] Published by permission of the Director of the National Bureau of Standards of the U. S. Department of Commerce.

[2] (a) Pier, *Z. Elektrochem.*, 15, 536 (1909); (b) **16,** 897 (1910); (c) Bjerrum, *ibid.*, **17,** 731 (1911); (d) 18, 101 (1912); (e) *Z. physik. Chem.*, **79,** 513, 537 (1912); (f) **81,** 284 (1913); (g) Siegel, *ibid.*, **87,** 641 (1914).

[3] Nernst, "Theoretical Chemistry," Macmillan Company, New York, 10th ed., 1923, p. 783.

The accuracy of explosion methods as employed by the investigators mentioned depends upon the favorable symmetry automatically assumed by the gross mechanism of the gaseous explosive reaction. The sharply localized zone of explosive reaction originating at the spark gap at the center of the spherical bomb is propagated in all directions from this point, as are also the sound and impulse waves resulting from it. Thus the zone of explosive reaction marked by flame and the disturbances and their reflections resulting from it, maintain during the reaction positions symmetrical with the spherical bomb. The equilibrium products of combustion thus remain enclosed within an expanding spherical shell of flame and are thereby protected as well as may be from heat losses due to the walls of the container till the end of the reaction and the attainment of maximum pressure. The maximum pressure of the equilibrium products filling the bomb at the instant the reaction is completed, corresponds to the equilibrium constant of the reaction

$$K = \frac{[A']^{n'_1}\,[B']^{n'_2}\,[C']^{n'_3}\ldots}{[A]^{n_1}\,[B]^{n_2}\,[C]^{n_3}\,\ldots.} \qquad (1)$$

Pier[4] has shown that the deviation from this constant due to the presence of an inert gas permits the specific heat of that gas to be determined at reaction temperature; and Siegel[5] has shown that from a knowledge of the pressure of the bomb and the reaction constant the degree of dissociation of combustion products may be found. For example, in the case of the trimolecular explosive reaction, $2CO + O_2 \qquad 2CO_2$, Equation 1 may be written for constant volume conditions

$$K = \frac{[CO]^2\,[O_2]}{[CO_2]^2} \qquad (2)$$

and if x is the degree of dissociation of carbon dioxide, then

$$K = \frac{[CO]^2\,[O_2]}{[CO_2]^2} = \frac{P}{2RT} \times \frac{x^3}{(1-x)^2\left(1+\frac{x}{2}\right)} \qquad (3)$$

In a previous communication[6] a simple device was described that was found to function as a bomb of constant pressure; it thus provides the complement to the bomb of constant volume referred to above. It expresses the initial and final condition of the explosive reaction in terms of volume at constant pressure instead of pressure at constant volume. The thermodynamic relation between the two forms of device is expressed in the equation of state, $pv = nRT$.

Besides the advantages attending the use of constant pressure methods as applied to'thermodynamic studies of gaseous explosive reactions, the experimental procedure in the use of the constant pressure bomb has the

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[4] Ref. 2 a, p. 538.

[5] Ref. 2 g, p. 654.

[6] Stevens, THIS JOURNAL, 48, 1896 (1926).

advantage of being unusually simple and direct. The labor and care necessary in evacuating and recharging a bomb of constant volume and of securing constant initial pressures and temperatures in the operations are tedious and time consuming. In the use of the constant pressure device and method these difficulties are practically eliminated. It is not difficult, using this device, to secure fifteen or twenty reaction records, giving initial and final volumes at constant pressure, within an hour. By securing so large a number of observations there is the advantage of using average results in computations.

The term volume here used in connection with the constant pressure bomb does not refer, as it does in the case of the constant volume bomb, to the actual volume of the temporary soap film container. The symmetry of form and movement automatically assumed by the reaction zone in the case of a homogeneous mixture of explosive gases fired from a point and under conditions of constant pressure, offers a much more accurate way of determining initial and final volumes involved in the transformation. The zone of explosive reaction originating at a point within a homogeneous mixture of explosive gases maintained at a constant pressure advances in all directions from this point at a constant linear speed. It thus forms an expanding spherical shell of flame that remains concentric with the point of ignition till the end of the reaction. This sphere of reaction products enclosed by the reaction zone is thus protected as well as may be from heat losses during the reaction, due to conduction and convection. By reference to Fig. 1 it will be seen that the initial volume of active gases whose transformation is photographically followed by the method used, is the volume of an ideal sphere 2r determined by the horizontal diameter of the container passing through the point of ignition and not the actual volume of the container itself, for this is never a sphere. The final volume is this initial volume transformed at a uniform linear rate into the sphere of equilibrium reaction products, $2r'$. The continuous volume changes during this reaction are recorded photographically together with time intervals of a calibrated fork.

The final volume represented by r'—as does the final pressure in the case of a constant volume bomb—corresponds to the equilibrium constant, K, of the reaction (Equation 1). Likewise the other thermodynamic relations characteristic of the reaction at constant volume conditions are expressible for conditions of constant pressure.

The conditions that determine uniform flame movement in a gaseous explosive reaction, whether for the slower reaction rates or for the more rapid rates of the Berthelot explosive wave, are a homogeneous mixture of the explosive gases and a constant pressure; for under these conditions only is it possible for the mass movement of the active gases and for their concentrations to remain constant during the reaction.

Kinetics

The photographic record (Fig. 1) of the gross mechanism and progress of the reaction at constant pressure, upon which equal time intervals have been impressed, is a time–volume record of the reaction and hence may provide some general information as to the kinetics of the gaseous explosive transformation.

If the rate of movement of the zone of explosive reaction is to be connected in any way with the rate of molecular transformation and hence with the rate of energy liberation, it is obvious that its rate should be determined relative to the active gases it is transforming and not relative to space. And it should likewise be recognized that unless the method employed makes it possible to follow the composition and concentrations of the active gases which the zone of explosive reaction is entering, a kinetic relation connecting the movement of the reaction zone with the composition and concentration of the explosive gases could hardly be expected to result from its use.

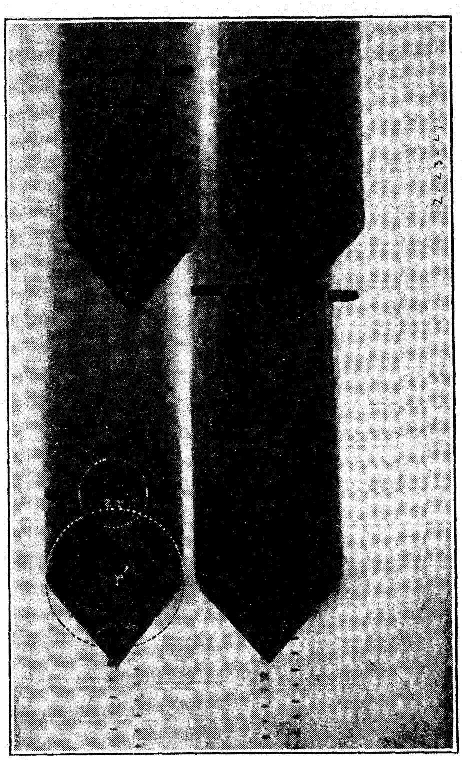

Fig. 1.—A reproduction of a photographic time–volume record of four gaseous explosions at constant pressure. $2r$ gives the dimensions of the sphere of initial active gases considered. $2r'$ the dimensions of the sphere of its reaction products at the instant the reaction is completed. Equal time intervals are recorded on the photographic film during the reaction process.

An examination of a great number of records similar to that reproduced in Fig. 1, obtained with different active gases at different concentration ratios, has shown that at constant pressure the rate of movement, s, of the zone of reaction, measured relative to the active gases, is constant and is proportional to the product of the initial concentrations (partial pressures) of those gases

$$s = k_1[A]^{n_1}\,[B]^{n_2}\,[C]^{n_3}\ldots. \qquad (4)$$

In this expression k_1 is a proportionality factor. The bracketed symbols represent initial concentrations or initial partial pressures of the active gases; their product expresses their impact probability, Γ; s is the linear rate of propagation of the reaction zone measured relative to the active gases it is entering.

It was of interest to examine the effect of inert gases on the rate of propagation of the zone of reaction in the light of the statistical relation expressed in (4) and by a method suggested by that employed by the investigators mentioned in determining the effect of inert gases upon the thermodynamic equilibrium. It is the purpose of this paper to record the results obtained in this endeavor.

Experimental Procedure

From the photographic figures of the progress of the reaction it will be seen that the constant rate of flame movement, s', in space may be determined at any instant during the transformation. It is equal to the radius, r'_i, at any instant divided by the time interval between ignition and the attainment of r'_i

$$s' = \frac{r'_i}{t} \tag{5}$$

But this is not the rate at which the flame is entering the gases. The rate, s, at which the flame is entering the gases may be found for the case of a spherical shell of flame expanding at uniform rate s' as follows.

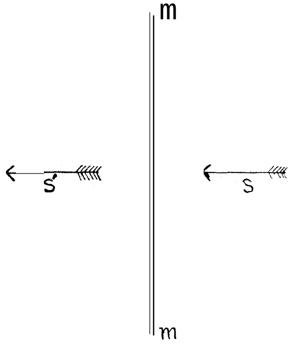

Fig. 2.

Let m, m, Fig. 2, be an element of the flame surface held at rest by the uniform flow s of the active gases against it; then s will be the rate at which the reaction zone enters the gases and s' will be the rate at which the transformed gases leave the flame area. If ρ and ρ' are the initial and final densities of the gases then from the equality of masses

$$\rho s = \rho' s' \tag{6}$$

For the case of the initial and final spheres in the reaction, we also have from the equality of masses

$$\frac{4\pi\rho r^3}{3} = \frac{4\pi\rho' r'^3}{3} \tag{7}$$

hence,

$$\frac{s}{r^3} = \frac{s'}{r'^3} \tag{8}$$

$$s = s' \frac{r^3}{r'^3} \tag{9}$$

For a test of these relations the gaseous explosive reaction at water vapor saturation

$$2CO + O_2 \rightleftharpoons 2CO_2 \tag{10}$$

was selected. For this special case Equation 4 may be written

$$s = k_1[CO]^2\,[O_2] \tag{11}$$

Including Equation 5

$$s = s' \frac{r^3}{r'^3} = k_1[\mathrm{CO}]^2\,[\mathrm{O_2}] \tag{12}$$

and

$$k_1 = \frac{r^3}{r'^2 t\,[\mathrm{CO}]^2\,[\mathrm{O_2}]} \tag{13}$$

Since the sum of the partial pressures of the gaseous components present in the reaction at pressure p must equal p, Equation 11 may be written for atmospheric pressure

$$s = k_1[\mathrm{CO}]^2\,[1 - \mathrm{CO}] \tag{14}$$

without designating the composition of the term [1–CO] further than to indicate that the sum of the partial pressures of its components remains the same as the partial pressure of the component $[\mathrm{O_2}]$ in Equation 11; and that under the same circumstances the products $[\mathrm{CO}]^2\,[\mathrm{O_2}]$ and $[\mathrm{CO}^2]$ [1–CO]'represent the same impact probability, Γ, though not the same proportion, k_1, of effective impacts nor the same potential energy. In case the component [1–CO] is made up of the fraction a of the active gas $\mathrm{O_2}$ and the fraction 1–a of some inactive gas, the partial pressure of the component [1–CO] may be expressed as

$$[1 - \mathrm{CO}] = \underset{\text{active}}{[1 - \mathrm{CO}]a} + \underset{\textbf{inert}}{[1 - \mathrm{CO}](1 - a)} \tag{15}$$

Equation 11 may then be written

$$s = k_1[\mathrm{CO}]^2\,[1 - \mathrm{CO}]a + k_1\,[\mathrm{CO}]^2\,[1 - \mathrm{CO}]\,(1 - a) \tag{16}$$

If, now, all of the impacts involving the inert gas are futile and the possible effect of its various physical properties, as specific heat, heat conductivity, etc., on the course of a thermal reaction be disregarded, then the last term in the above expression may be neglected and the effect on reaction probability of replacing the fraction $(1 - a)$ of an active gas by an inactive one be written

$$s = k_1[\mathrm{CO}]^2\,[1 - \mathrm{CO}]a \tag{17}$$

This expression takes into account the effect of the remaining active components only, and this is the major effect to be expected; but while the inert gas introduced may take no part in the molecular transformation, its presence in the zone of explosive reaction and in the active gases adjacent to it would naturally affect the heat distribution in that region. The effect of different inert gases upon the thermodynamic equilibrium is not the same; a quantitative estimate of their different effects permits their specific heats to be determined under the conditions resulting from the explosive reaction of the active gases. It might therefore be expected that the presence of inert gases in the zone of reaction would likewise have different effects upon the propagation of the reaction zone due to their individual characteristics.

In carrying out the observations the experiments were so arranged that the explosive transformation of the same partial pressures of the active gases, carbon monoxide and oxygen, could be observed on the same partial pressure of each of the inert gases used—and this over the entire range of mixture ratios of the gases that would ignite. The inert gases made use of were helium, argon, nitrogen and carbon dioxide. In the table below some of the physical properties of the gases involved in the transformations studied are set down. The values given for heat conductivity are taken from Taylor's "Treatise on Physical Chemistry," Vol. I, p. 92. The values for molecular heats are from Partington and Schilling, "Specific Heats of Gases."

Table I

Molecular Heats and Heat Conductivities of Gases Referred to in this Paper

Gas	He	A	N_2	O_2	CO.	CO_2
Mol. heat	5.07	5.07	6.90	6.90	6.90	9.0
Heat conductivity	336.0	39.0	56.6	57.0	54.2	33.7

Table II, below, gives results obtained for the $CO - O_2$ explosive reaction when no inert gas is present.

Table II

Experimental Results Obtained for the Rate of Flame Propagation in the $2CO + O_2$ Explosive Reaction at Constant Pressure

Record 9–7–27 No.	Partial pressure in atmospheres. [CO]	$[O_2]$	Γ $[CO]^2 [O_2]$	$s' = \frac{r_i}{t}$, cm./sec.	$s = s' \frac{r^3}{r'^3}$, cm./sec.	$k_1 = \frac{s}{\Gamma}$
1 to 3	0.224	0.776	0.0389	191	27.6	709
4 to 7	.260	.740	.0500	226	**34.7**	694
8 to 11	.279	.721	.0561	279	37.5	668
12 to 15	.310	.690	.0663	335	45.3	683
16 to 19	.325	.675	.0713	365	50.3	705
20 to 23	.359	.641	.0826	434	55.5	672
24 to 27	.388	.612	.0921	487	63.3	687
28 to 31	.416	.584	.1011	561	71.1	703
32 to 35	.460	.540	.1140	632	80.3	703
36 to 39	.491	.509	.1227	660	84.3	687
40 to 43	.523	.477	.1305	715	88.4	678
44 to 47	.574	.426	.1404	794	99.8	711
48 to 51	.622	.378	.1463	858	100.6	688
52 to 55	.688	.332	.1480	870	102.8	694
56 to 59	.726	.274	.1444	849	101.9	706
60 to 63	.775	.225	.1351	814	92.2	682
64 to 67	.810	.190	.1247	733	86.4	693
68 to 71	.840	.160	.1129	632	79.2	701
72 to 75	.848	.152	.1093	614	77.7	711
76 to 79	.883	.117	.0912	463	63.9	700
80 to 83	.903	.097	.0791	320	50.1	633
					Av. k_1	691

The results given in the above table may be expressed in graphic form by plotting the values of s as ordinates and either the corresponding partial pressures—shown in Fig. 3—or the corresponding values of $\Gamma = [CO]^2 [O_2]$, shown in Fig. 4 as abscissas. The method followed in Fig. **3** is the more familiar and will be used in expressing the results that follow. In Fig. **3** the observed values of $s = s'(r^3/r'^3)$ are represented by solid circles. Theoretical values of s, $s = k_1 [CO]^2 [O_2]$, are represented by open circles connected by a continuous line. This curve will be reproduced as a convenient reference in the other coordinate figures indicating the effect of inert gases on the CO — O_2 explosive reaction.

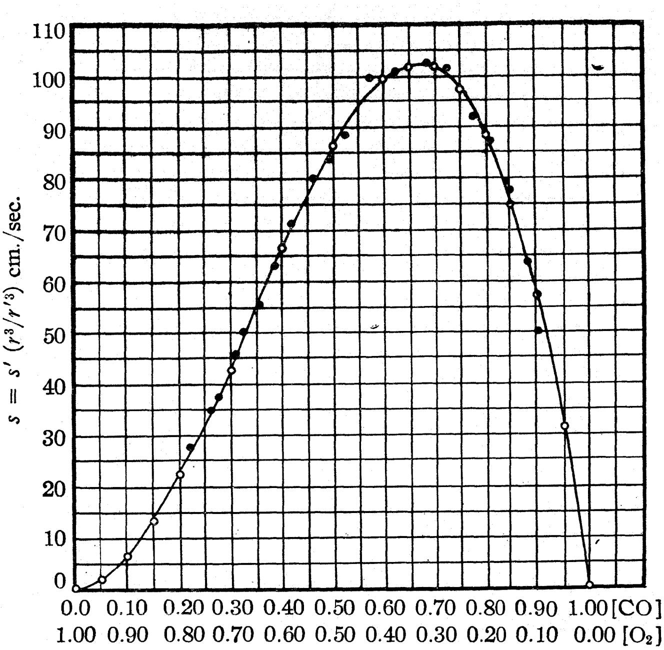

Fig. **3** shows the relation between the linear rate of propagation, s, of the zone of reaction, measured relative to the explosive gases, and the partial pressures of the gases, [CO] and [O_2], in the explosive mixture. The solid circles represent observed values, $s = s'(r^3/r'^3)$. The open circles and continuous line represent calculated values of $s = k[CO]^2 [O_2]$.

In Table III there are given the experimental results obtained when 10% of the component [1 — CO] consists of the inert gas A. These results are represented graphically in Fig. 5 by the mark $\vee$. The upper continuous curve in this figure gives velocity values of the reaction zone when no inert gas is present. The lower curve, indicated also by a continuous line, corresponds to Equation 17, s = 691 $[CO]^2$ [1 — CO] 0.9, for the case where 10% of the component [1 — CO] consists of an inert gas—

the possible effect of its physical properties being disregarded. There is also plotted on this figure the experimental values found when 10% of the component [1 − CO] consisted of nitrogen, marked X on the figure, carbon dioxide, marked ■, and helium marked A.

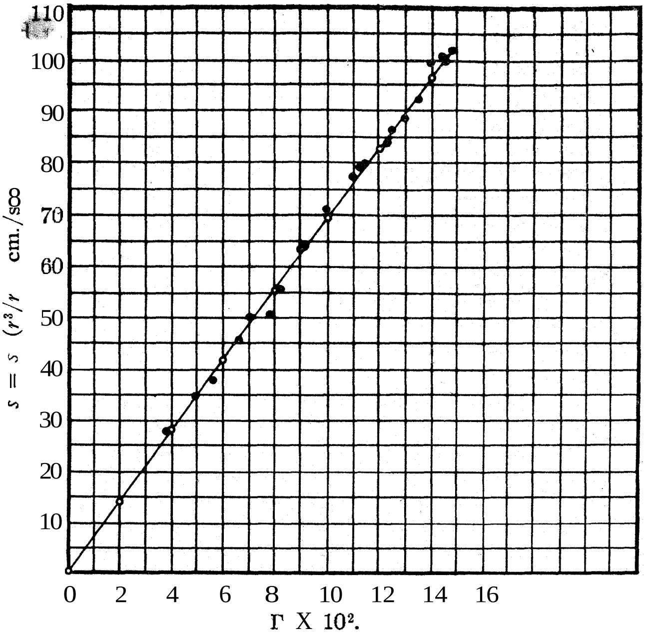

Fig. 4 **shows the relation between the linear rate of propagation of the reaction zone, *s*, and impact probability, Γ.**

Table III

Experimental Results Obtained When 10% of the Component, [1 − CO] Consisted of the Inert Gas Argon

Record 5–28–28 No.	Partial press., atm. [CO]	[1 − CO]	[A]	Γ $[CO]^2\,[1 - CO]$	$s' = \frac{r_i}{t}$, cm./sec.	$s = s'\frac{r^3}{r'^3}$, cm./sec.	$k_1 = \frac{s}{\Gamma}$
5 to 8	0.282	0.718	0.0718	0.0571	276	40.0	702
9 to 12	.326	.674	.0674	.0716	394	50.5	705
13 to 16	.373	.627	.0627	.0872	500	59.3	680
17 to 20	.426	.574	.0574	.1043	596	70.9	681
21 to 23	.472	.528	.0528	.1176	671	79.9	679
24 to 27	.521	.479	.0479	.1297	722	85.6	659
28 to 31	.572	.428	.0428	.1395	767	90.4	648
32 to 35	.625	.375	.0375	.1465	908	90.8	620
36 to 39	.674	.326	.0326	.1502	934	93.4	622
40 to 42	.726	.274	.0274	.1439	907	90.7	628
43 to 46	.775	.225	.0225	.1351	752	86.2	638
47 to 50	.824	.176	.0176	.1195	663	80.9	674
51 to 54	.876	.124	.0124	.0952	443	61.2	643

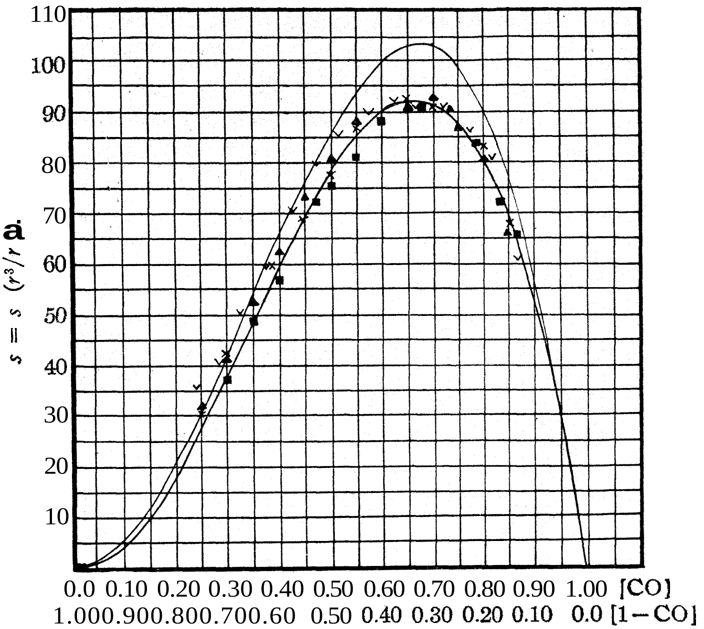

Fig. 5.—The upper continuous curve in this figure gives velocity values of the reaction zone when no inert gas is present. The lower curve, indicated also by a continuous line, corresponds to the equation, $s = 691\,[CO]^2[1-CO]\,0.9$, for the case where 10% of the component [1 − CO] consists of an inert gas, its possible physical effects being disregarded. The observed results when 10% of the component [1 − CO] consisted of N_2 are indicated by the mark ×, A by the mark V, He by the mark ▲, and CO_2 by the mark ■.

TABLE IV

EXPERIMENTAL RESULTS OBTAINED WHEN 20% OF THE COMPONENT [1 − CO] CONSISTED OF THE INERT GAS NITROGEN

Record 4–22–27 No.	Partial press., atm. [CO]	[1 − CO]	$[N_2]$	Γ $[CO]^2[1-CO]$	$s' = \frac{r_i}{t}$, cm./sec.	$s = s'\frac{r^3}{r'^3}$, cm./sec.	$k = \frac{s}{\Gamma}$
1 to 4	0.300	0.700	0.140	0.0630	245	36.2	575
5 to 9	.369	.631	.126	.0859	358	49.1	572
10 to 13	.420	.580	.116	.1023	440	58.2	569
14 to 17	.470	.530	.106	.1171	495	66.0	564
18 to 21	.521	.479	.096	.1300	581	73.2	563
22 to 25	.569	.431	.086	.1895	627	79.9	573
26 to 29	.616	.384	.077	.1457	651	82.8	592
30 to 33	.670	.330	.067	.1482	693	82.6	558
34 to 37	.718	.282	.056	.1453	666	81.8	563
38 to 41	.782	.218	.044	.1228	601	75.2	565
42 to 45	.822	.178	.036	.1203	529	65.2	542
46 to 49	.877	.123	.025	.0946	408	56.9	601

Table IV gives the experimental results when 20% of the component [1 − CO] was made up of the inert gas nitrogen. The observed values are indicated in the coordinate Fig. 6 by the mark ×. The upper continuous curve in this figure again represents velocity values of the reaction zone when no inert gas is present. The lower continuous curve in this figure corresponds to Equation 17, $s = 691\ [CO]^2\ [1 - CO]\ 0.8$. The observed results when the inert gas used was helium instead of nitrogen are represented by the mark A; when the inert gas was argon, by the mark V, and when the inert gas was carbon dioxide, by the mark **I**.

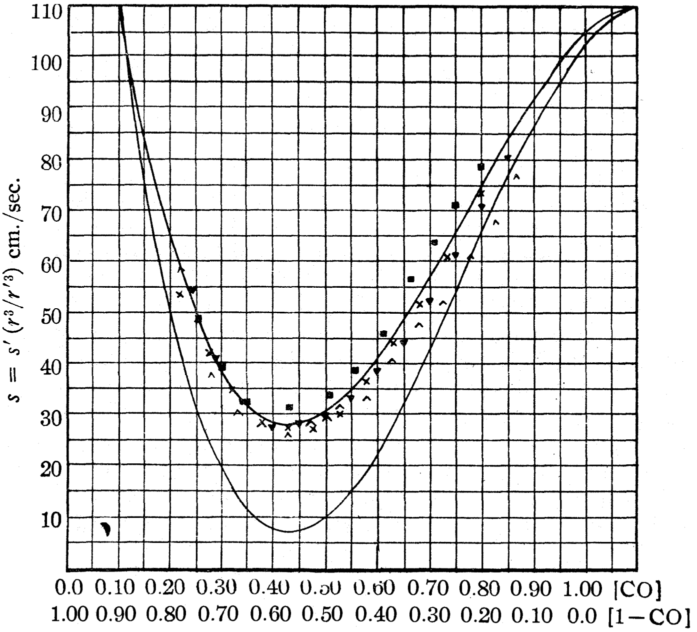

Fig. 6.—The upper continuous curve gives velocity values of the reaction zone when no inert gas is present. The lower continuous curve corresponds to the equation, $s = 691[CO]^2[1 - CO]0.8$; observed results when the inert gas present was N_2 are indicated by the mark X, when the inert gas was He, by the mark ▲, A, by the mark V, CO_2, by the mark ■.

In Table V are given the experimental results obtained for $s = s'\ r^3/r'^3$ when 40% of the component [1−CO] consisted of the inert gas helium. In Fig. 7 these results are shown graphically together with results obtained when the other inert gases were used in the same proportion. The marks employed to designate the s-values of the different inert gases in this figure are the same as those previously given.

From these results it may be seen that when small amounts (partial pressures) of different inert gases are present in the explosive mixture, not much difference in their individual effects is to be noticed; their different physical properties do not mask the effect of the active gases; but as the relative amounts (partial pressures) of the different inert gases become greater, a difference in their effect on the same $CO-O_2$ reaction becomes apparent. This is to be seen in the results given in Table V and shown in Fig. 7. The observed s-values not only diverge more widely from values indicated by Equation 17; they also differ characteristically from each other. It is further to be noticed that this divergence in each case is the greater, the greater the amount (partial pressure) is of the inert gas in the mixture. In Col. 4 of Table V is given the partial pressure of helium in each mixture ratio of [CO] and [1 − CO]. In Col. 8 of this table are given the corresponding values of $k_1 = s/\Gamma$. The values of k_1 in this

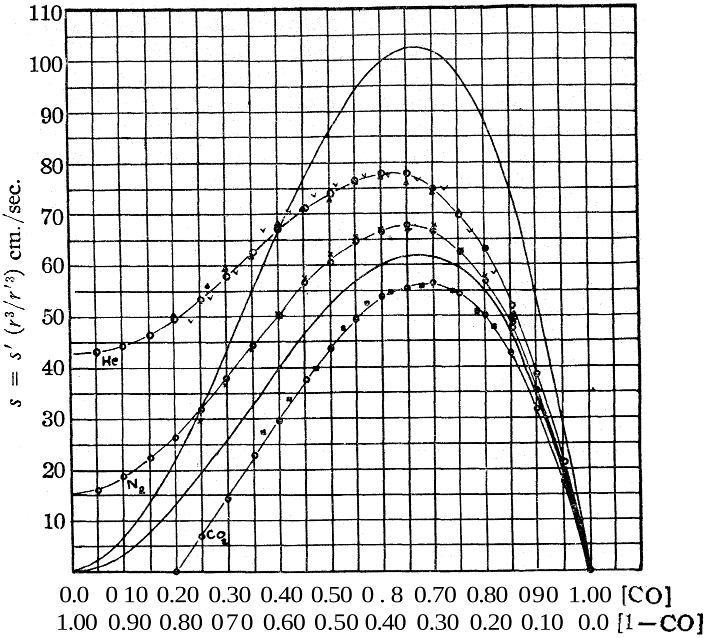

Fig. 7.—The upper continuous curve gives velocity values of the reaction zone when no inert gas is present. The lower continuous curve, without other marks, corresponds to the equation $s = 691 [CO]^2[1 - CO]$ 0 6, where 40% of the component [1 − CO] is made up of an inert gas whose effect upon the reaction rate is disregarded. Observed values when 40% of the component [1 − CO] consisted of A are marked V. Like values for N_2 are marked ×, He, ▲, and CO_2, ■. The curves in this figure marked He, N_2 and CO_2 shown by open circles and continuous lines correspond to Equation 18 when the experimental values for β found for the inert gases are introduced.

Table V

Experimental Results ObTainEd when 40% op the Component [1−CO] Consisted or the InErT Gas Helium

Record 2–6–27 No.	Partial press., atm. [CO]	[1 − CO]	[He]	Γ $[CO]_2 [I-CO]$	$s' = \frac{r_i}{i}$, cm./sec.	$s = s' \frac{r^o}{r'^3}$, cm./sec.	$k_1 = \frac{s}{\Gamma}$	$\beta = \frac{s - k_1 a [CO]^2 [1 - CO]}{[He]}$
8′ to 11′	0.217	0.783	0.313	0.0369	262	49.5	1342	109
5′ to 8′	.265	.735	.294	.0516	339	56.1	1088	118
4 to 7	.302	.698	.279	.0637	376	59.9	940	120
8 to 11	.351	.649	.260	.0811	449	61.4	757	107
12 to 15	.400	.600	.240	.0960	498	68.0	708	117
16 to 19	.450	.550	.220	.1114	541	71.8	645	116
20 to 23	.500	.500	.200	.1251	567	72.3	578	102
24 to 27	.550	.450	.180	.1362	631	75.8	557	107
28 to 31	.600	.400	.160	.1441	613	76.5	531	105
32 to 35	.650	.350	.140	.1479	612	76.6	518	114
36 to 39	.700	.300	.120	.1470	591	73.9	503	108
40 to 43	.750	.250	.100	.1406	538	69.5	506	112
44 to 47	.800	.200	.080	.1280	446	61.3	479	102
48 to 51	.850	.150	.060	.1084	298	51.0	471	101
							Av. β =	109

column, according to the assumption made in Equation 17, should be constant and equal to 415. The values of k~are seen to be far from constant in this case and only approach the theoretical value for no effect of an inert gas as the partial pressure of helium in the mixture decreases. The highest value of k_1 is seen to correspond to the greatest amount of helium in the explosive mixture and vice *versa.*

It was conceived that the relationship shown in the table between the values of helium and k_1 could be due to characteristic physical properties, whatever they might be, of the inert gas present in the mixture and that the magnitude of their different effects upon the $CO - O_2$ reaction might be directly proportional to the partial pressure of the inert gas in the mixture, that is

$$s = s' \frac{r^3}{r'^3} k_1 [CO]^2 [1 - CO] a + \beta [G_i] \tag{18}$$

where $[G_i]$ is the partial pressure of the inert gas. The observed results were examined for this relationship. The last column of Table V gives the estimated value of β for each mixture ratio of [CO] and [1−CO] that would ignite

$$\beta = \frac{s - k_1 a [CO]^2 [1 - CO]}{[He]} \tag{19}$$

When the average value of β so found, 109, is substituted in Equation 18 the curve represented by open circles and a continuous line, marked He in Fig. 7, is determined. In a similar way it was found that the value for

β for each of the other inert gases used was also a fair constant. Its value for 40% of N_2 in this reaction is 41, for CO_2, **−41.8** and for A, **112.**

In carrying out the experimental work involved in these studies, the inert gases helium, nitrogen and carbon dioxide were first employed. **A** comparison of the results obtained with these gases indicated that their effect upon the $CO - O_2$ reaction was of an order roughly paralleling the order of their heat conductivities, but following also the order of their molecular heats. It was therefore desirable to compare the effects of the two monatomic inert gases, helium and argon, having the same molecular heat but very different heat conductivities. A sample of argon was later obtained and the comparison made. The results indicate that the sample of argon used has practically the same effect on the rate of propagation of the reaction zone in the $CO - O_2$ explosive reaction as the inert gas helium. These two gases being monatomic have the same molecular heat independent of temperature, but the heat conductivity of helium is **8.6** times that of argon.

The mixture ratio for maximum flame velocity for the conditions expressed by Equations 14 and 17 is that given by position 0.667 in the coördinate figures; but for Equation **18** this position will be displaced to the left according to the positive magnitude of the last term, and to the right according to its negative magnitude. This may be seen in the results given in Fig. 7. It is also of interest to note that it might be possible to have a mixture of two inert gases whose individual effects upon the rate of propagation of the reaction zone were in opposite sense and balanced each other. For such a case the last term in Equation 18 would be negligible. The conclusion could be drawn from a special case of this kind that the rate of propagation of the zone of reaction is proportional to the product of the concentrations of the active components as in the case of the pure gases $CO–O_2$. This conclusion might also seem warranted from experimental results obtained when the inert gas is present in the explosive mixture in comparatively small quantities as shown in Figs. 5 and **6** and for all results where the value of [CO] is large and the partial pressure of the inert gas small. It was therefore essential in carrying out the investigation to determine in each case the effect of the same partial pressure of each of the inert gases on the same mixture ratio of [CO] and [1−CO], and this over the entire range of mixture ratios that would ignite. In Fig. 7 the results of this procedure when 40% of the component [1−CO] consists of an inert gas is shown for the inert gases helium, argon, nitrogen and carbon dioxide.

The writer desires to express here his gratitude to the National Advisory Committee for Aeronautics for interest, encouragement and support extended him during an investigation of gaseous explosive reactions. This report deals with the effect of inert gases on the reaction.

Summary

1. Attention is called to previous investigations of gaseous explosive reactions carried out under constant volume conditions, where the effect of inert gases on the thermodynamic equilibrium was determined. The advantage of constant pressure methods over those of constant volume as applied to studies of the gaseous explosive reaction is pointed out and the possibility of realizing for this purpose a constant pressure bomb mentioned.

2. The application of constant pressure methods to the study of gaseous explosive reactions made possible by the use of a transparent constant pressure bomb, led to the discovery of an interesting kinetic relation connecting the rate of propagation of the zone of explosive reaction within the active gases, with the initial concentrations of those gases

$$s = k_1[A]^{n_1}\ [B]^{n_2}\ [C]^{n_3}\ldots.$$

3. By a method analogous to that followed in determining the effect of inert gases on the equilibrium constant K, the present paper records an attempt to determine their kinetic effect upon the expression given above. It is found that this effect on the $CO - O_2$ reaction for the inert gases investigated, helium, argon, nitrogen and carbon dioxide, may be expressed as

$$s = k_1[A]^{n_1}\ [B]^{n_2}\ [C]^{n_3}\ldots. + \beta[G_i]$$

where $[G_i]$ represents the initial concentration of the inert gas in the mixture.

4. An example of the utility of the constant pressure bomb for the study of the kinetics of the gaseous explosive reaction is offered in the results given in the present paper.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PURDUE UNIVERSITY]

THE EQUILIBRIUM OF SILVER OXIDE AND SILVER CHLORIDE WITH AQUEOUS POTASSIUM CHLORIDE AND POTASSIUM HYDROXIDE

BY ROY F. NEWTON

RECEIVED AUGUST 6, 1928 PUBLISHED DECEMBER 10, 1928

Lewis and Randall,[1] in one of their calculations of the free energy of formation of water, have made use of Noyes and Kohr's[2] measurements on the equilibrium between silver oxide, silver chloride, potassium hydroxide, potassium chloride and water. They point out that it would be much simpler to use the dissociation of silver oxide into silver and oxygen, and the electromotive force of a silver–silver oxide electrode against the hydrogen electrode, but that the silver–silver oxide electrode is quite variable

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[1] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Company, New York, 1923, p. 482.

[2] Noyes and Kohr, *Z. physik. Chem.*, 42, 336 (1902).

and leads to results quite different from those obtained by other sets of reactions. However, Noyes and Kohr's results are not very consistent and it seemed worth while to redetermine the equilibrium between silver oxide, silver chloride, potassium hydroxide, potassium chloride and water.

Materials

Silver oxide was prepared (*a*) by precipitation at room temperature of dilute solutions of barium hydroxide and silver nitrate, (*b*) by heating precipitate (*a*) for several hours at 300°, (c) by precipitating from nearly boiling solutions of the above reagents, (d) by addition of silver nitrate to boiling sodium hydroxide solution and boiling the precipitate in excess sodium hydroxide solution and (*e*) by precipitation from the silver ammonia complex hydroxide by vacuum distillation of the ammonia. Preparation (*e*) was made to see if silver oxide so prepared showed evidence of greater stability than the samples precipitated in the more usual ways. On the contrary, as judged by the concentration ratio of chloride to hydroxide in equilibrium with it in presence of water and silver chloride, it behaved as if it were less stable, or more soluble, than the other four preparations, and for this reason little work was done with it.

The silver chloride was prepared by mixing moderately dilute solutions of silver nitrate and hydrochloric acid and washing thoroughly by decantation. The silver chloride was prepared and stored in a dark room, was kept in a moist condition and did not darken.

The water used was distilled and made free of carbon dioxide by prolonged passage of carbon dioxide-free air. The potassium chloride was a c. p. grade recrystallized and fused. The potassium hydroxide was sometimes made from electrolytically prepared potassium amalgam, and sometimes by precipitating c. p. potassium hydroxide with excess barium hydroxide, filtering and removing the excess barium hydroxide by addition of the required quantity of potassium sulfate as determined by analysis. The potassium sulfate was a recrystallized c. p. product. The sulfuric acid was standardized by titration with weighed quantities of recrystallized borax, using methyl yellow (dimethylamino-azobenzene) as indicator.[3] The hundredth normal silver sulfate solution was standardized against recrystallized fused potassium chloride by electrometric titration as described later.

Procedure

Varying proportions of silver oxide and silver chloride were put into 250-cc. ground-glass-stoppered Pyrex Erlenmeyer flasks, the desired quantities of potassium hydroxide, potassium chloride and water added, and the samples were then rotated in a 25.00 ± 0.02° thermostat for periods varying from several hours to three days. The equilibrium was approached from both sides. No consistent differences were observed. Samples consisting of most of the liquid contents of the flasks were filtered from them, using filters made by sealing disks of alundum into Pyrex glass tubes. First portions of ten to twenty cubic centimeters were rejected to avoid error due to possible selective adsorption. The flasks and filters remained in the thermostat during the filtrations. Potassium hydroxide was determined by titration of the entire samples (about 200 cc.) with 0.5 N sulfuric acid, using phenolphthalein as indicator. The solution was then

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[3] Kolthoff, THIS JOURNAL, 48, 1447 **(1926).**

carefully evaporated to small bulk and titrated electrometrically with 0.01 N silver sulfate solution, using a silver–silver chloride electrode and connecting to a saturated potassium sulfate–mercurous sulfate–mercury electrode. Standardizations of the silver sulfate were made by titrating weighed quantities of potassium chloride mixed with amounts of potassium sulfate comparable with those encountered in the analyses. While steady potentials were obtained only slowly, and the titrations were tedious, the end-points were definite, the standardizations were reproducible and since the samples were practically identical in composition and concentration with the solutions titrated during standardization, systematic errors in the analyses are not to be expected.

TABLE I

EQUILIBRIUM RATIOS OF CHLORIDE AND HYDROXIDE

Sample no.	Prepn. Ag_2O	Concn of OH^-, mole/kg. water	Concn. of Cl^-, mole/kg. water	Concn. ratio, Cl^-/OH^-	Activity ratio
1	a	0.0939	0.000852	0.00907	
2	a	.0978	.000875	.00895	
3	b	.1072	.000944	.00881	
4	b	.1065	.000945	.00887	
5	b	.1054	.000942	.00894	
6	b	.1011	.000925	.00915	
7	c	.1098	.000981	.00893	
8	c	.1130	.000999	.00884	
9	c	.1035	.000961	.00929	
10	c	.0997	.000921	.00924	
11	d	.1112	.000986	.00887	
12	d	.1065	.000996	.00935	
13	d	.1038	.000973	.00937	
Average for solutions approx. 0.1 molal				.00905	0.00892
14	a	.0529	.000471	.00889	
15	a	.0542	.000483	.00891	
16	b	.0520	.000465	.00894	
17	b	.0531	.000481	.00906	
18	c	.0536	.000485	.00905	
Average for solutions approx. 0.05 molal				.00897	.00897
Final weighted mean				.00903	.00893
Mean of Noyes and Kohr's results				.00937	.00930

The activity ratios were calculated by multiplying the corresponding concentration ratios by $\gamma^2_{KCl}/\gamma^2_{KOH}$, where γ is chosen to correspond to the *total* ion concentration.[4]

It may be noted that while individual samples are variable, the samples prepared in different ways do not differ significantly from one another, and while the general average is somewhat below the values of Noyes and

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[4] Ref. 1, p. 362. The individual ion activity coefficients, p. 382, have been derived in the same way, but the values have been so rounded that the difference in activity coefficients of Cl^- and of OH^- in 0.1 molal solution have been exaggerated from barely over 1 to 2%.

Kohr, they probably agree within the limits of error, considering the individual variability, which is characteristic of the results both of Noyes and Kohr, and of the author. While the difference of the equilibrium ratio from that of Noyes and Kohr does not justify a recalculation of the free energy of water based in part on this equilibrium, it may be noted that the free energy calculated from the above results agrees with that obtained by other methods somewhat better than that calculated from the results of Noyes and Kohr.

Summary

The equilibrium of AgCl, Ag_2O, KOH, KCl and H_2O, previously studied by Noyes and Kohr, has been redetermined, using Ag_2O prepared in a variety of ways, and determining the chloride by electrometric titration. While the individual values are somewhat variable, the method of preparation has no significant effect on the equilibrium ratio of chloride and hydroxide. Within experimental error the equilibrium ratio is the same in 0.05 molal solution as in 0.1 molal solution.

LAFAYETTE, INDIANA

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

A HIGHLY ACCURATE METHOD FOR THE ANALYSIS OF UREA

BY MILLICENT TAYLOR

RECEIVED AUGUST 6, 1928 PUBLISHED DECEMBER 10, 1928

There are many problems in physical and colloid chemistry which require for their experimental solution the use of a reference substance capable of analysis to a high degree of accuracy. Such a reference substance must also be chemically inert and a non-conductor of electricity. These problems include methods of indirect analysis, determination of solvation by the method of ultrafiltration[1] and the determination of the hydration of the ions by measurement of the displacement of the reference substance during electrolysis, as suggested by Nernst in 1900. In Washburn's[2] well-known work on this latter subject, only one substance, raffinose, was considered to possess the requisite properties and it is subject to the drawback that a highly sensitive polarimeter of a type not generally accessible is required to estimate it.

The high molecular weight of raffinose is also a disadvantage. The decimolar solution contains more than 50 g. to the liter, a quantity sufficient to cause considerable increase in the viscosity of the solution and consequently to affect the migration velocities of the ions. Also, it is

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[1] McBain and Jenkins, *J. Chem. Soc.*, 121, 2325 (1922).

[2] Washburn, THIS JOURNAL, 31, 322 (1909); Washburn and Millard, *ibid.*, 37, 694 (1915).

conceivable, in view of Coehn's[3] observation of the Tyndall cone in sucrose solution and of his statement that sucrose moves in the electric field, that the large molecules of raffinose may tend to become colloidal and to adsorb charged ions in the presence of a considerable quantity of electrolyte. Thus doubt is thrown on the value of raffinose as a reference substance in migration experiments.

The possibility of using urea for this purpose does not appear to have been considered, yet it has properties which render it almost ideal for the purpose. Its equivalent weight is low, it is easy to obtain pure and its aqueous solution is stable at room temperature in the absence of ferments. Moreover, its basic dissociation constant,[4] $[CO(NH_2)_2H][OH]/[CO(NH_2)_2HOH]$, at 25° is 1.5×10^{-14}, the conductivity of its solution is approximately equal to that of water and the effect of its presence in potassium chloride solution is merely a slight lowering of the conductivity, which can be accounted for by the increased viscosity of the solution.

It only remained to find a suitably accurate method of estimating it in solution. A search through the literature revealed the fact that no method has afforded results which would establish an accuracy exceeding 1% of the urea present. The method favored by physiologists at the present time consists in the fermentation of urea by urease[5,6] in the presence of potassium dihydrogen phosphate and subsequent liberation and distillation of the ammonia formed. This method appears to be satisfactory for small quantities of physiological fluids for which an accuracy of 1% is sufficient, but it presents difficulties when a degree of accuracy of the order of 0.1% is desired. As is well known, the removal of the last traces of ammonia by boiling and aerating an aqueous alkaline solution is a matter of some uncertainty, even when no colloidal organic matter is present to induce frothing and bumping. In distilling off the ammonia produced by urease fermentation, the frothing is very marked and, though it can be decreased to some extent by the addition of wax or oil, the escape of ammonia is checked and the titration of the excess of acid in the absorber is rendered less accurate, owing to the fact that a small quantity of the wax distils over with the steam and removes the indicator from the aqueous layer. A further drawback is the long boiling required for the complete expulsion of the ammonia from the mixture, resulting in the extreme and variable dilution of the acid in the absorption flask.

In view of these disadvantages, it was decided to revert to the method of Benedict and Gephart,[7] which depends on the hydrolysis of urea by acid

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[3] A Coehn, *Z. Elektrochem.*, *15*, 622–624 (1909).

[4] Walker and Wood, *J. Chem. Soc.*, *83*, 484–491 (1903).

[5] E. K. Marshall, J. *Biol. Chem.*, 17,351 (1914).

[6] Plimmer and Skelton, *Biochem.* **J.**, **8**, 70 (1914).

[7] Benedict and Gephart, THIS JOURNAL, 30, 1760 (1908).

under a pressure of four atmospheres. The authors state that the results obtained with pure urea solutions leave no doubt that the urea is completely hydrolyzed. The one experiment quoted consists in the hydrolysis of 5 cc. of a *2.5%* urea solution which yielded 0.0575 g. of nitrogen, whereas the theoretical yield is 0.0583 g., an experimental deficit of more than 1% of the total urea. Wolf and Osterberg,[8] using the same method and a 2% solution of urea, also obtain values lower than the theoretical by 1%. It is obvious that these investigators, having in view the composition of physiological fluids, are not concerned with accuracy exceeding 1%.

Experiments by the writer with larger quantities of urea than those used by Benedict and Gephart have indicated that for the purpose of estimating urea unmixed with other hydrolyzable nitrogen compounds, the autoclave method gives a high degree of accuracy. This accuracy depends on the facts that the reaction goes to completion in the presence of very slight excess of hydrochloric acid, and that the acid does not vaporize under the conditions in the autoclave. Thus the distillation with soda can be avoided by mixing a known quantity of standard acid with a known quantity of the solution to be analyzed and directly titrating the excess of acid with dilute soda. By making the excess of acid small, the effect of any slight error in the concentration of the soda becomes insignificant, and consequently the possible accuracy of estimation of the urea depends only on the accuracy of weighing out the urea and acid solutions concerned, and on the accuracy of making up the hydrochloric acid solution.

Experimental

The digestion is carried out in a 500-cc. stoppered conical flask made of Pyrex glass or silica and provided with an exit tube of an inverted U-shape sealed in near the top of the flask. The flask is weighed and the urea solution and standard acid are pipetted (see p. 3264) into it, the weight being noted after each addition. A Pyrex test-tube containing a little water into which the side tube dips acts as scrubber to the escaping carbon dioxide. The latter is absorbed by the distilled water in the autoclave, to which a few cc. of soda solution has been added. This precaution renders unnecessary any subsequent aeration or boiling of the reaction mixture for the expulsion of carbon dioxide.

The flask and scrubber tube are covered with tinfoil in the autoclave and after displacing all the air, heating for half an hour under two atmospheres, and for four hours under four atmospheres, the apparatus is allowed to cool. The autoclave is then opened, the glass stopper of the flask is removed, and replaced by a rubber bung carrying a tube, by means of which the water in the scrubber tube is sucked back and the scrubber tube rinsed several times into the flask. The titration is carried out in the presence of two drops of 0.02% methyl red indicator.

In the experiments described below, the standard hydrochloric acid was prepared by the distillation method of Hulett and Bonner,[9] and the soda was standardized against the acid to three tints of the indicator, giving three different concentrations of the soda of which the extremes differed by less than 0.02%. Thus it was unnecessary always to titrate the soda to the same tint.

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[8] Wolf and Osterberg, THIS JOURNAL, 31,425 (1909).

[9] Hulett and Bonner, *ibid.*, 31,390 (1909).

The first experiments were carried out volumetrically using calibrated instruments; the later ones gravimetrically, using weight burets. The results are corrected for the buoyancy of the air.

The solutions of urea and hydrochloric acid contained about 0.2 and 0.4 equivalents per liter, respectively, and each experiment was carried out with about 50 cc. of urea solution. The soda solution used for back titration was about 0.2 N. The urea was Kahlbaum's purest material, m. p. 132.2–133.2°, which had been kept in a desiccator for some days before use. Results are recorded in Tables I to III.

In the experiments recorded in Table I, the urea was hydrolyzed by ordinary concentrated hydrochloric acid and the ammonia estimated by distillation with soda and absorption by standard hydrochloric acid. In each of these two experiments, 50.28 cc. of 0.22509 N urea was digested with 5 cc. of pure concentrated acid.

TABLE I

RESULTS OF EXPERIMENTS

Expt.	HCl concn. in abs., *N*	HCl soln., cc.	Concn. of soda	Vol. of soda, cc.	Equiv. of urea per liter of soln. Found	Taken
1	0.51606	25.03	0.21790	7.41	0.23478	0.22508
2	.41671	30.03	.13591	8.87	.22490	.22508
				Mean =	.22484	

In the second set of experiments (Table 11), 50.28 cc. of the same urea solution was digested each time with varying quantities of 0.41671 N hydrochloric acid and titrated directly with 0.13584 N soda.

TABLE II

RESULTS OF EXPERIMENTS

Expt.	Acid, cc.	Soda, cc.	Equiv. of urea per liter of soln. Found	Taken
3	50.28	71.00	0.22489	0.22508
4	50.28	71.02	.22482	.22508
5	30.03	8.94	22474	,22508
		Mean =	22482	

The method was then applied gravimetrically to determine the concentration of three urea solutions, A, B and C, each of unknown concentration but approximately 0.2 N_w. In all cases, 0.40756 N_w hydrochloric acid was used. The results are recorded in Table III.

Of all the solutions analyzed only one failed to give concordant results. In this case one sample of the urea solution was poured, not pipetted, into the digestion flask, and though excess of hydrochloric acid was added, the water in the scrubber tube became alkaline. The sample of the solution which was pipetted in the usual way was found to contain 0.20147 gram equivalents of urea per 1000 g. of solution, while the second sample gave only 0.20103 gram equivalents, a deficit of 0.2%. It seems probable

TABLE III

RESULTS OF EXPERIMENTS

Expt.	Urea soln., g.	HCl soln., g.	Concn. of soda soln., N_w	Soda soln., g.	Equiv. of urea per liter of soln.
			Solution A		
6	51.2844	50.5605	0.2383 (33)	44.544	0.194870
7	51.2857	35.4112	.2383 (33)	18.614	194901
8	51.2511	25.1701	.2383 (54)	1.1379	.194794
				Mean =	.194855
			Solution B		
9	51.2300	25.9771	.2383 (54)	2.4635	.195196
10	50.8790	26.0405	.2383 (13)	2.8615	.195208
				Mean =	.195202
			Solution C		
11	51.0923	25.9704	.2383 (33)	1.8615	.198482
12	50.9424	26.6487	.2383 (33)	3.2235	.198526
				Mean =	.198504

that urea is rapidly hydrolyzed by water alone at the autoclave temperature of 150° and, consequently, since it is not convenient to shake up the mixture in the digestion flask, some of the ammonia escaped combination with acid.

With this exception, the extreme divergence between any values for the same solution is 0.05%, and if those results which were obtained gravimetrically and by the use of only slight excess of acid are considered exclusively, the agreement throughout is within 0.02%.

No special precaution other than the use of calibrated weights has been observed and it is probable that using more dilute solutions of acid and alkali, and titrating to a larger number of intermediate indicator tints, a considerably higher degree of accuracy could be obtained. The difference of 0.12% shown in Table I between the urea weighed out and that obtained by analysis is undoubtedly real, owing to the fact that no extreme precautions were taken to dry and purify the urea. The method is now being employed in this Laboratory in experiments on the hydration of the ions, and is found to be extremely convenient owing to the short time required for actual manipulation, the ease of removal of the ammonium chloride and to the fact that the process is at no stage precarious.

Summary

Urea is an excellent reference substance for use in physico-chemical and colloidal problems, being a non-electrolyte of low equivalent weight and chemically indifferent. A simple method of analysis whereby it is converted into ammonium chloride and carbon dioxide is described. The accuracy obtained is at least 0.02% of the urea used.

BRISTOL, ENGLAND

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

THE PARTITION COEFFICIENT IN THE FRACTIONAL CRYSTALLIZATION OF RADIUM–BARIUM BROMIDE SOLUTIONS[1]

BY ZACHARY T. WALTER WITH HERMAN SCHLUNDT

RECEIVED AUGUST 20, 1928 PUBLISHED DECEMBER 10. 1928

The latter stages in the preparation of a pure radium salt have usually been carried out by the fractional crystallization of a radium–barium chloride or bromide solution. From a consideration of the alkaline earth group of the periodic table, the general trend of the solubilities of radium salts may be safely predicted. True to expectation, the solubilities of radium bromide,[2] chloride, sulfate[3] and chromate[4] have been found to be less than the corresponding barium compounds and this factor has been generally quoted to account for the enrichment of radium in the crystalline phase. Furthermore, since the solubility of the alkaline earth hydroxides increases with increasing atomic weight, the radium in this instance should remain in the mother liquor. McCoy[5] has satisfactorily demonstrated this prediction.

At least two other theories have been advanced to explain the mechanism of the enrichment of radium in the crystalline phase. One of these theories,[6] advanced by Germann, would explain the phenomenon on the basis of adsorption. The other theory stated by Doerner and Hoskins would explain the mechanism of the enrichment of the crystalline phase as one in which radium atoms replace barium atoms in isomorphous crystals of the barium salt.

Further, irrespective of any theory, at least three different equations have been proposed to explain the regularities observed in the enrichment of radium by the process of fractional crystallization or precipitation.

The experimental part of this paper will present some evidence to test the validity of the respective equations and will include a new procedure by means of which the crystals separated are more completely freed from the mother liquor.

Experimental

(A) Source of Material.—The source material which was used in these experiments consisted of a sample of purified barium chloride, 250 g.,

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[1] Abstract of a thesis submitted by Z. T. Walter in partial fulfilment of the requirements of the degree of Master of Arts, Graduate School, University of Missouri, 1928.

[2] John L. Nierman, *J. Phys. Chem.*, 24, 192 (1920); Clarence F. Scholl, THIS JOURNAL, 42,889 (1920).

[3] S. C. Lind, J. E. Underwood and C. F. Whittemore, *ibid.*, 40, 465 (1918); H A. Doerner and William M. Hoskins, *ibid.*, 47, 662 (1925).

[4] L. M. Henderson and Frank C. Kracek, *ibid.*, 49,738 (1927).

[5] H. N McCoy, U. S. Patent 1,103,600 (1914).

[6] Frank E. E. Germann, THIS JOURNAL, 43,1615 (1921).

which contained approximately a total of 26×10^{-5} g. of radium element. This material had previously been used in radioactive researches at the University of Missouri. Before its use in this study it was converted to radium–barium bromide by first making radium–barium carbonate. This carbonate was then treated with hydrobromic acid and the pure crystals of radium–barium bromide were obtained upon the evaporation of the hydrobromic acid solution.

(B) Method of Treatment.—The purified radium–barium bromide was taken into solution and the solution made up to exactly one thousand grams. This solution was then analyzed for both its radium and its barium content. The radium in the solution was determined by the emanation method in carefully calibrated electroscopes. The barium in the solution was determined by the sulfate method. This solution throughout this paper is called the stock solution.

(C) Method of Growth and Separation of Crystals.—A suitable quantity of this stock solution was weighed into a fused quartz evaporating dish. The solution was then evaporated on the water-bath until it was saturated. The crystals were then grown from the solution by removal of water with slow evaporation, the process requiring two to four hours depending upon the quantity of crystals removed from the solution. During the separation of the crystals the solution was continuously stirred. When the desired quantity of crystals had been separated, the dish was weighed and the loss of weight during evaporation was obtained. A sample of mother liquor was next decanted from the liquor above the crystals, weighed and made up to 1000 g. for analysis for radium content.

The next step in the process consisted in the complete removal of all mother liquor from the crystals. The usual plant process at this point is merely to decant all of the mother liquor that can be conveniently poured from the crystals, thus leaving them wet with impoverished liquor. The procedure used in this investigation was to centrifuge the crystals in a hand centrifuge. The manner in which the crystals were completely separated from the mother liquor is considered to be the distinctive feature of this work, for in previously reported papers this point had not been given sufficient attention. The dry crystals were finally weighed as the hydrate, $Ra–BaBr_2 \cdot 2H_2O$.

Now from the previously determined content of the stock solution and from the values of the radium content of the mother liquor and quantity of barium bromide separated, the value for K, the partition constant, may easily be obtained.

(D) Data Expressed in Terms of Doerner and Hoskins' Equation.—In Table I all of the information necessary for the calculation of the partition constant, K as defined by Doerner and Hoskins, is given. The equation given by them is as follows: $K = (\log y/a)/(\log n/b)$, where y is the total radium (element) remaining in the mother liquor left after fractionation and separation of crystals; a equals the quantity of radium (element) in the sample of stock solution used in the fractionation; n represents the quantity of anhydrous radium–barium bromide remaining in the mother liquor after fractionation; b is the quantity of anhydrous barium bromide in the sample of stock solution fractionated. All weights are expressed in grams.

TABLE I

EXPERIMENTAL DATA FOR THE DOERNER-HOSKINS FORMULA

Expt.	Crystals sepd., %	Y	a	n	b	K
1	5.36	35.01×10^{-6}	47.76×10^{-6}	35.47	37.48	5.63
2	8.85	31.73×10^{-6}	47.76×10^{-6}	33.76	37.48	3.91
3	10.98	11.11×10^{-6}	23.88×10^{-6}	16.68	18.74	6.58
4	17.55	58.62×10^{-7}	$23\ 88 \times 10^{-6}$	15.45	18.74	7.27
5	18.12	38.45×10^{-7}	13.06×10^{-6}	9.87	12.05	6.13
6	24.55	46.2×10^{-7}	23.88×10^{-6}	14.14	18.74	5.83
7	30.65	33.83×10^{-7}	23.88×10^{-6}	13.00	18.74	4.35
8	35.79	9.98×10^{-7}	13.06×10^{-6}	7.74	12.05	5.83
9	45.25	5.93×10^{-7}	13.06×10^{-6}	6.59	12.05	5.13
10	45.75	5.75×10^{-7}	26.12×10^{-6}	13.08	24.10	6.25
11	54.59	3.07×10^{-7}	13.06×10^{-6}	5.47	12.05	4.75

(E) Data Expressed in Terms of the Equation of Chlopin and Nikitin.[7]—Another equation has been developed by Chlopin and Nikitin in which a relation is expressed between the concentration of radium per unit volume of crystals separated and the concentration per unit volume of mother liquor. Chlopin and Nikitin state that none of the equations previously given expresses very closely the experimental results. The equation favored by Chlopin and Nikitin is modeled after the Nernst–Berthelot distribution or partition equation. In this equation, K, the partition coefficient, has a somewhat different meaning than is usually given to it. Here it is the ratio of the concentration of radium per unit volume of crystals separated to the concentration of radium per unit volume of mother liquor. The equation follows: $XS_1/m = K(1 - X)S_0/q$. X is the fraction of radium in the crystals separated; $1 - X$, fraction of radium remaining in mother liquor; S_0, density of mother liquor, 1.63; S_1, density of the crystals separated, 3.58; m is the weight of the crystals separated; and q is the weight of the mother liquor remaining after fractionation.

In order to apply the equation of Chlopin and Nikitin to our experimental results, it was necessary to determine the density of the mother liquor and thus calculate the volume of the solution obtained after the crystals were removed. The value used for the density of barium bromide crystals (hydrate) was taken from "International Critical Tables." The

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[7] W. Chlopin and B. Z. Nikitin, *Z. anorg. allgem. Chem.*, **166**, 311 (1927).

experimental results expressed in the symbols employed by Chlopin and Nikitin are given in Table II.

TABLE II

EXPERIMENTAL RESULTS EXPRESSED IN SYMBOLS OF THE CHLOPIN-NIKITIN EQUATIONS

Expt.	Crystals sepd., %	q	m	X	$(1 - X)$	K
I	5.36	80.00	2.01	0.267	0.733	31.91
2	9.93	78.62	3.315	.336	.664	28.24
3	10.98	38.99	2.311	.521	.479	40.40
4	17.55	36.51	3.688	.748	.252	64.40
5	18.12	20.72	2.45	.706	.294	44.5
6	24.55	34.24	5.16	.807	.193	60.8
7	30.65	31.76	6.44	.858	.142	77.8
8	35.79	16.59	4.83	.924	,076	91.4
9	45.25	14.46	6.11	.950	.050	106.4
10	45.75	27.64	1236	.977	.023	218.9
11	54.59	12.24	7.55	.977	.023	148.2

(F) Data Expressed in Terms of Schlundt's Exponential Equations.[8] The calculation of the values of K, the partition constant, as given in Schlundt's exponential equation is comparatively simple. The equation is, $Q_1 = Q_0e^{-Kp}$, where p is the fraction of the crystals separated, K is the distribution or partition coefficient; e is the natural log base; Q_1 is the fraction of radium remaining in mother liquor, and Q_0, the initial quantity of radium, may here be taken as unity. The values of K as calculated by this equation are given in Table III.

TABLE III

EXPERIMENTAL RESULTS IN TERMS OF EXPONENTIAL EQUATION

Expt.	Crystals sepd., %	Q_1	K	Expt.	Crystals sepd., %	Q_1	K
1	5.36	0.733	5.80	7	30.65	0.142	6.37
2	885	.664	4.60	8	35.79	076	7.19
3	10.98	.479	6.70	9	45.25	.050	6.62
4	17.55	.252	7.86	10	45.75	.023	8.24
5	18.12	294	6.74	11	54.59	.023	6.91
6	24.55	.193	6.70				

Discussion

From an examination of the experimental tables it will be noticed that the Chlopin-Nikitin equation definitely does not express a true partition coefficient, for the values of K increase as larger fractions of the crystals are removed from the stock solution. It will also be noticed that, while the values for the partition coefficient as expressed by the Doerner-Hoskins equation and the Schlundt exponential equation do not coincide, they do express a fairly exact relation between the radium in the crystals separated

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[8] Herman Schlundt, "Mesothorium," Technical Paper 265, U. S. Bureau of Mines, 1922.

and the salt remaining in the mother liquor. The average value for the partition constant, K, Schlundt equation, is 6.66, while the Doerner and Hoskins constant is 5.64. The corresponding values for the distribution of radium in other systems using the Doerner-Hoskins equation are: for the radium–barium sulfate system K is equal to about 1.8; for the radium–barium chloride system K is equal to 2.74.[9] It is evident that of these three systems the radium–barium bromide system gives by far the most efficient enrichment of radium by fractional crystallization, and indeed it has been found so in practice, but these results show that it can be made more than twice as efficient as the chloride system.

Summary

1. The theories which attempt to explain the mechanism of fractional crystallization are outlined.
2. Three equations are cited to show the mathematical expressions advanced in the literature to represent the partition of radium salts between mother liquor and crystals separated in the process of fractionation.
3. A method of completely freeing the crystals from mother liquor by use of a centrifuge is described.
4. The average value for the partition coefficient in the Schlundt equation was found to be 6.66.
5. The average value for the partition coefficient in Doerner and Hoskins' equation was found to be 5.6.
6. Both the Schlundt and the Doerner-Hoskins equations seem to express equally well the partition relation, namely, that in the process of fractionation the distribution of radium between crystals and mother liquor takes place continuously in constant ratio.

COLUMBIA, MISSOURI

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[9] Unpublished experiments by Dr. G. F. Breckenridge, University of Missouri.

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

THE CHEMICAL EFFECTS OF CATHODE RAYS ON OXYGEN, AIR, NITRIC OXIDE ARD CARBON DIOXIDE

BY WARREN F. BUSSE AND FARRINGTON DANIELS

RECEIVED AUGUST 27, 1928 PUBLISHED DECEMBER 10, 1928

The problem of chemical reaction can be studied to advantage through ionic gas phase reactions. The most important progress in this field has been made by Lind,[1] using α-particles, but large quantities of radium are necessary for measurable quantities of chemical products. The limitations are even more severe for β- and γ-rays, and Errera and Henri[2] obtained traces of material only after exposures of about fifty hours to the β- and γ-rays from 500 mg. of radium.

The electrical discharge offers another method for producing ionization and chemical reaction in gases but the phenomena are complicated. In this Laboratory the effect of the electrodes has been studied first by increasing the electrode area[3] and then by reducing it to a minimum.[4] Attempts were made, also, to study reactions brought about by electron bombardment in the absence of electrodes.[5]

Krueger and Utesch[6] studied the formation of ozone by Lenard rays in a small apparatus and reported 20 to 40 molecules of ozone for each ion pair.

The development of the Coolidge cathode ray tube[7] marks an important advance in this field for it is now possible to pass electrons at a high voltage through a window and into a reaction chamber to give a sufficient quantity of product for chemical analysis. The authors are greatly indebted to Dr. W. D. Coolidge of the General Electric Company for the cathode ray tube used in this work.

In this communication a series of gas reactions is reported, comprising the action of cathode rays on oxygen, air, nitric oxide and carbon dioxide. The extent of each reaction was determined by chemical analysis. It was impossible to measure directly the number of ions formed in the gas and the M/N ratios (that is, number of molecules $\div$ number of pairs of ions) could not be determined, but the yields were computed in terms of the number of molecules per electron passing through the cathode ray tube,

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[1] Lind, "Chemical Effects of Alpha Particles," 2d ed., Chemical Catalog Co., New York, 1928.

[2] Errera and Henri, *3. Phys. Radium*, 7,225 (1926).

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

[4] Hunt, *ibid.*, in press.

[5] Runt, "Thesis," University of Wisconsin, 1926.

[6] Krueger and Utesch, *Ann. Physik*, 78, 114 (1925).

Coolidge, *J.* Franklin *Inst.*, 202,693 (1926).

giving what may be called an M/C ratio. This ratio was then compared for a given reaction under different conditions, and for different reactions under the same conditions. This M/C ratio was often of the order of one hundred times the M/N ratio.

Apparatus

The Coolidge cathode ray tube is shown at "a" in Fig. 1 and it has been described in detail by Dr. Coolidge." The cathode end is similar to that of the Coolidge x-ray tube with a heated tungsten filament in the focusing cup. The electrons travel from the filament under a high potential gradient to the anode and pass through the thin nickel window (0.0012 cm. thick). The window is supported by a grid so that it can stand a full atmosphere's pressure. A copper tube protects the glass of the anode arm from the electrons. An invar tube holding the grid is sealed to the tube by a metal-to-glass seal.

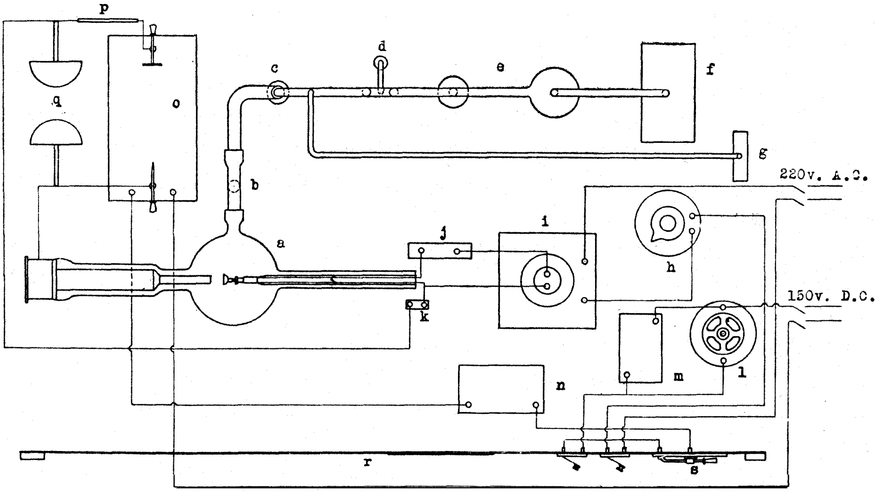

Fig. 1.—Schematic diagram of apparatus for Coolidge electron tube.

The tube was evacuated with a mercury pump, e, backed by an oil pump, f, and a liquid-air trap, c, was used to prevent diffusion of mercury vapor into the tube. A vacuum of less than 10^{-6} mm. could be obtained, but when the tube was operating the pressure increased to about 3×10^{-5} mm. The McLeod gage is shown at g.

The coustruction of the tube is such that potentials up to 200,000 volts can be applied to its terminals and a space current of several milliamperes can be sent through the tube if it is operated intermittently.

A Weston induction coil, o, capable of giving a heavy spark of over 50 cm. between dull points was used as the source of the high voltage. It was operated on direct current with a mercury turbine interrupter, 1, giving about sixty breaks per second. The voltage was determined from the sparking distance between 25-cm. brass hemispheres, q, using the tables of Peeks for spheres of this size.

The filament current was supplied by a step down insulation transformer, i. The space current or electron emission was regulated with an adjustable self-inductance,

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[8] Peek, "Dielectric Phenomena at High Voltage," 1921, p. 90.

h, in the primary circuit of the filament current transformer. The space current was measured with a calibrated ammeter, k, having a range from 0 to 2 milliamperes.

The heat generated in the window was so great that the current could be turned on only about onc-fourth of the time, and an automobile timer, n, was used as an intermittent contact in the circuit of the primary.

A lead screen, r, 2 by 1.5 meters and 3 mm. thick, protected the operator from the x-rays. A window of lead glass 6 mm. thick, permitted a view of the apparatus and readings of the meter were taken with the aid of a telescope.

A condenser, m; a charcoal tube, b; a resistance, p and an ammeter, j, for the filament current made up the rest of the equipment.

Since there was danger of corroding the nickel window- of the cathode ray tube with the gases used in the experiments, the reaction cellswere not attached to the cathode-ray tube. This arrangement had the disadvantage that the electrons had to pass through two windows and a short air space but it made the manipulation of the cells much easier and increased the life of the nickel window. Only two windows have been necessary while the tube has been in practically constant use for two years. The reaction cells were made of soft glass tubes 7 5 cm. in diameter and of two lengths, 22 and 34 cm. Side arms with stopcocks were provided for sweeping out the gases One end of the cell was sealed off and the other end was closed with a thin window of cellophane (a commercial product of cellulose xanthate), aluminum or mica. The cellophane ancl the aluminum were 0.02 mm. thick and the mica was 0.01 mm. thick. The windows were attached with the help of paraffin and a brass ring. None of the windows reduced the range of the electrons in air more than a few centimeters and the slight differences in the absorption of the different windows did not affect the results appreciably.

Range and Absorption of Cathode Rays

The maximum range of the cathode rays was determined by the red fluorescence of lime, which could be distinguished from the weak green fluorescence caused by x-rays. Fig. 2 shows the relation of the maximum range of the voltage. By extrapolating back to zero range, one finds that it takes 70 kilovolts (peak voltage) to take the electrons through a nickel window 0.013 mm. thick. Application of Thomson's[9] formula, $V_0^2 - V_x^2 = bx$, gives a value of 3.85×10^{12} for the absorption coefficient, b, for nickel. In this formula V_0 is the voltage at the start of the path and V_x is the velocity of the electron expressed in volts after the electron has traversed the distance, x. Dividing this caefflcient by the density of nickel, a value of 4.32×10^{11} is obtained for the mass absorption coefficient of the nickel window and this value is very close to the mass absorption coefficient obtained by Terrill[10] for aluminum, copper and gold.

The maximum voltage as determined by the spark gap was used in these computations since it determines the maximum range of the electrons.

Although the maximum range for 185 kv. electrons was found to be about 50 cm., the number of electrons which reach this distance is very

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[9] J. J. Thomson, "The Conduction of Electricity Through Gases," University Press, Cambridge, 1911, p. 378.

[10] Terrill, *Phys. Rev.*, 22, 101 (1923).

small. The velocity of electrons falls off in such a manner that the decrease in the fourth power of the velocities is proportional to the distance, but the number of electrons crossing a unit area decreases exponentially with the distance at a rapid rate. Accordingly it is possible to use reaction cells shorter than 50 cm. Experiments showed that for *short* exposures there was no detectable difference in the yields with reaction cells of 22 cm. or 34 cm.

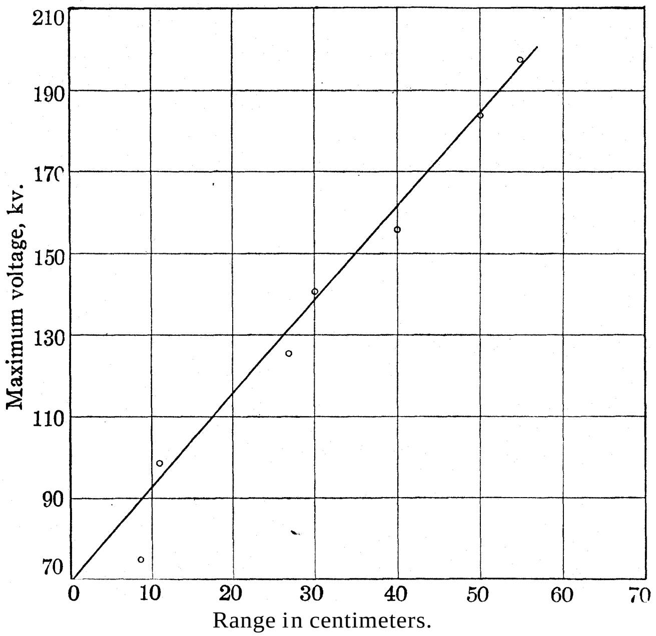


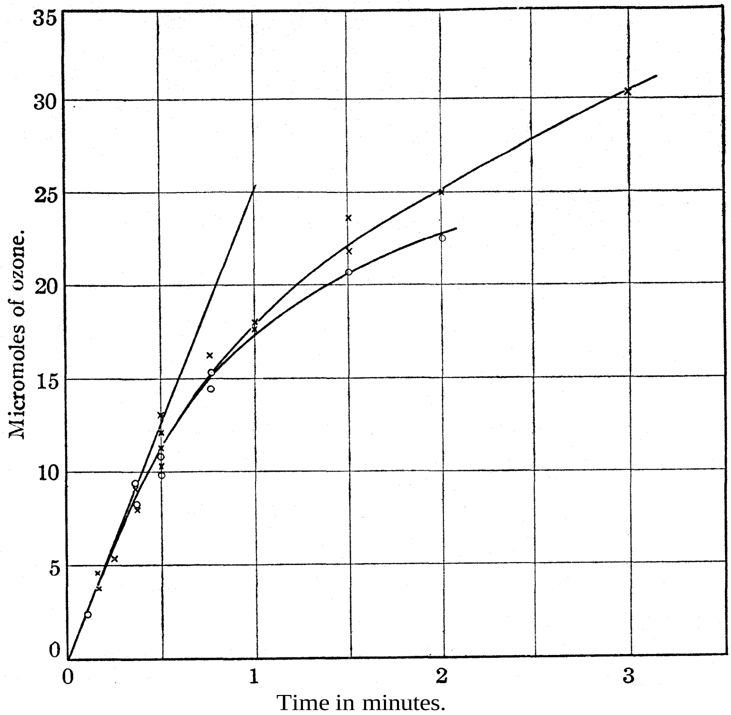
Fig. 2.—Range of electrons as measured by the fluorescence of lime in total darkness.

Action of Cathode Rays on Different Gases

Oxygen.—The action of cathode rays on oxygen was studied intensively because ozone, which is the only product, can be determined accurately in small amounts and because an extensive study of ozone formation in the electrical discharge has been made in this Laboratory. The reaction is not as simple as could be desired, however, because the decomposition of ozone very soon affects the yields.

In carrying out these experiments, the reaction cells were filled by sweeping through a rapid stream of oxygen from a tank for an hour or more and then placing the reaction cell in front of the window of the cathode-ray tube. Unless otherwise noted, the distance from the reaction cell to the window of the cathode-ray tube was 2 to 3 mm. The oxygen was then exposed to the cathode rays for the desired time, after which the ozone was determined by sweeping the gas through two bottles containing neutral 5% potassium iodide solutions. The iodine was titrated with 0.005 *N* sodium thiosulfate, 1 cc. of which is equivalent to 2.5 micromoles of ozone.

All the factors which might affect the yield were studied. It was found that for short exposures the yield was a function of the voltage of the cathode-rays, the space current, the time of treatment, the distance from the cathode-ray tube to the reaction cell and the source of the oxygen. The surface of the reaction cells, whether of glass or paraffin, had little effect and no appreciable difference in yield could be detected when using mica, aluminum or cellophane windows for the reaction cells. The yields were not appreciably influenced by the speed of the mercury turbine interrupter, the speed of the intermittent switch, the time the ozone remained in the reaction cell (except after several hours) or the moisture content of the gas.



○, Short reaction cells; X, long reaction cells.

Fig. 3.—Ozone yield from oxygen (0.4 ma.; 185 kv.).

The results of a typical series of experiments are shown in Table I and Fig. 3. In this series the influence of time was studied while the space current ahd voltage were kept constant.

With exposure of less than a minute the yields do not depend on the length (volume) of the tube. In all cases, time was given for diffusion so that the concentration would be nearly uniform throughout the chamber. The exposures were intermittent so that the total time of the exposure was ten to thirty times as long as the net exposure. The experiments marked "b" and "c" show that there is very little difference in the ozone yield when a 90-second exposure is spread over a period of one hour with the shorter tube or spread over a period of two hours with the longer tube. The experiments marked "a" show that only about a third of the

TABLE I

OZONE YIELD IN OXYGEN AS A FUNCTION OF TIME

Space current = 1 mil. amp. Voltage = 185 Kv.

Tube length, cm.	Time, sec.	Yield, micro-moles	Tube length, cm.	Time, sec.	Yield, micro-moles	Tube length, cm.	Time, sec.	Yield, micro-moles
22	7.5	2.4	22	30	10.8	34	60	18.0
34	10	3.8	34	30	11.2	22	90	20.8[b]
34	10	4.6	34	30	6.8[a]	34	90	21.9[c]
34	15	5.5	22	30	7.8[a]	22	120	22.5
34	22	8.0	34	30	12	34	120	25.0
22	22.5	9.5	22	45	15.5	34	150	31
22	22.5	8.0	34	45	16.4	22	150	23.5
22	30	9.8	22	45	14.5	34	180	30.5
34	30	13.2	34	60	18.0			

[a] Ozone stood in reaction cell overnight before analysis.
[b] Exposure extended over one hour.
[c] Exposure extended over two hours.

ozone decomposes on standing overnight, so that only a negligible amount can decompose thermally during an ordinary experiment.

The curves of Fig. 3 show that the rate of ozone formation soon falls off markedly, because the ozone is decomposed as well as produced by the cathode rays. The shorter tube with the smaller volume gives a higher concentration of ozone and hence a greater rate of decomposition. This condition gives a lower yield of ozone but the difference is not apparent until after fairly long exposures have built up appreciable concentrations of ozone. The important thing from a theoretical standpoint is not the actual ozone yield for any given exposure but the true rate of formation, that is, the yield that would be obtained if none of the ozone was decomposed. These values can be obtained by taking the tangents to the yield–time curves at zero time, since under these conditions there is no ozone to decompose. On account of the rather large percentage error at the low concentrations the curve and its tangent cannot be drawn with precision but the values are probably accurate to within 10%.

The initial rate of ozone formation, given by the tangent at zero time, is 25 micromoles of ozone per minute with a space current of 0.4 mil. amp. and a potential of 185 kv.; 25 micromoles contains 1.51×10^{19} molecules ($25 \times 10^{-6} \times 6.06 \times 10^{23}$) and 0.4 milliampere for one minute gives 1.5×10^{17} electrons ($0.4 \times 10^{-3} \times 60 \div 1.59 \times 10^{-19}$) and the M/C ratio is, therefore, 100. In other words, 100 molecules of ozone are formed for every electron that crosses the cathode-ray tube.

The influence of the space current is shown in Fig. 4, with the time kept constant at one-half minute and the voltage kept constant at 185 kv. The curve shows that in these short exposures the yield is directly proportional to the space current. This series was made under slightly different conditions than in the preceding series, so that the absolute values of the two series cannot be compared directly.

Figure 5 shows how the ozone yields change with time, when higher currents and longer exposures than those given in Fig. 3 are used. Each point shown on the curves is the average of from two to ten determinations. The long exposures had to be extended over several hours to allow time for diffusion. The short reaction cells gave yields (not shown in Fig. 5) considerably lower than the yields in the large cells because the concentration was higher and the decomposition was greater. It may be noted that with long exposures the ozone yield is not proportional to the space current through the tube.

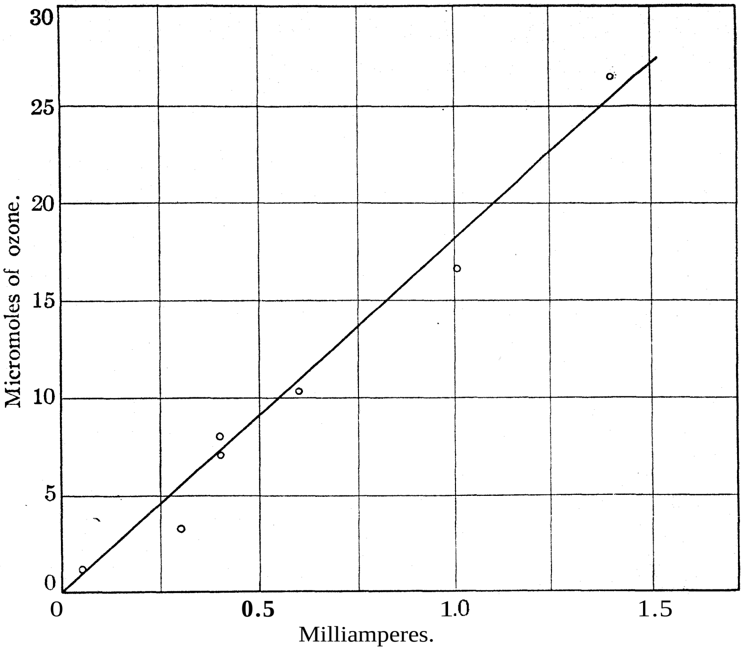


Fig. 4.—Ozone yield from oxygen with various space currents (voltage, 185 kv., time of exposure, 0.5 min.).

The curve for 1 mil. amp. space current seems to be approaching an asymptote at a yield somewhere near 75 micromoles of ozone. Since the reaction cell was 7.5 cm. in diameter and 34 cm. long, this yield corresponds to an ozone concentration of about 0.1%.

The ozone yields obtained with different voltages were studied next. All of these experiments were made with a tank of oxygen which gave low yields, probably due to an oxidizable impurity, but the relative values for the different voltages are comparable. The initial rates of ozone formation as determined by the tangents at zero time are given in Table II, together with the M/C ratios.

TABLE II

EFFECT OF VOLTAGE ON THE INITIAL RATE OF OZONE FORMATION

Voltage, kilovolts	140	102	185	200
Rate of O_3 formation, micromoles per min.	3.2	12	19	27
M/C	12.6	48	76	107

Another factor which affected the ozone yield was the distance between the window of the reaction chamber and the window of the cathode-ray tube. A series of experiments made to test this factor showed that the yield was reduced by about one-half whenever the distance between the reaction cell and the cathode-ray tube was increased by 3.5 cm.

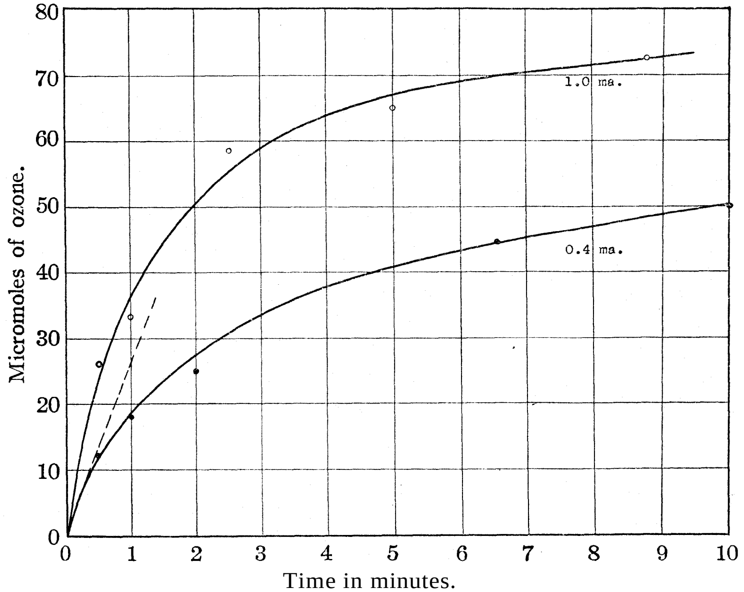


Fig. 5.—Ozone formation in oxygen (large reaction cells, 185 kv.).

Air.—When the cathode rays pass through air, they form not only ozone but also nitrogen oxides which can be determined by absorption in standard alkali before absorbing the ozone in the potassium iodide.

In carrying out these experiments the reaction cell was first filled with carbon dioxide-free, dry air, taken from outdoors to avoid the possible catalytic effect of impurities which might be present in the air of the laboratory. After treating the air with the cathode rays, the air in the cell was sucked out through a bottle of 0.01 N sodium hydroxide and two bottles of potassium iodide. Any nitric oxide formed by the cathode rays was oxidized by the ozone to nitrogen pentoxide and absorbed in the alkaline solution. The excess of sodium hydroxide was titrated with standard acid and each cc. of 0.01 N sodium hydroxide neutralized by the gases from the reaction chamber was equivalent to 5 micromoles of nitrogen pentoxide or 10 micromoles of nitric oxide.

Figure 6 gives the ozone yields for the large and small reaction cells with 186 kv. zero time with 1 mil. amp the yield is 26 micromoles of ozone per minute and the initial rate of ozone formation with 0.4 mil. amp. is 11 micromoles per minute. These data give an M/C ratio of 44, which is about half the M/C ratio in pure oxygen. The initial rates of formation are proportional to the space current but the direct proportionality does not hold for the longer exposures which involve the decomposition of ozone.

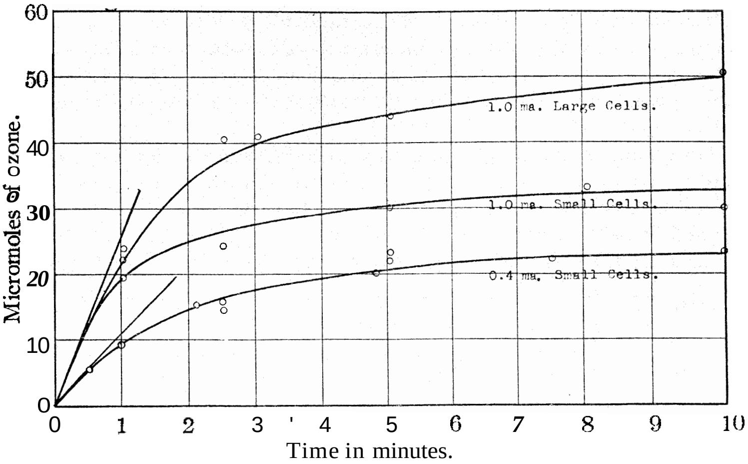
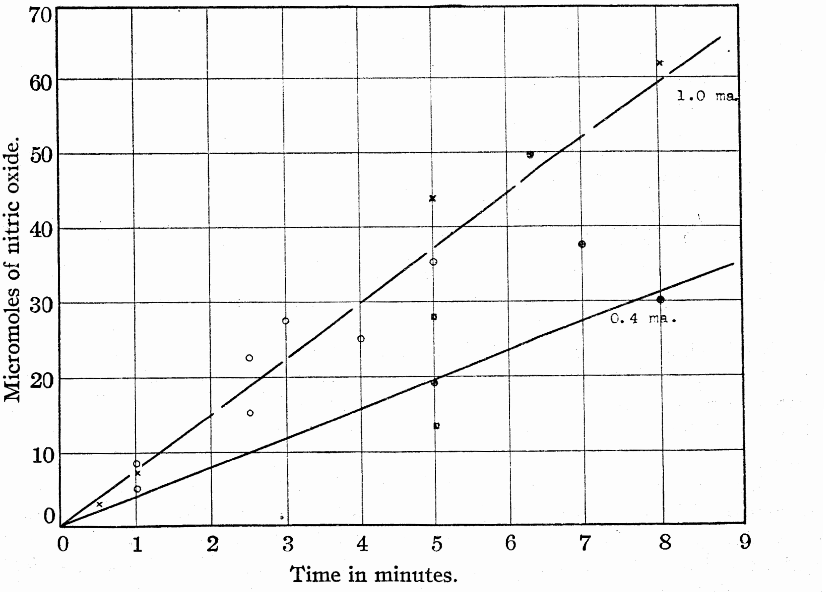


Fig. 6.—Ozone yields with air, (185 kv.).



O,⊕—Large cells; ×,□—small cells.

Fig. 7.—Nitric oxide yield with air, (185 kv.).

The nitric oxide yields, expressed in terms of micromoles of nitric oxide, are shown in Fig. 7. While the ozone curves of Fig. 6 soon flatten out on account of the decomposition of ozone, the curves for the nitric oxide show no tendency to reach an equilibrium. There were rather wide variations in the nitric oxide yields, indicating that some unknown factor was affecting the yields, but the rate of formation may be taken as about 8 micromoles per minute with 1.0 mil. amp. and 4 micromoles per minute with 0.4 mil. amp. These data give an M/C ratio of 13.5 and 16.0, or an average value of about 15 molecules per electron

The large and small cells gave the same yields within the limit of accuracy of the experiments, a result which is in accord with the fact that the rate of formation does not decrease at the higher concentrations (Fig. 7). It is probable that the nitrogen pentoxide formed from the nitric oxide is decomposed by the electron bombardment but that it is reoxidized by the excess of ozone. No attempt was made to test for nitrous oxide.

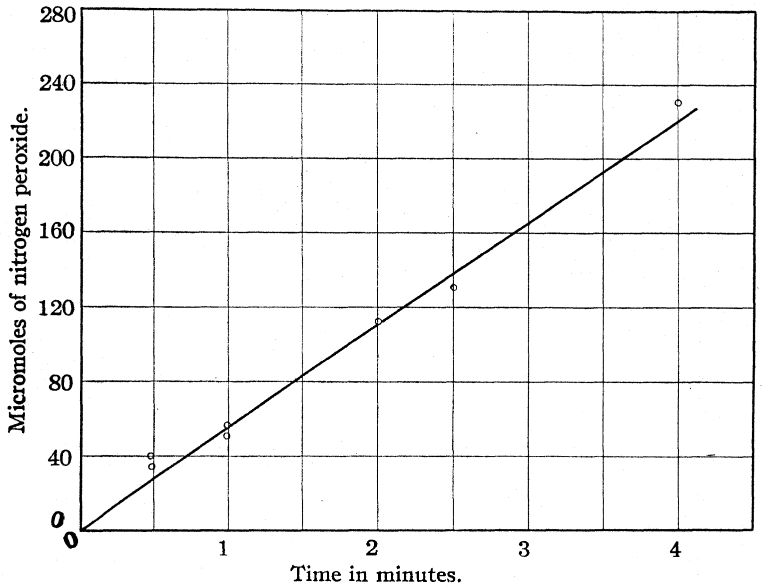


Fig. 8.—Decomposition of nitric oxide (0.4 ma., 185 kv.).

Nitric Oxide.—The nitric oxide was prepared by the action of nitric acid (1.2 sp. gr.) on copper and purified by bubbling through concentrated sulfuric acid. Any nitrogen dioxide was absorbed by the sulfuric acid. To avoid the initial oxidation of the nitric oxide by the air in the reaction cell, the air was first swept out of the cell with nitrogen.

Decomposition of the nitric oxide involved the liberation of oxygen, which then combined with the excess nitric oxide to form nitrogen dioxide. After an exposure to the cathode rays the nitrogen dioxide was determined by sweeping the gas through sodium hydroxide with nitrogen and titrating the excess alkali with 0.1 N sulfuric acid, using methyl red as an indicator.

The reactions are taken to be

$$2NO = N_2 + O_2$$
$$O_2 + 2NO = 2NO_2$$
$$NO_2 + NO + 2NaOH = 2NaNO_2 + H_2O$$

One cc. of 0.1 N alkali is equivalent to 50 micromoles of nitrogen dioxide or 50 micromoles of nitric oxide decomposed.

Great care was necessary to prevent the access of air to the nitric oxide, as it would also give nitrogen dioxide. It was necessary to displace the air in the absorption bottle with nitrogen and to prevent back-diffusion of air with a second wash bottle.

The nitrogen used in these experiments contained a small amount of oxygen and blank experiments were necessary to determine the amount of nitrogen dioxide produced by this oxygen impurity. The same procedure was followed as in a regular experiment except that the nitric oxide was not exposed to the cathode rays. The four blank determinations gave **2.8, 2.9, 2.7** and ***2.6*** cc. of 0.1 N sodium hydroxide. In the last experiment ***(2.6*** cc.) the nitric oxide remained in the cell overnight before being swept out through the alkali, and the close agreement with the other values proved that the cell was air tight and that the cellophane windows were not porous.

The influence of the time of treatment is shown in Fig. **8** and the influence of the magnitude of the space current on the decomposition was studied also. These curves show no equilibrium effect up to four minutes with 0.4 mil. amp. and 185 kv. and indicate either that nitrogen dioxide is not easily decomposed by the cathode rays or more likely that the decomposition products recombine on standing. The rate of nitric oxide decomposition is **57** micromoles per minute with 0.4 mil. amp. space current at 185 kv. and the corresponding M/C ratio is 230.

Carbon Dioxide.—The reaction cells were filled from a tank with carbon dioxide which had been purified by passing through concentrated sulfuric acid and chromic acid and then through phosphorus pentoxide. After treatment with the cathode rays, the gas was swept out with carbon dioxide through a 10% potassium iodide solution to remove any ozone. The exit gases passed through a tube of iodine pentoxide heated to 150° in an oil-bath, and then through 10 cc. of 10% potassium iodide solution to absorb the iodine liberated by carbon monoxide according to the reaction

$$5CO + I_2O_5 = 5CO_2 + I_2$$

The ozone and the carbon monoxide were both determined by titration with $N/200$ sodium thiosulfate.

It was necessary to make a considerable correction for the iodine carried over from the iodine pentoxide when the untreated gas was passed through.

The results were very unsatisfactory and in the first experiments appreciable hut inconsistent amounts of ozone were found. The last two experiments extending over a longer period of time are thought to be more reliable. The rays were passed into the carbon dioxide for a net time of ten minutes at 200 kv. and 1.0 mil. amp. The blank correction amounted to about one-fourth of the total titration; 0.35 and 0.60 mg. of carbon monoxide were obtained. The average, 0.47 mg., corresponds to 10^{19} molecules and the current of 1.0 mil. amp, corresponds to 3.8×10^{18} electrons. The M/C ratio is, therefore, ***3*** molecules per electron crossing the tube when the maximum potential drop across the tube is 200 kv.

Calorimetric Determination of Energy of Cathode Rays

It was desired to study the relation between the energy of the cathode **rays** and the chemical reactions produced, but the wave form produced by the induction coil was so distorted and the loss of energy so great that the energy delivered to the reaction chamber could not be calculated from the voltage and amperage in the cathode-ray tube. A rough measurement was obtained, however, with the help of a special calorimeter placed at a position corresponding to the end of the reaction chamber. It was assumed that all the electrons which would have entered the reaction chamber were stopped by the small calorimeter and converted into heat. It was assumed also that the number of secondary electrons emitted backward was small and sufficiently constant so that no appreciable error was introduced by using copper in the calorimeter and aluminum or cellophane in the reaction cell. Experiments had shown that cellophane and aluminum windows gave the same yield.

A flat, circular chamber was made of thin copper, 7.5 cm. in diameter and 0.7 cm. thick. A horizontal glass capillary was attached to the copper chamber and the apparatus was filled with nitrobenzene and operated simultaneously as a thermometer and a calorimeter. When the cathode rays were stopped by the copper chamber, the heat generated caused the nitrobenzene to expand and move out along the capillary tube. The capillary was calibrated in terms of centigrade degrees by setting the calorimeter into a water-bath at definite temperatures. The distance traveled by the nitrobenzene in the capillary was practically a linear function of the temperature. The heat capacity of the copper was 4.08 and that of the nitrobenzene 6.97, giving a total heat capacity of 11.05 calories per degree.

Heating and cooling curves were plotted and the temperature change was found to be quite uniform after a short initial period. The measurement was complicated by the fact that the framework supporting the window of the cathode-ray tube became hot after a while and radiated heat to the calorimeter, necessitating a somewhat arbitrary correction amounting usually to between 10 and 20% of the total value.

The results are summarized in Table III.

TABLE III

ENERGY OF CATHODE RAYS RECEIVED BY CALORIMETER

Dist. from window to calorim., cm.	Max. voltage, kv.	Current, mil. amp.	Temp. rise in calorim. per min., °C.	Energy rec'd. with intermit. curr., cal./min.	Energy received if current were continuous, cal./min.
0.5	200	1.0	1.50	16.5	66.0
2.0	200	1.0	0.76	8.4	33.6
2.0	200	1.0	.90	10.0	40.0
2.0	200	0.5	.43	4.8	19.2
2.0	200	0.5	.42	4.6	18.4
2.0	185	1.0	.49	5.4	21.6
2.0	185	1.0	.49	5.4	21.6
2.0	185	0.5	.25	2.7	10.8
2.0	162	1.0	.35	3.8	15.2

The energy actually measured per minute while the tube was in operation is given in the next to the last column and these values are multiplied by 4 to give the figures of the last column. The current was on for about $^1/_8$ second and off $^3/_8$ second to keep the window cool, so it was flowing for only one-fourth of the actual time of an exposure.

The results are quite consistent, the temperature rise for 1.0 mil. amp. being twice as great as the rise for 0.5 mil. amp., but the constant error due to the thermal radiation from the window of the tube may be fairly large.

The greatest energy, amounting to 66 calories per minute, was introduced when the calorimeter was half a centimeter from the window. The measurements at 2 cm. are more valuable for the calculations because the absorption by the cellophane window of the reaction chamber was found to be equivalent to 2 cm. of air.

The average value at 2 cm. with 1 mil. amp. and 200 kv. was 36.8 cal. per minute; and at 185 kv. it was 21.5.

The energy registered by the calorimeter is very much smaller than the product of the maximum voltage and the current measured in the cathode-ray tube. At 200 kv. it is 1.3%, and at 185 kv. it is 0.8%. The chief reason for the low percentage lies in the fact that the *maximum* voltage of the induction coil as registered by the spark gap is much greater than the voltage during the rest of the period. Furthermore, the energy reaching the calorimeter or the reaction chamber was less than that in the cathode-ray tube because some of the electrons were stopped by the grid and the window and some were deflected to one side by air molecules before reaching the chamber. The loss of energy was assumed to be the same in both the chemical measurements with the chamber and the energy measurements with the calorimeter.

Conclusions

For the sake of comparison, representative data on the different gases are collected in Table IV.

TABLE IV

SUMMARY OF EFFECTS OF CATHODE RAYS ON VARIOUS GASES

Reaction	Voltage, kv.	Curr., mil. amp.	Micromoles per min.	M/C	Cal. per min.	Cal. per mole
$O_2 \longrightarrow O_3$	185	0.4	25	100	8.6	3.4×10^5
Air $\longrightarrow O_3$	185	.4	11	44	8.6	7.8×10^5
Air $\longrightarrow$ NO	185	.4	4	14	8 6	22×10^5
NO $\longrightarrow O_2$	185	.4	57	230	8 6	1.5×10^5
$CO_2 \longrightarrow$ CO	200	1.0	2	3	37	$180 \times 10''$

In Col. 1 is given the reaction which was measured chemically and in Col. 2 the maximum voltage across the tube as measured with a spark-gap. Col. 3 gives the space current or electron current across the tube. Col. 4 contains the yields in micromoles per minute as obtained by chemical analysis. In cases where known secondary reactions occurred corrections were made. In Col. 5 are found the M/C values or the ratio of the number of molecules of product to the number of electrons passing across the cathode-ray tube. The actual number of electrons entering the reaction chamber is less than C and undetermined in this research, but it is directly proportional to C because the conditions were alike in all the experiments. In the next to the last column the energy of the cathode rays entering the reaction chamber is recorded in calories per minute. The values were obtained by stopping the electrons with a calorimeter. In the last column is given the energy of the cathode rays in calories necessary to give a gram molecule of the product.

An examination of Table IV shows that of these reactions the decomposition of nitric oxide proceeds the most readily and the decomposition of carbon dioxide proceeds the least readily. After the decomposition of nitric oxide, the formation of ozone from oxygen proceeds most easily, followed by the formation of ozone from air, and nitric oxide from air. All these reactions are endothermic reactions but there seems to be no simple connection between the response to cathode rays and the heat of formation, or the free energy of the different gases.

The chemical action of the cathode rays appears rather inefficient in the systems studied. In some cases the efficiencies are low because the cathode rays are used up in producing effects which are not detected by the chemical test employed. For example, the ozone yield in air is less than the ozone yield in oxygen because in air some of the electrons are used up in making nitric oxide instead of ozone.

No direct determinations were made on the decomposition of ozone but it was found that an equilibrium existed at about 0.1% ozone under the cathode-ray bombardment. Since there were about 1000 times as many oxygen molecules as ozone molecules at equilibrium, the decomposition of ozone must be approximately 1000 times as fast as the formation, under the conditions of the experiment. The decomposition of ozone is an exothermic reaction and proceeds much more readily than the endothermic reactions which have been studied. Extensive experiments were carried out also with another exothermic reaction (the union of nitrogen and hydrogen to form ammonia) but the yields were so small and so inconsistent that the data have not been reported.

The total number of ions produced in the reaction chamber could not be determined, although attempts were made to obtain a saturation current with a 2000-volt dry battery. It is possible, however, to estimate from the energy measurements the maximum number of ions which could have been obtained. From the ionization potential of 15 volts it can be calculated that the formation of a pair of ions of molecular oxygen requires 2.4×10^{-11} ergs. The input of 8.6 calories (or 3.6×10^{8} ergs) of energy in the form of cathode rays can produce no more than $3.6 \times 10^{8} \div 2.4 \times 10^{-11}$ or 1.5 X

10^{19} pairs of ions. The 25 micromoles of ozone produced by the same cathode rays contain 1.5×10^{19} molecules. These calculations show that within the limits of accuracy of the thermal measurements the number of molecules is equal to the number of pairs of ions. This estimate checks with the M/N ratio for ozone obtained by Lind[11] using a-ray bombardment, but it is not in agreement with the results of Krueger and Utesch[6] in which the M/N ratio was found to be about 40. If the ionization potential of **23** volts for atomic oxygen is taken, there are 1.5 molecules for every ion pair, and if the resonance potential of 8 volts is taken, there is about one molecule of ozone for every two excited oxygen molecules.

It is to be noted that the M/C ratios discussed before are purely empirical values used for purposes of comparison of different gases under similar conditions. C represents the average number of electrons crossing the tube and it is considerably larger than the number of electrons entering the reaction chamber.

The results of this investigation indicate that the chemical behavior of high voltage electrons is essentially the same as that of a-particles. This similarity in behavior is to be expected because the greater part of the chemical action of a-particles is effected through electrons of high velocity driven out from molecules in the path of the a-particle, and these electrons are the same as the electrons shot out from the cathode-ray tube. The M/N ratio for ozone obtained in oxygen with cathode rays was calculated to be the same within the limits of experimental error as that obtained with a-particles. Moreover, the decomposition of carbon dioxide was found to be very slight and this fact checks well with the facts of radioactivity. Alpha-particles do not produce any change in this gas[12] on account of reversion of the CO_2^+ ions to CO_2. The high yield in the decomposition of nitric oxide is to be expected also, because the ionization potential is only 9 volts instead of the 15 volts for oxygen.

It might he expected that an appreciable part of the energy of the moving electron would be used up in displacing the electrons in molecules rather than in expelling them. From the close relation between ion pairs and molecules and the checks with experiments using a-particles, it appears that nearly all of the energy of the cathode ray goes to complete ionization rather than to the displacements which correspond to resonance potentials. As long as the electron has energy equal to or greater than the ionization potential, most of the effects will be ionizations.

The chemical effects produced by cathode rays of definite voltage depend on the ionization potential of the gas and on the stoichiometrical reactions which follow the ionization, and they are very similar to the chemical effects of a-particles.

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[11] **Ref. 1, p. 92.**

[12] **Ref. 1, p. 155.**

The authors are glad to acknowledge assistance received from the Coffin Foundation in the form of a scholarship to one of us.

Summary

1. The chemical effects produced in gases by electrons from a Coolidge cathode-ray tube have been studied. The gases were enclosed in separate vessels not in contact with the window of the tube. The influence of time, voltage and space current has been studied.

2. Ozone was obtained from oxygen and the ozone was in turn decomposed. The rate of ozone formation was obtained by extrapolation to "zero time."

3. The chemical effects were expressed as the ratio of molecules produced per electron crossing the cathode-ray tube. These M/C ratios are as follows: nitric oxide decomposition 230, ozone from oxygen 100, ozone from air 44, nitric oxide from air 14, carbon dioxide decomposition 3.

4. The energy of the cathode rays was obtained with a small calorimeter and it varied from 3 to 16 calories per minute.

5. A calculation of the maximum number of ions was made using the energy input and the ionization potential of oxygen. This estimate gives a ratio of molecules to gas ions approximately the same as has been found with a-particles.

6. The close similarity in chemical behavior of cathode rays and α-particles has been emphasized. The yield depends on the ionization potential of the gas and the stoichiometrical reactions which follow ionization.

MADISON, WISCONSIN

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

THE HEAT CAPACITY AND ENTROPY OF BARIUM BROMATE FROM 16 TO 300° ABSOLUTE. THE ENTROPY OF BROMATE ION

BY BERNARD S. GREENSFELDER AND WENDELL M. LATIMER

RECEIVED SEPTEMBER 10, 1928 PUBLISHED DECEMBER 10, 1928

This work is a part of the program for the evaluation of entropy of aqueous ions as a means of facilitating the thermodynamic treatment of solutions. The general theory has been treated in previous papers by Latimer and coworkers.[1]

The present paper initiates work in the field of the halogenate ions, ClO_3^-, BrO_3^- and IO_3^-, and it is planned to use the entropy values obtained with experimental reaction heats in order to obtain the free energies of these ions. The experimental method follows the general plan of study

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[1] (a) Latimer and Buffington, THIS JOURNAL, 48, 2297 (1927); (b) Latimer, *ibid.*, 48, 2868 (1926); (c) Latimer, *J. Phys. Chem.*, 31, 1267 (1927); (d) Latimer and Greensfelder, THIS JOURNAL, 50, 2202 (1928); (e) Latimer and Kasper, unpublished material.

of cesium alum by Latimer and Greensfelder,''wherein complete references to specific heat technique and laboratory technique are given.

Material.—Barium bromate monohydrate, $Ba(BrO_3)_2 \cdot H_2O$, was selected because of its low solubility, well-defined monoclinic crystal structure and purity. "C. P." material free from heavy metals, iron and bromide was obtained from the Mallinckrodt Company. A water determination gave 4.42% of water; theoretical, 4.38%. The specific heat measurements were made on a sample weighing 145.80 g.

Measurements.—The molal heat capacity values fall smoothly on a curve with two points of double inflection at 150°K. and at 190°K., too slight to be noticed on the accompanying diagram.

The gold resistance thermometer proved adequate to fix the temperature differences down to 13.92°K., the initial temperature of the first run. The calibrations continuously made against thermocouple No. 109 agreed exactly with two previous sets of comparisons, except in the range 30 to 105°K., wherein the resistance showed a regular deviation, reaching a maximum of 0.012 ohm/ohm at 37°K. This is, incidentally, the point of maximum deviation from rectilinearity of resistance as a function of temperature.

It was also noted that the thermocouple e.m.f. at the temperatures above 200°K. was altered by a change in the temperature of the surrounding block and radiation shield, necessitating the selection of a mean value corresponding to equal temperature of block and radiation shield with respect to the calorimeter. As a check, eight special calibrations were made with an average temperature difference between block and calorimeter of 0.05 degree. The resulting points accurately confirmed the previous mean values.

TABLE I

HEAT CAPACITY OF BARIUM BROMATE

Molecular weight of $Ba(BrO_3)_2 \cdot H_2O$ = 411.22

T, °K.	Sp. heat, cal./g./deg.	Molal heat cap., cal./mole/deg.	T, °K.	Sp. heat. cal./g./deg.	Molal heat cap., cal./mole/deg.	T, °K.	Sp. heat, cal./g./deg.	Molal heat cap., cal./mole/deg.
16.36	0.0052	2.15	94.24	0.0666	27.39	187.42	0.1038	42.70
19.57	.0077	3.15	99.63	.0692	28.47	193.33	.1052	43.27
23.65	.0116	4.77	103.82	.0718	29.54	202.51	.1069	43.98
28.06	.0160	6.57	109.30	.0748	30.77	209.79	.1096	45.07
33.12	.0212	8.71	114.58	.0775	31.87	217.41	.1113	45.77
37.42	.0257	10.56	119.87	.0795	32.71	229.40	.1144	47.02
41.49	.0294	12.08	138.11	.0868	35.68	237.35	.1160	47.69
47.34	.0343	14.17	145.05	.0884	36.35	245.19	.1184	49.13
58.57	.0421	17.30	151.70	.0910	37.41	252.67	.1205	49.57
63.67	.0480	19.74	156.76	.0925	38.05	269.19	.1236	50.83
69.80	.0530	21.76	162.71	.0956	39.30	280.97	.1255	51.60
77.91	.0573	23.55	168.33	.0974	40.07	288.24	.1270	52.20
83.68	.0609	25.03	174.28	.1014	41.69	295.88	.1294	53.21
88.91	.0638	26.25	181.06	.1016	41.76			

TABLE II

ENTROPY OF BARIUM BROMATE

0–3°K.	Debye T^3 Rule	0.010 E. U.
3–10°K.	Extrapolation	0.432 E. U.
10–298.1°K.	Graphical	80.276 E. U.
		80.718 E. U.

Entropy of barium bromate at 298.1°K. = 80.72 E. U.

Heat Capacity and Entropy of Barium Bromate

The experimental data are given in Table I, accompanied by a summary of the entropy calculations and illustrated by Figs. 1 and 2.

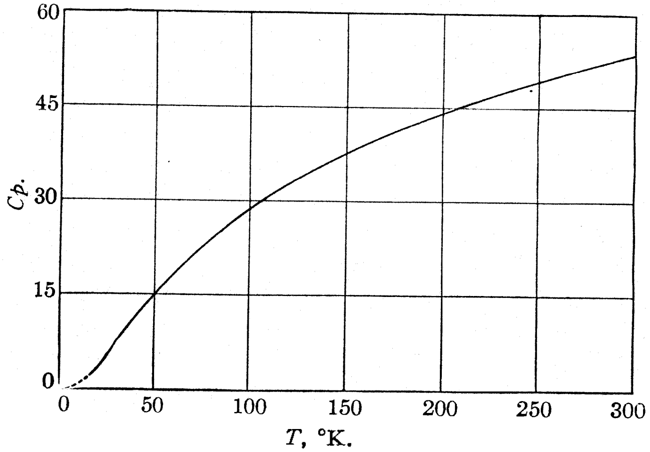

Fig. 1.—Molal heat capacity of barium bromate.

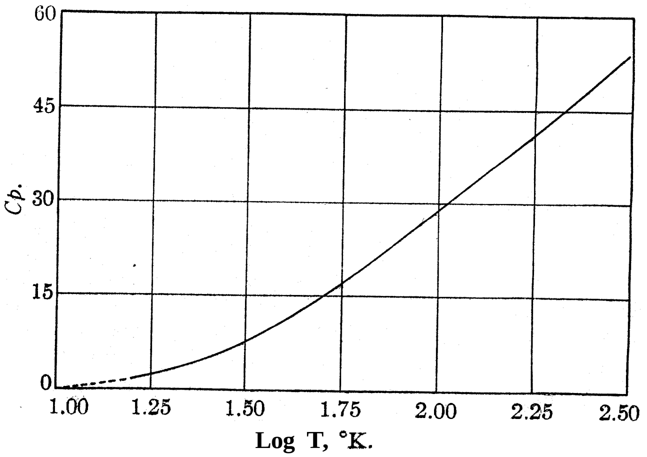

Fig. 2.—Molal entropy of barium bromste.

Heat of Solution.—The ΔH of solution of barium bromate may be calculated from the solubility-temperature coefficient as based on the solubility data of Trautz and Anschütz[2] and Harkins,[3] shown in Fig. 3. The single point of Harkins at 25° closely checks that of Trautz and Anschütz. The equation, originally applied by van't Hoff, may be given in the convenient form $\Delta H = -(R\, d(\ln K)/d(1/T)$.

The validity of the expression is dependent entirely upon the approximation of the given system to the laws of the ideal or perfect solution. In the absence of such complicating factors as hydrolysis and specific ion association, the ionic activity coefficients should accurately correct for the Debye-Hückel deviation. If such activities are then included in the equilibrium constant, K, ΔH will then presumably correspond to the true experimental value.

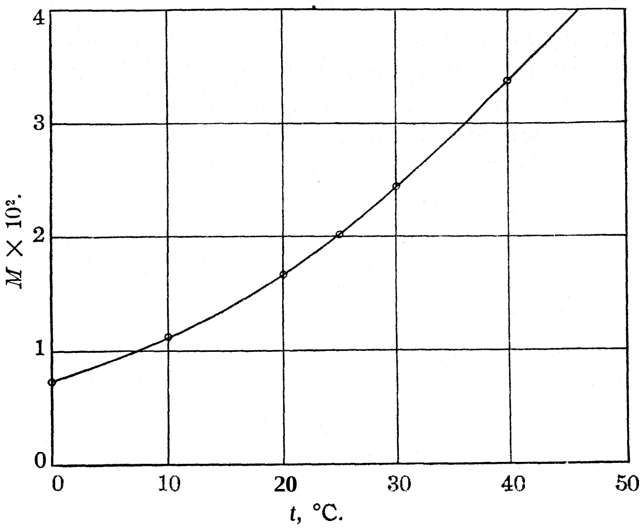

Fig. 3.—Solubility of barium bromate.

In the present case $Ba(BrO_3)_2 \cdot H_2O$ is considered free from hydrolysis or any ion association sufficient to exert perceptible influence on the heat of solution. The activity coefficients have been obtained with the aid of Professor M. Randall after a survey of similar ion types, and also from the data given by Lewis and Randall.[4]

It then follows that $\Delta H = -[4.5746\ d \log (\gamma\, m)^3]/d(1/T)$ and $\Delta H = +15{,}064$ calories.

From the solubility at 25°, we find $\Delta F = -RT \ln K = -1363.7 \log 4 \times (0.550 \times 0.02023)^3 = +7171$ calories.

Then $\Delta S_{\text{sol.}} = (\Delta H - \Delta F)/T = (15064 - 7171)/298.1 = 26.48$ E. U.

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[2] Trautz and Anschütz, *Z. physik. Chem.*, 56, 236 (1906).

[3] Harkins, This Journal, **33**, 1815 (1911).

[4] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, 1923, p. 382.

Entropy of Bromate Ion.—Now $Ba(BrO_3)_2 \cdot H_2O = Ba^{++} + 2BrO_3^- + H_2O$. Using the value for Ba^{++} given by Latimer and Buffington,[1a] and that for water obtained by Latimer and Greensfelder[1d] from the data of Simon and others, we find $S^\circ_{BrO_3^-} = {}^1/_2(80.72 + 26.48 - 15.92 - 4) = +43.6$ E. U., and the entropy of BrO_3^- at 298.1°K. = +43.6 E. U., with respect to $S^\circ_{H^+} = 0$.

The greatest uncertainty is the value for the heat of solution and it is planned to check this value by a direct experimental determination.

The authors wish to thank Mr. J. Elston Ahlberg of this Laboratory for assistance in the experimental work and calculations.

Summary

The specific heat of $Ba(BrO_3)_2 \cdot H_2O$ has been measured from 16 to 300°K. These values, together with the heat and free energy of solution of barium bromate, have been used to calculate the entropy of bromate ion in hypothetical one molal aqueous solution.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY, HARVARD UNIVERSITY]

THE COMPRESSIBILITY OF THALLIUM, INDIUM AND LEAD[1]

BY THEODORE W. RICHARDS AND JOSEPH D. WHITE

RECEIVED SEPTEMBER 18, 1928 PUBLISHED DECEMBER 10, 1928

Introduction

Existing data on the compressibility of thallium are in apparent conflict. The first pertinent experimental work[2] on this metal (about twenty years ago) gives the value 2.85 × 10^{-6} for the cubic compressibility at 20° over the pressure range 100–500 megabars. Fifteen years afterwards, P. W. Bridgman published a determination[3] seeming to indicate that the cubic compressibility under the same conditions may be considerably larger—about 3.5 × 10^{-6}. This latter determination was based upon the linear compressibility, actually measured, which was multiplied by three on the assumption that thallium is isotropic. Bridgman pointed out that the large difference between his value and the earlier

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[1] Note by *the* Editor.—This research was completed in 1927 under the direction of Professor Theodore W. Richards but the present account of it was prepared after the death of Professor Richards by Dr. Lawrence P. Hall.

[2] Richards and Stull, *Carnegie* Institution *of* Washington, Pub. No. 76, 1907, p. 65. The value there given, 2.6, after correction for the new compressibility of mercury, for slight errors in the pressure gage and to the megabar standard, becomes 2.85 X 10^{-6}. The value given on page 62 is wrong through typographical error—a misprint which has unfortunately been copied elsewhere (for example, THIS JOURNAL, **37,** 1646 (1915)).

[3] Bridgman, Proc. Am. *Acad.* Arts *Sci.,* 58, 198 (1922).

one "strongly suggested that the crystal system cannot be cubic."[4] If this were the case, of course, his determination of the linear compressibility means little unless the direction in relation to the crystal axis is known; and since the specimen was an extruded one, definiteness in this respect is unlikely.

The discrepancy prompted further experimental investigation, especially desirable since compressibility has acquired important significance in relation to internal pressure. The earlier work referred to above was of a pioneering nature and was made to discover rather the order of magnitude of various compressibilities than the precise values, although indeed the results have nearly all of them, except this one, been confirmed within a narrow limit of error by subsequent investigators. Accordingly, the present investigation was carried out with greater care.

The earlier result was in fact found to be very close to the true value. Bridgman's inference as to the cause of the discrepancy of his value and ours is supported; it has been confirmed, moreover, very recently by Terpstra, and others,[5] who have shown that the crystal structure of metallic thallium is face-centered tetragonal, similar to that of indium and gallium. Becker and Ebert state that the axial ratios are almost unity, but according to Terpstra the ratio is 1.58. This would account for the wide discrepancy in values for the compression coefficient.

The compressibility of indium also was studied, because of the fact that only a very small amount of the metal had been available for the use of previous experimenters. This outcome also, verified the earlier work at Harvard within a reasonable limit of error.

The compressibility of lead was redetermined as a test of the methods used.

Preparation of Materials

Mercury was purified in the usual fashion by passing it in fine drops through dilute nitric acid and by final distillation, according to Hulett. Toluene was purified by shaking a commercially pure sample with three successive portions of concentrated sulfuric acid, each time washing with water, dilute sodium hydroxide and again with water. After standing over anhydrous calcium chloride, it was shaken with separate quantities of clean mercury until no further tarnishing of the mercury took place; subsequently the toluene was distilled. The middle fraction (mean boiling point, 110° at 760 mm.) was preserved over sticks of sodium hydroxide in a glass-stoppered bottle and used in the determinations.

The lead was a very pure specimen, most of which had previously been used for the purpose.[6]

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[4] In an anisotropic crystal there is a marked difference in linear compressibility ong its different axes. See, for example, Bridgman's values for zinc, ref. 2, p. 217.

[5] (a) P. Terpstra, *Z. Krist.*, 63, 318 (1926), quoted in *C. A.*, 20, 3105 (1926): (b) Becker and Ebert. *Z. Physik*, **16**, 165 (1923).

[6] Richards and Bartlett, THIS JOURNAL, 37, 470 (1915).

Thallium

The purification of the thallium offered much difficulty. Several hundred grams of crude thallium containing several per cent. of impurities (mostly lead and zinc) served as a starting point. This was dissolved in hot dilute nitric acid and the crystals of nitrate were treated with concentrated sulfuric acid in slight excess. After all of the nitric acid had been expelled at a high temperature and fumes of evaporating sulfuric acid were evolved, the sulfate paste was dissolved in excess of pure water and the residual lead sulfate was separated. Small amounts of thallic oxide formed were reduced with sulfurous acid. The sulfate was once crystallized and from its solution thallium was deposited electrolytically, having present an excess of sulfuric acid sufficient to prevent the deposition of zinc at the cathode and thallic oxide at the anode. It was necessary to make this solution very dilute to avoid the inclusion of sulfate and the current density **was** kept low in order that the metal should be precipitated as compact, well-defined crystals. As usual, great current density produced only a spongy product. From time to time the crystals were removed by means of a small glass fork from the cathode to a casserole, in which they were leached free of salt and acid by many successive additions of pure, boiled but cool water, and preserved in a glass-stoppered bottle filled to the neck with freshly boiled water. These precautions are necessary; otherwise the substance on subsequent fusion will contain sulfate and oxide, rendering fusion difficult and the product impure.

When ready for fusion the thallium was shaken free of all superficial water by centrifuging, dried as rapidly as possible in a vacuum desiccator and fused in a steady flow of pure hydrogen at a temperature of 400°, whereby traces of mercury and other volatile impurities were driven off. The surface of the fused and cooled mass was scraped free of most of the slag (presumably thallium oxide) and the porcelain boat which served to contain the metal was transferred to a specially designed slag funnel. On remelting by uniform heating, the thallium was quickly poured into a clean glazed boat, the slag remaining behind. Finally, the purified metal was cast into a cylinder and turned in a lathe to fit the piezometer.

Indium

The method of preparation of the allied metal, indium, was not dissimilar, although not quite identical. The source was a large quantity of material obtained in several lots as a by-product from a recent research on the atomic weight of gallium.[7] Part had been prepared in preliminary fashion during vacation by Dr. Craig, who very kindly gave it to us for the present purpose. The original source of all was the Oklahoma residues described elsewhere.

The particular specimens used had been largely freed from lead, copper, gallium and arsenic, as well as much of the zinc. Further steps were necessary, however, to obtain adequate purity. The first lot of this material was dissolved by an excess of sulfuric acid and the warm, dilute solution treated with hydrogen sulfide. The precipitate was removed; after partially neutralizing with ammonia, the filtrate was again saturated with hydrogen sulfide, and the small amount of precipitated indium sulfide mixed with impurities was again filtered off. Zinc and iron still remained to be separated, at least in part. For this purpose fractional electrolysis was tried. Neither a strongly acid nor a completely neutralized solution gave satisfactory results, but electrolytic deposition could be effected when the solution was about half normal in acid.

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[7] Richards and Craig, THIS JOURNAL, 45, 1155 **(1923).**

With suitable current density (easily regulated) the indium was deposited in compact form on stout platinum wires (about 1 cm. long) sealed into soft glass tubing. At first only the tip of the cathode was covered with electrolyte. During six or seven hours, somewhat less than 1 g. per hour could conveniently be deposited on each electrode. The small pieces of indium were washed with water and preserved under freshly prepared distilled water. All the fractions contained zinc, since the current density was too great to separate this metal from indium.

These nuggets, although they had been somewhat protected against oxidation, were so much oxidized that they refused to melt together in a current of hydrogen. To effect coalescence, the drops of melted indium were rubbed together under paraffin at the temperature of about 170° (melting point of indium, 156°).[8] Stirring the material under this protecting environment caused the slag to be suspended in the paraffin, whereas the melted metal easily united into a bright, coherent globule. Some of the material is, of course, lost with the slag, but at least 70% may be recovered.

The clean metal thus prepared, after being all melted together and freed from paraffin with benzene, was re-melted and cast into a cylinder of a proper diameter to fit the piezometer. The tube for casting, of proper bore, containing the indium, was allowed to cool very slowly by being gradually lowered through a ring burner, the solidification of the metal taking place from below upward. Thus the formation of cavities within the cast metal was prevented. The cylinder thus obtained weighed approximately 35 g. and was used for preliminary determinations of compressibility.

Since neither the quantity nor the purity of this specimen was adequate for the best possible results, a larger specimen of purer material was prepared for the final determinations. The 35 g. specimen itself formed part of the raw material for the new sample. It was fractionally crystallized as metal three times, 22 g. of purer material being thus recovered. The several fractions poured off as liquid, which contained much of the zinc, were then dissolved in dilute sulfuric acid, filtered from a trace of lead sulfate, treated with hydrogen sulfide, again filtered and freed from the gas, precipitated as indium hydroxide, leached with 5 separate portions of dilute pure caustic potash to remove as much as possible of the residual gallium and zinc and then washed a number of times by decantation with water. This solution was then combined with other similar ones to be described.

The most impure of the residues were brought to a state of moderate purity before the process of further purification described above in detail was applied. In this preliminary treatment the sulfite method was used to eliminate iron. Several other specimens of indium residue were also worked up by substantially the same method, and added to the material. A number of solutions, all of about the same degree of purity and containing a total of about 105 g. of indium, were combined and electrolyzed; nearly 90 g. of metal was separated and fused together in the way already described.

The solidifying point at this stage averaged 145.1°, as found by the method commonly used for organic compounds, while a sample of the pure indium used by Richards and Sameshima[9] gave a value 156°+ by the same method. Spectrographs were now made by an accurate Féry spectrometer, in order to determine the nature and quantity of the impurities. As was expected, considerable zinc still remained, but only faint traces of gallium were to be seen and nearly all of the lead also had been eliminated.

For final purification the method described by Richards and Craig for freeing gallium from zinc was used. Indium, like gallium, has a very high boiling point, whereas zinc, even from an alloy, has considerable vapor pressure at a bright red heat. Hence,

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[8] This device was suggested by Dr. Craig, based upon his experience with the material.

[9] Richards and Sameshima, THIS JOURNAL, 42, 49 (1920).

by heating sizable portions of the sample in a large evacuated silica test-tube, the zinc was easily distilled into the upper part of the tube, taking with it only a very small amount of indium. Determinations of the zinc in the sublimates from weighed portions (by titration with ferrocyanide standardized against pure zinc) gave an average of 2.7% of zinc in the original metal. The melting points of different almost non-volatile residues varied from 154 to 156°. A cooling curve of the combined preparations (85 g.) gave a nearly constant temperature (155") for four minutes, during which time almost all of the melted mass solidified (or, on warming, almost all of the solidified mass melted). The specific gravity of the metal thus prepared and very carefully cooled was found to be 7.296. Richards and Wilson[10] found the density to be 7.277, but their samples had not been cooled so carefully and may have contained minute air bubbles. Spectrographs of the non-volatile metallic mass showed it to be free from zinc. The amount of gallium remaining was only a trace and other likely metals were sought for but not found. Thus, although the claim cannot be made that this 85-gram specimen was absolutely pure, it was evidently more than pure enough to serve the purpose in hand. Zinc had been the only substance really difficult to eliminate and that was wholly eliminated by the process of heating to high temperature *in vacuo*.

Standardization of Absolute Gage

Since the exactness of standardization of pressure is important, the weights used in the absolute pressure gage were all carefully compared with a weight standardized by the Bureau of Standards at Washington. A second set of weights was also calibrated for use with a second (auxiliary) absolute gage, which was used only for comparison and calibration of the first gage, as will presently be discussed.

The pistons of both gages were accurately measured with Brown and Sharpe micrometer calipers and with a Newall measuring machine at the Taft-Pierce Co. of Woonsocket, R. I. The diameters of the cylinders to hold the gages were determined by measurement of closely fitting plugs. The first piston (used throughout the experiments) had a diameter of 0.6360 cm. and its cylinder had a diameter of 0.6368 cm. Hence, the value 0.6364 cm. was indicated as the effective diameter.[11] The second piston was 1.4003 cm. in diameter and its cylinder 1.4008 cm., with an effective diameter of 1.4006 cm. Since this second gage had almost five times the area of the first, the percentage accuracy of measurement was greater.

For comparison these two pistons were mounted in the usual way and "in parallel." The weights required to maintain an equilibrium between the two pistons were determined over a range of pressures and the effective area of the first piston was found in terms of the larger one.[12] This method of comparison proved to be an exceedingly sensitive one. By it the effective diameter of the working piston appeared to be 0.6366 cm. From a mean of these two estimates the effective area may be taken as

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[10] Richards and Wilson, *Carnegie Institution of Washington,* Pub. No. 118, 1909, p. 13.

[11] The effective diameter is taken as the mean of the diameters of cylinder and piston, cf. Richards and Shipley, THIS JOURNAL, 38, 992 (1916).

[12] See Bridgman, *Proc. Am. Acad. Arts Sci., 44,* 214 (1909).

0.31824 sq. cm. One kilogram, then, on the absolute gage, would correspond to 3.0813 megabars (if based in 980.4 as the factor of gravity at Cambridge).

Method

The method employed was essentially identical with that invented twenty-five years ago and used by former workers in the Wolcott Gibbs Memorial Laboratory.[13]

The piezometer was of glass. All precautions (frequently reiterated in the past) were taken to avoid errors from hysteresis, etc. Under these circumstances the glass piezometer has appeared to yield as good results as the more complicated steel one.[14] The piezometer was filled with great care. Bubbles of air were excluded as completely as possible. At first a small amount of a lubricant of rubber and paraffin was used on the stopper of the piezometer. However, because this was so easily dissolved in the toluene, in later experiments either a sirup of phosphoric acid or a warm mixture of dextrose and glycerine[15] was substituted. The thermostat was kept at 24.540 ± 0.002'.

The piezometers were standardized with mercury. Since the metals under investigation were protected from mercury by toluene, the compressibility of toluene also had to be investigated. With piezometer No. 1 filled with mercury alone a change of 0.2685 g. of mercury was made in the side arm in going from 100 to 500 megabars. The constant at 24.84° for the toluene (density = 0.8616) was found to be 0.4219 g. Hg/g. of toluene from 100 to 500 megabars, because 26.5 g. of toluene needed 11.42 g. of mercury in the side tube over the pressure range. These values are the averages of many trials.

Hence, $w' = 0.269$ and $m = 0.4219$ for piezometer No. 1, using the equation $\beta = \frac{(W - w' - mK)}{5425\ W} D + \beta'$, where β is the compressibility sought, w the weight of mercury added in the particular case, w' the weight of mercury added when mercury alone is present, m the additional weight of mercury needed (in the side arm) when one gram of another liquid replaces an equal volume of mercury (within the piezometer), K the weight of the other liquid, D the density of the specimen, W its weight and β' is the compressibility of mercury; 5425 is 400 times the density of mercury at 25° between 100 and 500 megabars.

The value of β at 24.84' for this specimen of toluene is 70.9 X 10^{-6}. Richards and Shipley[16] found 69 X 10^{-6} at 20° for toluene.

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[13] For examples, see (a) ref. 2; (b) ref. 6; (c) a diagram of the apparatus will be found in *J. Franklin Inst.*, July, 1914, p. 7.

[14] For comparison of glass and steel piezometers, see (a) ref. 6, p. 471; (b) Richards, Bartlett and Hodges, THIS JOURNAL, 43, 1538 (1921).

[15] Tyrer, *J. Chem. Soc.*, 103, 1678 (1913).

[16] Richards and Shipley, THIS JOURNAL, 38, 998 (1916).

Compressibility of Lead

To standardize methods and to relate the results for indium and thallium with older work, the compressibility of lead was redetermined, using a cylinder which had been cast, hammered to remove possible imperfections in casting, and turned on a lathe to fit the piezometer. Its density was 11.346. Toluene was used as the confining fluid to transmit pressure to the specimen and to prevent lead from coming in contact with mercury. Sirupy phosphoric acid was used for lubrication of the stopper. The first experiment to measure the compressibility of lead was interrupted and therefore rejected. The successful experiments are recorded in Table I.

TABLE I

COMPRESSIBILITY OF LEAD AT 25°

Expt.	Wt. of toluene, g.	Wt. of lead, g.	Mercury, 100–500 meg., g.	$\beta \times 10^6$ (meg.)
1	2.663	314.140	1.153,[a] 1.153	2.41, 2.41
2	2.519	314.135	1.096, 1.084	2.43, 2.35
			Av.	2.40

[a] The two values given for each experiment are the weights of mercury required in the side arm. The first represents the weight in going from 100 *up* to 500 megabars, the second from 500 *down* to 100.

The value for β, 2.40 X 10^{-6} (in megabar units), at 25° may be compared with 2.35 X 10^{-6} at 20° found by Richards and Bartlett,[17] who used lead under water and mercury in a steel piezometer. When the value of these experimenters is corrected to 25°, 2.41 × 10^{-6} is obtained. The earlier value of Richards and Stull[2] corrected to present-day standards is also 2.4 X 10^{-6}. Bridgman[3] found 2.40 X 10^{-6} (in megabar units) at 30°.

The agreement of the values found by these new experiments on lead with the values presented in the literature indicated that the experimental method had been correctly executed and gave added weight to the significance of the new values obtained for thallium and indium.

Compressibility of Thallium

In the determination of the compressibility of thallium the value of w' for the piezometer used (No. 2) was found to be 0.2816 as the average of three experiments. The density of the casting used in the determinations was 11.85. In the first experiment a relatively large amount of toluene was used. This was lessened in the second by the addition of a small button of thallium to the piezometer. Sirupy phosphoric acid was used as a lubricant on the stopper.

Experiments 1 and 2 (Table II) were performed in June, 1025. Four months later the compressibility of this casting of thallium was redeter-

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[17] Ref. 6, p. 479.

mined (Expts. 3, 4 and 5) and essentially the same result for compressibility was obtained as before.

TABLE II

COMPRESSIBILITY OF THALLIUM AT 25°

Expt.	Toluene, g.	Thallium, g.	Mercury, 100-500 meg.	$\beta \times 10^6$
1	4.541	301.25	2.087	3.06
			2.022	2.74
2	3.913	309.70	1.772	2.89
			1.775	2.87
			Av.	2.89
3	4.650	301.59	2.090	2.89
			2.090	2.89
4	4.384	301.29	1.992	2.99
5	4.587	300.66	2.063	2.88
			2.073	2.60
			Av.	2.87
6	3.504	315.36	1.590	2.78
			1.584	2.82
7	3.398	315.35	1.541	2.79
			1.541	2.79
			Av.	2.80
			Av. of all	2.85

It was discovered during the second series of experiments that there was a minute "pipe" hole in one end of the casting. Although it did not appear that a significant error could be caused by this flaw, the metal was recast. Much experimentation was required to perfect a method of obtaining a casting free from flaws. The final procedure was to pour the melted thallium into a pyrex tube of proper bore, with a lining of magnesium oxide to prevent sticking of metal to glass. The tube had been previously heated. With its molten charge it was lowered vertically through an electric furnace. Cooling was effected from the lower tip very slowly as the tube descended. In this carefully controlled manner there was obtained a casting free from flaws. The specimen was cleaned, hammered, and fitted to the piezometer. The data for the determinations made from this specimen are found under Experiments 6 and 7. Although from these experiments β appears slightly lower than in the previous ones, the average of all the experiments (2.85×10^{-6}) cannot be far from the truth. If the mean is weighted by giving double credit to the last two experiments, since they were performed with a better cast specimen, the average 2.83×10^{-6} is obtained.

Compressibility of Indium

Indium–Zinc Alloy.—A preliminary series of determinations was carried out with a 35-g. sample of indium, containing about 3% of zinc (density 7.292). An iron cylinder was used in the lower part of the barrel of the piezometer to decrease the amount of toluene required. Although individual standardizations with the iron cylinder and also individual determinations of compressibility seemed satisfactory, there was exceedingly poor agreement of successive experiments for an unknown cause. From these preliminary experiments β for indium appeared to be about 2.4 X 10^{-6}.

Since part of the difficulty seemed to be in the lubricant used, Ramsay grease was used on the stopper, which necessitated the use of water as the confining liquid, although it reacts with indium very slowly, generating hydrogen. Contact of the indium with iron slightly accelerates the action. In a loaded piezometer left overnight an appreciable bubble of gas was found. However, a small amount of gas dissolves completely in the confining liquid and appears to cause no appreciable error.

A slight modification of procedure was made in starting at a pressure of 500 megabars, reducing the pressure to 100, and returning to the higher pressure. By this technique the same values of compressibility were usually obtained for "up" and "down" experiments. Standardization of the piezometer showed that 0.2045 g. of mercury was the added weight of mercury required in the side arm over the range 100 to 500 megabars due to the substitution of one gram of water for its volume of mercury within the piezometer (m in the equation), 0.4462 g. of mercury corresponding to 2.182 g. of water.

Mehl and Mair[18] found with a 25-g. sample of water the value 0.2044 at 25°. Three standardization experiments were made with approximately the same quantity of water used when the bar of indium was present. Over the pressure range of 100 to 500 megabars 0.1600 g. of mercury was required when 0.8576 g. of water was present; 0.1895 g. of mercury for 1.005 g. of water; and 0.1665 g. of mercury for 0.8838 g. of water. Hence, from the average of these results, the value of w' is 0.1605 on the basis of 0.8576 g. of water.

TABLE III

COMPRESSIBILITY OF 97% INDIUM ALLOY

Expt	Water, g.	Indium, g.	Mercury, 100–500 meg.	$\beta \times 10^6$
1	1.1896	35.357	0.1895[a]	2.52
2	1.1584	34.215	.1845	2.53
3	1.1110	34.211	.1734	2.48
			Av.	2.51

[a] Identical values were obtained for both the "up" and "down" experiments.

Pure Indium.—The 35-g. sample was purified and combined with more indium to form a larger and purer specimen, which would not re-

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

quire an auxiliary steel bar. The density of this larger casting was 7.296. Its density was redetermined several times during the course of the experiments, since on several occasions a slight amalgamation took place in the process of unloading the piezometer after a determination of compressibility. The spot amalgamated was immediately scraped free from mercury. Since no change in density resulted, it is unlikely that the small amount of surface amalgamation which occurred had any influence on the compressibility.

A piezometer of proper size for the cylinder of indium was standardized with mercury alone and the factor 0.1098 was found for the pressure range of 100 to 500 megabars. With 2.1820 g. of water there was required in the side arm over this pressure range 0.5560 g. of mercury; with 2.0541 g. of water, 0.5300 g. of mercury. This gives a value for m of 0.2045 and for w' a value of 0.5209 on the basis of 2.0541 g. water.

After Expt. 3 (Table IV), the indium was melted and recast, because after scraping of the amalgamated spots the cylinder fitted poorly and required a larger quantity of water. The new casting had a density of 7.297.

Table IV

Compressibility of Indium

Expt	Water, g.	Indium, g.	Mercury, 100-500 meg.	$\beta \times 10^6$
1	2 0059	81.538	0.4335	2.57
			.4375	2.64
2	2 2500	80.471	.4780	2.46
			.4780	2.46
3	2.2972	80.094	.4935	2.56
			.4935	2.56
			Av.	2.54
4	1.6500	85 070	.3540	2.52
				2.52
5	1.7102	84.727	.3700	2.58
			.3720	2.61
			Av	2.56
			Average of all	2.55

The previous value for the compressibility of indium[8] ($\beta = 2.7 \times 10^{-6}$ at 25°) was determined with a sample of only 6.7 g. Essentially in accord with it is the value more recently determined and here presented, which was made with an 80-g. specimen.

From the value 2.55×10^{-6}, β for indium, and the value 1.7×10^{-6} for zinc, it may be calculated that an alloy of 97% indium and **3%** zinc (approximately the amount indicated by analysis and density of the alloy) would have a compressibility of 2.52×10^{-6}, if the rule of mixtures holds. This calculated value is slightly higher than the value actually found for such an alloy (2.51×10^{-6}), as would be expected from the generalization that solid solutions have compressibilities somewhat lower than calculated by the rule of mixtures.[18]

Discussion

In Table V certain properties and constants of the members of the natural group which has recently been studied, together with those of

TABLE Va

COMPARISON OF PHYSICAL PROPERTIES OF CERTAIN NATURAL GROUPS

Element	At. wt.	Density at 20°	At. vol.	M. p., °A.	Scratch hardness Moh's scale	Cubic coeff. of expansion × 10^6
Cu	63.57	8.92	7.13	1356	3.0	50
Zn	65.38	7.14	9.15	693	2.5	82
Ga	69.72	5.91	11.80	303	1.5	[85]
Ge	72.38	5.36	13.50	1232	(3.0)	[22]
As (metal)	74.96	5.7	13.14	1073	(3.5)	16
Ag	107.88	10.5	10.26	1234	2.7	57
Cd	112.41	8.6	13.07	594	2.0	94
In	114.8	7.3	15.73	428	1.2	100
Sn (white)	118.70	7.31	16.24	505	1.8	67
Sb	121.77	6.68 (25°)	18.20	904	3.0	33
Au	197.2	19.3	10.21	1336	2.5	43
Hg	200.61	14.2^a	14.15^a	234	1.5	180^b
Tl	204.4	11.85	17.23	577	1.2	90
Pb	207.22	11.34	18.2	601	1.5	88
Bi	209.00	9.80	21.3	544	2.5	40

[a] At melting point.

[b] Cubic coefficient for solid mercury is 125.

TABLE Vb

COMPARISON OF PHYSICAL PROPERTIES OF CERTAIN NATURAL GROUPS

Element	Av. compress. × 10^6 at 20° 100–500 megabars	Latent heat of vap. in Kj. per g. atom	n'	$P\theta$ megabars	Π kilomegabars	Space lattice
Cu	0.75	467	5.64	19,390	376	FCC
Zn	1.7	99	5.3	14,130	178	HCP
Ga	2.0	...	[6.0]	[12,350]	[125]	FCT
Ge	1.4 (30°)	500(?)	2.6?	[4,600]	376	Dia C
As (metal)	4.5	139	...	1,040	104	H not CP
Ag	1.01	249	6.76	16,130	208	FCC
Cd	2.1	96(?)	7.03	13,120	117	HCP
In	2.55 (25°)	...	7.42	11,470	72.5	FCT or H?
Sn (white)	1.9	325	6.9	10,320	108	T not FC
Sb	2.4	190	..	4,025	109	H not CP
Au	0.65	368	9.10	21,800	243	FCC
Hg	3.1^a	59	7.91	13,100	41.3	H or FCT?
Tl	2.85 (25°)	120(?)	6.55	9,420	77	FCT or HCP
Pb	2.40 (25°)	193	7.75	10,340	72	FCC
Bi	3.0	176		3,920	77.5	H not CP

[a] At melting point.

neighboring groups in the periodic table of elements, are summarized. Most of these data are taken from "International Critical Tables," Vols. I and III. The values for cubic compressibilities and coefficients of expansion are, however, with the exception of germanium and mercury, those compiled by one of us some years ago.[19] The compressibilities of germanium and mercury have been calculated from Bridgman's data.[3,20]

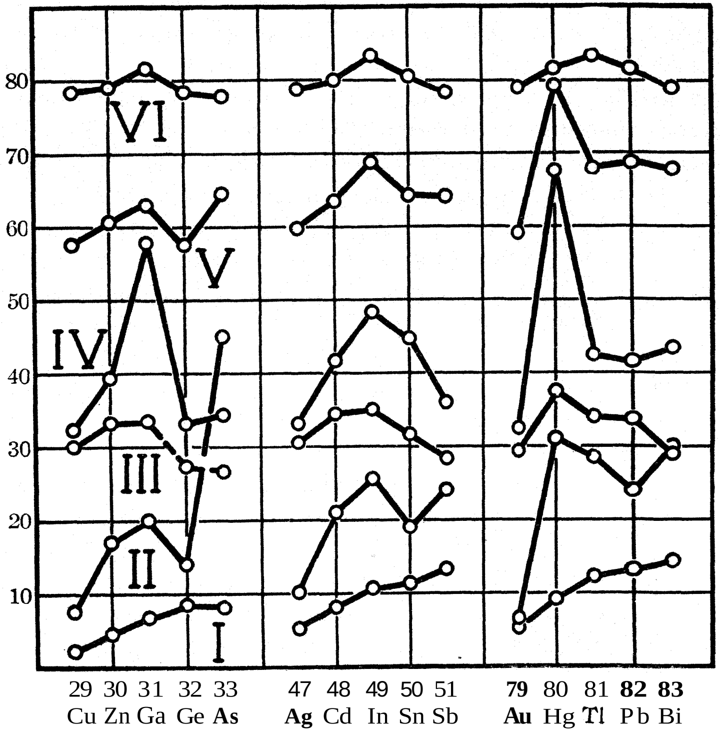

Fig. 1.—Curve I, atomic volume; II, compressibility ($\beta \times 10^7$); III, cubic coefficient of expansion ($\alpha \times 10^5 + 25$); IV, reciprocal of absolute melting point ($^1/_{T_m} \times 10^3 + 40$); V, reciprocal of internal pressure ($^1/_\pi \times 10^3 + 55$); VI, reciprocal of hardness ($\times 10 + 75$).

The hardness values are after Rydberg.[21] The numbers in brackets have been calculated from insufficiently supported data. The values for n', $P\theta$ (thermal pressure) and π (internal pressure) are obtained from calculations making use of Richards' equations of state for solids and liquids.[22] A value of 2 has been assumed for m throughout. The symbols m and n' are the exponents representing, respectively, the rate of increase of the

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[19] (a) Richards, THIS JOURNAL, 37, 1646 (1915); (b) *ibid.*, 43, 285 (1921).

[20] Bridgman, *Proc. Am. Acad. Arts Sci.*, 47, 347 (1911).

[21] Rydberg, *Z. physik. Chem.*, 33, 353 (1900).

[22] (a) Richards, THIS JOURNAL, 46, 1419 (1924); (b) *ibid.*, 48, 3664 (1926).

internal cohesive pressure and of the internal distending pressure with decreasing volume. Values for π for all the elements listed, except germanium, arsenic, antimony and bismuth, were calculated from coefficients of compressibility and expansion data. These four were, for good reasons, calculated from latent heats of vaporization data. The coefficient of expansion for germanium is not known; while the calculation of internal pressures for the anisotropic crystals of the other three elements would lead to only approximate if not very erroneous values. The expansion and compression coefficients for arsenic, antimony and bismuth vary according to the direction chosen in the crystal, which indicates that their internal pressures are distributed very unevenly.[23] This fact applies to members of other groups appearing in Table V but not so rigorously. Consequently it seemed justifiable for qualitative considerations to proceed with the calculations as outlined above. In Fig. 1 are plotted various properties of the members of the groups indicated in Table V in relation to their atomic numbers. In the diagram the lowest curve represents atomic volumes (Curve I) and the one just above it compressibilities (Curve II). In addition, are curves for cubic coefficients of expansion (Curve III), reciprocals of the melting points in degrees absolute (Curve IV), reciprocals of internal pressures in kilomegabars (Curve V), and the reciprocals of hardness (Curve VI).

An examination of the curves in the diagram shows with but few exceptions an approximate proportionality between atomic volumes of the elements of any one family and their other properties. Thus, if the succeeding elements in the group have larger atomic volumes than the first one, then their other properties also have larger values.

On the other hand, an examination of the two lowest curves shows that although the atomic volumes of the elements in the gallium–indium–thallium group are intermediate between the atomic volumes for neighboring elements in the periodic table, the compressibilities are greater than those for either the preceding or succeeding neighbor except for mercury which, being a liquid, has an anomalous behavior. The same relations hold when atomic volumes are compared with coefficients of expansion, reciprocals of melting points and (excepting a reversed relationship between thallium and lead) reciprocals of internal pressure. In other words the members of the gallium family seem to occupy sub-maximum points on the upward slope of the completed periodic curves given in an earlier publication from this Laboratory.[24] This is remarkable in view of the generally accepted conclusion that there is an approximate proportionality between atomic volumes and related properties. The peculiar behavior of the gallium family may be explained in the following

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[23] Richards, THIS JOURNAL, 47,739 (1925).

[34] Ref. **19** *a*, p. 1649.

manner. Whereas the atomic volumes of its members are intermediate between their neighbors, their compressibilities show a decided maximum because other factors overbalance the effect of atomic volume. That is, their coefficients of expansion are larger, their melting points lower, and their degree of hardness much less.[25] These properties depend upon the important fact that the net internal pressure (that is, the resultant of the cohesive pressure, inherent distending pressure and thermal pressure) of these three metals is decidedly less than the net internal pressures of either the zinc or germanium family.

Acknowledgment is made for essential financial assistance from the Carnegie Institution of Washington and an anonymous benefactor of this Laboratory.

Summary

The compressibility from 100 to 500 megabars at 25° has been measured for lead ($\beta = 2.40 \times 10^{-6}$), thallium ($\beta = 2.53 \times 10^{-6}$), indium ($\beta = 2.55 \times 10^{-6}$) and an indium–zinc alloy containing 97% indium ($\beta = 2.51 \times 10^{-6}$).

The preparation of the pure metals is described. The special precautions and modifications in procedure for determining the compressibility of these specimens are presented in detail.

The thermal pressure ($P\theta$), the internal pressure (Π), and the coefficient (n') of rate of change of the internal distending pressure have been calculated according to Richards' equation of state. The periodic variation of properties is discussed with particular bearing on the gallium, indium, thallium group, which occupies a sub-maximum position.

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[25] For a discussion of the relation of compressibility and hardness, see Mehl, *Am. Inst. Min. Met.*, Tech. Pub. No. 57.

[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY, HARVARD UNIVERSITY]

THE COMPRESSIBILITY OF SODIUM, BARIUM AND BERYLLIUM[1]

BY T. W. RICHARDS, L. P. HALL AND B. J. MAIR

RECEIVED SEPTEMBER 18, 1928 PUBLISHED DECEMBER 10, 1928

Determinations of the coefficient of compressibility have been made during the past twenty-five years for many of the elements by the "constant volume method" developed at the Harvard Laboratories. Values for the less common elements have been determined as such elements have become available. In this paper are presented values for barium, strontium and beryllium, and also for sodium. The latter was redetermined to demonstrate the reliability of the method with the modifications necessary in handling strontium and barium.

Bridgman, measuring the linear compressibility,[2] calculated the cubic compressibility of strontium to be 8.187×10^{-6} at 30° (in kg./cm.^{2}). Shortly after the initiation of the research here presented, Bridgman published values for barium and beryllium[3] of 10.19×10^{-6} and 0.855×10^{-6}, respectively, at 30° and in kg./cm.^{2} units. Nevertheless, corroboration by an independent method was deemed to be of sufficient importance to justify publication of the results.

Preparation of Materials

Barium.—The barium was obtained through the kindness of Dr. Francis C. Prary of the Aluminum Company of America. It was prepared in a special alloy furnace which was provided with a mild steel crucible so constructed that it could be evacuated and filled with some inert gas. Before the barium was melted, the crucible was evacuated to 2 mm. residual pressure and maintained thus until the temperature rose to about 400°.

The barium was then melted in an atmosphere of argon in the steel crucible, the pressure reduced to prevent blow-holes and the barium cast in a mold in the lid of the crucible.

After its receipt the barium was cut under kerosene oil with the aid of a small coping saw and knife into a size and shape suitable for the piezometer. The pieces of barium when not in use were stored in a vacuum desiccator under exceptionally pure kerosene.

During the manipulations involved in three determinations of compressibility over a period of four days, an eighteen-gram sample gained only 1.4 mg., showing that the methods of storage and manipulation ade-

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[1] As this research was completed shortly after the death of Professor Richards, this report was prepared by the junior authors.

[2] Bridgman, *Proc. Am. Acad. Arts Sci.*, 58, 151 (1923).

[3] Bridgman, *ibid.*, 62, 207 (1927).

quately prevented serious oxidation. The trace of oxide thus formed was present as a superficial layer, which would be without influence on the value for the compressibility.

An examination in a quartz prism spectrometer showed the barium to be of exceptional purity: no iron and only very slight traces of strontium. Analyses indicated a barium content of 99.95%.

Kerosene Oil.—The essential requirements of the kerosene used in the piezometer as a confining liquid for barium are absolute freedom from water, sulfur and unsaturated hydrocarbons. Treatment with sodium wire over a period of one week and subsequent distillation did not yield an anhydrous water-white product. For these reasons the kerosene oil was further treated by shaking with a potassium–sodium alloy (four parts potassium to one part sodium) followed by a careful fractionation. Only the fraction distilling between 185 and 225° was used. Since the potassium–sodium alloy was a liquid at ordinary temperatures, it continually presented a fresh surface to the kerosene. This surface, in conjunction with its great chemical activity, assured the removal of any substances liable to react with barium. The oil was stored over potassium–sodium alloy until ready for use.

Mercury.—The mercury was prepared in the usual manner by treatment in a nitric acid tower and finally by distillation, according to Hulett.

Method and Apparatus

The apparatus and methods used in this research have been described in adequate detail elsewhere.[4] Only modifications of apparatus or procedure will be described here. All measurements were made at 25.00°, instead of the customary 20°. The piezometer, of the type previously used for solids, was made of Pyrex instead of soft glass. This was advantageous in making it less liable to fracture, while its temperature and pressure hysteresis did not appear to be any greater than that of soft glass. One detail of its construction, the taper of the stopper, although mentioned before, seems worthy of repetition since in recent years it appears to have been overlooked. The taper found to be most satisfactory was one in eight. With this taper no difficulty was experienced in removing the stopper, while with less taper, one in twelve or one in sixteen, this difficulty occasionally resulted in breakage of the piezometer. This increased taper also resulted in greater reproducibility of volume.

The barium was held in a thin-walled test-tube which fitted snugly in the piezometer and prevented mercury from coming in contact with it.

The piezometer containing the glass tube, mercury and about 2.5 g. of kerosene (the amount used in actual measurement of the compressibility of barium) was standardized in the usual manner.

The stopper lubricant used was a heavy Ramsay grease. 0.3 ± 0.1 mg. was placed on one spot on the stopper, which was then inserted rapidly in position and turned with considerable pressure until further movement

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[4] Richards, *J. Franklin Inst*., 198, 25 (1924); Richards and Saerens, THIS JOURNAL, 46, 935 (1924).

was impossible. With this procedure practically none of the lubricant dissolved in the kerosene. A glucose–glycerine lubricant was tried but, although insoluble in kerosene, was much less satisfactory, possibly owing to the presence of small, solid particles which hindered a satisfactory seating of the stopper.

The data for the standardizations of the piezometer are tabulated in Table I in the customary manner.

Table I

Standardization of Piezometer with Oil

Expt	Oil. g.	Mercury, g. 100–500 meg.	Mercury on basis of 2.3132 g. of oil, 100–500 meg.
1	2.3132	1.0905	1.0905
2	2.3132	1.0890	1.0890
3	2.5652	1.2014	1.0882
4	2.7027	1.2645	1.0895
5	2.4408	1.1454	1.0881
		Av.	1.0891 g.

The weights of kerosene used in the different standardization experiments (Col. 2) were not identical. To reduce these to a common basis (Col. 4), it was necessary to determine a correction factor for the oil used. The following table presents the experimentally determined values for the weight of mercury in the side arm when one gram of oil replaces one gram of mercury in the piezometer.

Table II

Experimentally Determined Values

Expt.	Oil, g.	Mercury, g. 100–500 meg.	Oil in excess of 2.3132 g.	Mercury in excess of 10891	Ratio, Hg/oil
1	7.7294	3.5154	5.4162	2.4263	0.4480
2	7.8488	3.5848	5.5356	2.4957	.4508
3	7.2624	3.3106	4.9492	2.2215	.4488
4	7.6397	3.4860	5.3265	2.3969	.4500
				Av	.4494

This factor was also used in calculating the compressibility of sodium, barium and strontium.

Compressibility measurements were first made on a sample of "C. P." sodium to determine whether the special methods necessary for the work with barium would give results, in the case of sodium, in accordance with those generally accepted. As will be seen, the results thus obtained confirm the older value[6] of 15.6×10^{-6}.

The density of sodium (0.972) used was that determined by F. N. Brink.[6]

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[5] *Richards,* This Journal, *37,* 1652 (1915).

[6] *Richards,* Stull *and* Bonnet, *Carnegie Institution of Washington,* Pub. *No. 76,* 1907, p. 15.

TABLE III

COMPRESSIBILITY OF SODIUM

Oil used, g.	Mercury 100–500 meg.	$\beta \times 10^6$	Wt. of sodium in air, g.
3.3676	1.8645	15.68	4.6265
3.1311	1.7558	15.58	4.6268
	Av.	15.63	

When the details of experimental procedure had been perfected with sodium, the data recorded in Table IV were obtained with barium.

TABLE IV

COMPRESSIBILITY OF BARIUM

Expt.	Oil used, g.	Mercury, 100–500 meg.	$\beta \times 10^6$ (meg.)	Weight of barium in air, g.
1	2.3298	1.2741	10.46	18.5382
2	2.3315	1.2771	10.54	18.5388
3	2.5461	1.3721	10.49	18.5392
4	2.5694	1.3811	10.44	18.5392
		Av.	10.48	

When Bridgman's value for barium is corrected to 25° to the pressure units here used, and to the same range of pressure, β equals 10.34×10^{-6}, a reasonably good agreement for the two diverse methods.

Determination of Weight and Density of Barium

The determination of the weight of the sample of barium presented one of the most difficult problems of the research. A special apparatus was designed for complete removal of kerosene in an inert atmosphere. Argon of 99.95% purity was further purified by passage over activated charcoal chilled with solid carbon dioxide in ether. A diagrammatic sketch of the

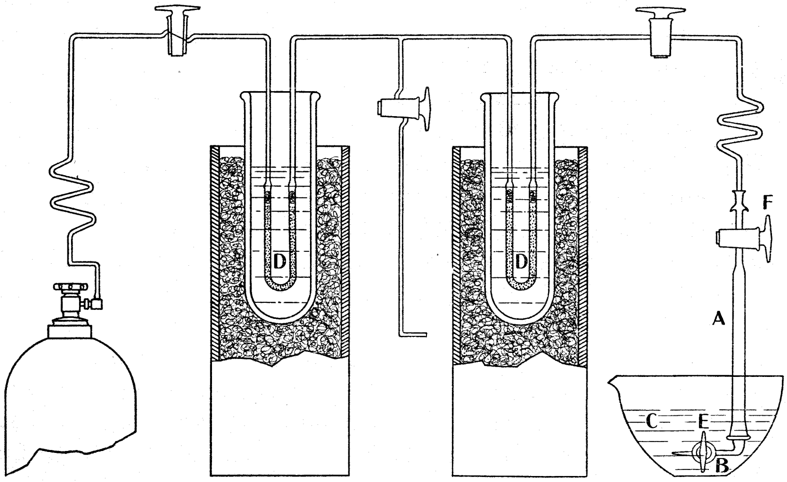

Fig. 1.

apparatus is depicted in Fig. 1. The charcoal in tubes (D,D) was first completely outgassed by heating to 500° in a high vacuum for forty-eight hours. When pure argon was desired, Dewar vessels with carbon dioxide and ether were placed over these tubes. Next, the sample of barium in the tube with kerosene was immersed in a bath of anhydrous, sulfur-free petroleum ether (C), into which the weighing tube (A) dipped. After the apparatus was swept out with pure argon, the cylindrical pieces of barium were introduced into A and the end piece (B) inserted in position. The bath of petroleum ether was removed and the barium dried in a current of argon. The stoppers E and F were closed, the tube was removed and weighed. The sample was again transferred to kerosene and the tube refilled with argon. The difference in weight gave the weight of barium in argon. A buoyancy factor was applied to obtain the weight of barium *in vacuo* and in air. The weight of barium in air was used to compute the weight of oil in the piezometer by difference.

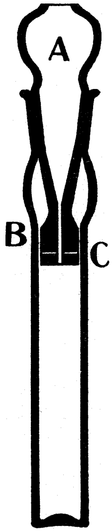

Fig. 2.

The density was determined in a new kind of pycnometer for solids, a modification of a type suggested by Dr. J. C. Woodhouse. The pycnometer used is illustrated in Fig. 2. The ground-glass stopper (A) was of the same type as that used in the piezometer, which had been found to yield a reproducible volume. A capillary tube (B) etched with a fine mark (C) extended into the piezometer. The level of the liquid was adjusted to the mark by means of a capillary pipet inserted through the hollow stopper. Excellent reproducibility of weight was obtained, a maximum variation of only 0.3 mg. being found in successive fillings and settings. The density of the kerosene was determined as 0.79424 by this method, whereas 0.79430 was obtained with a small Ostwald-Sprengel pycnometer. Even greater reproducibility might be possible by the use of a small ground-glass cap fitting on the stopper to prevent evaporation.

Two determinations of the density of barium at 25.00' gave the identical value, 3.661. This value appears to be the most reliable yet obtained.[7]

Strontium, also provided by the Aluminum Company of America, was prepared in a way similar to that used for barium. Since there were some inclusions of strontium hydroxide in the sample, it was more difficult to cut it up. It was undoubtedly on account of these inclusions that the density found (2.737) was higher than is usually reported.[8] The coefficient of compressibility at 25° was found to be 7.22×10^{-6} as the average of

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[7] Considerable discrepancy exists in the literature for the density of barium. Guntz, *Compt. rend.*, 141, 1240 (1905), found 3.78. Biltz and Huttig, *Z. anorg. Chem.*, 114, 247 (1920), found values ranging from 3.44 to 3.70, using samples of 0 5 to 1.5 g. Kern, *Chem. News*, 31,243 (1875), found 3.75 with an impure sample.

[8] C. E. Glascock, THIS JOURNAL, 32, 1222 (1910).

three experiments. This is distinctly lower than Bridgman's value of 8.32 × 10^{-6} (corrected for temperature and pressure units).

This lowering of the value is in agreement with the high density caused by the presence of compounds. Hence, this value is presented only as a preliminary one.

These determinations complete the compressibility and density data for the family group of Ca, Sr and Ba.

Comparison of their atomic volumes and compressibilities is of interest.

	Mg	Ca	Sr	Ba
Atomic weight	24.32	40.07	87.62	137.37
Density	1.73	1.53	2.55[a]	3.66
Atomic volume	13.3	25.3	34.36	37.52
Compressibility ($\beta \times 10^6$)	2.9	5.7	8.32[b]	10.48

[a] Glascock, ref. 8.

[b] Bridgman, *Proc Am. Acad. Arts Sci.*, *58*, 201 (1923).

Beryllium

A cylinder (1.1 × 9 cm.) of beryllium, over 99% pure, was made by the Beryllium Corporation of America. It was coherent and finely crystalline. The density was found to be 1.85. Since in this case water was used as the confining liquid, it was necessary to standardize the piezometer with water. The results of these experiments will be found in Table V. The factor for the replacement of water for mercury in the piezometer has been determined[9] as 0.2044 and this factor was used to correct the weights of mercury in Table V to a common basis.

TABLE V

STANDARDIZATION OF PIEZOMETER WITH WATER

Expt	Water, g.	Mercury. g. 100–600 meg.	Mercury on basis of 2.7604 g. of water 100–500 meg.
1	2.7604	0.6319	0.6319
2	2.9156	.6643	.6326
3	2.9166	.6638	.6319
4	2.9064	.6603	.6325
5	2.8742	.6561	.6328
		Av.	.6323

TABLE VI

COMPRESSIBILITY OF BERYLLIUM:

Expt.	Water used, g.	Mercury, g. 100–500 meg.	$\beta \times 10^6$
1	2.9884	0.5355	0.930
2	3.1357	.5307	.890
3	2.9743	.5334	.948
4	3.1119	.5661	.918
5	2.9871	.5360	.947
		Av.	.927

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[9] Mehl and Mair, THIS JOURNAL, 49, 1892 (1927).

The data for the compressibility of beryllium are presented in Table VI.

Acknowledgment is made for generous financial assistance from the Carnegie Institution of Washington and an anonymous benefactor of this Laboratory.

Summary

1. Coefficients of compressibility were measured by the "constant volume" method at 25° as follows: sodium, $\beta = 15.6 \times 10^{-6}$; barium, $\beta = 10.48 \times 10^{-6}$; strontium (preliminary) 7.22×10^{-6}; beryllium, $\beta = 0.93 \times 10^{-6}$.

2. The densities of the specimens used were for barium, 3.66; for strontium, 2.74; for beryllium, 1.85.

3, Special methods were developed for determining the weight and density of barium and strontium.

ST. LOUIS, MISSOURI, AND
BRYN MAWR, PENNSYLVANIA

NOTE

Use of the Hildebrand Hydrogen Electrode in Biological Solutions.—We have found that in certain biological solutions the ordinary Hildebrand[1] hydrogen electrode may attain equilibrium so slowly as to be entirely worthless. The Hildebrand type is obviously inferior to the enclosed electrode involving complete saturation of the solution with hydrogen, but the latter device greatly changes the P_H (as is well known) of mixtures containing reducible substances, or of mixtures partly buffered by hemoglobin or by volatile substances such as carbon dioxide and hydrogen sulfide.

We have put an ordinary rubber bulb from an "atomizer" into our hydrogen supply line so that the hydrogen flows through the bulb. By squeezing the bulb repeatedly the Hildebrand electrode is repeatedly saturated with hydrogen. Obviously, because of possible air leaks, the system should be operated so that at all times the pressure in the hydrogen supply line is slightly greater than atmospheric. It is very important that the solution level be periodically forced entirely below the bottom of the platinum, this being regulated by the rate of squeezing the bulb. In this way nearly constant readings are obtainable within five minutes with a small amount of hydrogen, while the usual arrangement sometimes did not give the right sign of e.m.f. even after an hour with a vigorous stream of hydrogen. This difference is strikingly observed by passing the hydrogen at first without touching the bulb, the e.m.f. being erratic and sometimes off by 0.5 volt. The correct reading is then quickly attained by pressing

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[1] J. H. Hildebrand, THIS JOURNAL, 35,349 (1913).

the Bulb a few times. We claim no new principle,[2] but give this note for the benefit of those who may own an electrode of the Hildebrand type.

CONTRIBUTION FROM THE
ANATOMICAL LABORATORY OF THE
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA
ROBERT E. CORNISH

RECEIVED SEPTEMBER 17, 1928
PUBLISHED DECEMBER 10, 1928

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF STANFORD UNIVERSITY]

THE CARBAZYLIC ACIDS: THE AMMONIA ANALOGS OF THE CARBOXYLIC ACIDS[1]

BY E. F. CORNELL

RECEIVED JUNE 25, 1928 PUBLISHED DECEMBER 10, 1928

The Ammonia System.—Liquid ammonia shows a striking similarity to water in many of its properties, particularly as an electrolytic solvent. This close correspondence purely as solvents has been extended so as to include similarities between derivatives of ammonia and the analogous water compounds. A system of acids, bases and salts related to ammonia as the aquo acids, bases and salts are related to water has been developed by Franklin.[2]

The Carbazylic Acids.—In this paper is given an account of the investigation of a class of ammono acids which are to be regarded as the ammonia or nitrogen analogs of the carboxylic acids. Just as aquo-acetic acid, for example, may be looked upon as being derived from a hypothetical ortho-acetic acid by the loss of a molecule of water, so a analogous ammono-acetic acid may be regarded as being derived from a hypothetical ortho-ammono-acetic acid by the loss of a molecule of ammonia, as represented by the parallel equations

$$2CH_3C(OH)_3 \longrightarrow 2CH_3COOH \longrightarrow (CH_3CO)_2O$$
$$CH_3C(NH_2)_3 \longrightarrow CH_3C(NH)NH_2 \longrightarrow CH_3CN$$

The acid amidines and the nitriles have come to be known as carbazylic acids and acid anammonides inasmuch as they represent the nitrogen analogs, respectively, of the carboxylic acids and acid anhydrides. In the following discussion, it will be shown that the carbazylic acids and their derivatives are identical in several of their reactions with the carboxylic acids or their derivatives.[3]

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[2] See Michaelis and Rona, *Biochem. Z.*, 18, 317 (1909).

[1] The material in this paper is from a thesis submitted to the Department of Chemistry and the Committee on Graduate Study of Stanford University in partial fulfilment of the requirement for the degree of Doctor of Philosophy, 1926.

[2] Franklin, Am. *Chem.* J., 47, 285 (1912); Eighth Int. Cong. App. Chem., 6, (1912); THIS JOURNAL, 46, 2137 (1924).

[3] Franklin in his earlier papers [THIS JOURNAL, 27, 800 (1905); Am. *Chem.* J., 47, 291 (1912)] mistakenly refers to acetamide and diacetamide as ammono-acetic acids,

Salts of the Carbazylic Acids.—Pinner[4] describes the formation of the silver salt of benzamidine by the action of silver nitrate on a water solution of benzamidine hydrochloride. The sodium and potassium salts cannot be prepared in such a manner since they are very readily hydrolyzed. Benedict[6] first prepared a salt of benzamidine in liquid ammonia solution by the action of potassium amide on benzamidine. The close analogy between this reaction and that involved in the formation of potassium benzoate by the action of potassium hydroxide on benzoic acid is clear from inspection of the equations

$$C_6H_5C(NH)NH_2 + KNH_2 = C_6H_5C(NH)NHK + NH_3$$
$$C_6H_5COOH + KOH = C_6H_5COOK + H_2O$$

Action **of Ammono** Bases on Acid **Anammonides.**—The preparation of a number of salts of the carbazylic acids by the action of metallic amides on the nitriles will be described in the experimental part of this paper. Just as acid anhydrides react with bases to form salts, so should one expect the analogous reaction to take place when the acid anammonides are treated with ammono bases in liquid ammonia solution.

$$(RCO)_2O + 2KOH = 2RCOOK$$
$$RCN + KNH_2 = RC(NH)NHK$$

The carbazylic acids are formally tribasic acids and as such might be expected to form di- or possibly tri-metallic derivatives. It was found possible, however, to form only the monometallic derivative.

Action of Hydrocyanic Acid on Potassium **Amide.**—Hydrocyanic acid may be looked upon as the anammonide of formic acid and as such might be expected to react with metallic amides in liquid ammonia solution to form salts of ammonoformic acid. Hydrocyanic acid may also be considered as an ammonocarbonous acid,[6] and might be expected to react with an ammono base to form an ammonocarbonite and ammonia. As a matter of fact, this is what happens, for when a solution of hydrocyanic acid in liquid ammonia solution is treated with potassium amide, potassium cyanide is formed and not potassium formamidine.

Action of Cyanogen on Potassium **Amide.**—Cyanogen may be looked upon as the anammonide of oxalic acid. However, when a solution of cy-

to urea as an ammonocarbonic acid and to calcium cyanamide as a salt of ammonocyanic acid. Of course, we now speak of the first two compounds as aquo-ammono-acetic acids and of the latter two as an aquo-ammono-carbonic acid and a calcium ammono-carbonate, respectively. The term carboxazylic acid is now used to denote the mixed aquo-ammono-carboxylic acids of which acetamide is an example, since they represent compounds derived simultaneously from water and ammonia.

[4] Pinner, *Ber.*, 11, 6 (1878).

[5] Benedict, Master's "Thesis," Stanford University, 1924.

[6] Franklin, J. *Phys. Chem.*, 27, 168 (1923), has discussed in detail a number of reactions which have been interpreted in support of the view that hydrocyanic acid is a carbonous acid of the ammonia sytem.

anogen in liquid ammonia is treated with potassium amide, the potassium salt of ammono-oxalic acid is not formed. The products are potassium cyanide and potassium cyanamide, the potassium salts of ammonocarbonous and ammonocarbonic acids, respectively. Cyanogen thus behaves toward potassium amide as a mixed carbonous and carbonic anammonide, C=N—C≡N, rather than as an oxalic acid anammonide.

Action of Aquo Bases on Acid Anammonides.—We have seen that the nitriles react with metallic amides in liquid ammonia solution to give salts of carbazylic acids. It is reasonable to expect that they would also react with aquo bases in liquid ammonia solution to give salts of the carboxazylic acids. Potassium hydroxide does react, slowly at room temperature and fairly rapidly if heated to 100°, with benzonitrile and propionitrile in liquid ammonia solution to give potassium benzamide and potassium propionamide, respectively.

$$C_6H_5CN + KOH = C_6H_5C(NH)OK$$
$$C_2H_5CN + KOH = C_2H_5C(NH)OK$$

Ammonation of the Acid Anammonides in the Presence of Acid.—Benzonitrile and propionitrile, when heated in liquid ammonia solution containing ammonium chloride,[7] are ammonated to benzamidine and propionamidine, respectively, according to the equations

$$C_6H_5CN + NH_3 = C_6H_5C(NH)NH_2$$
$$C_2H_5CN + NH_3 = C_2H_5C(NH)NH_2$$

Attempts to ammonate hydrocyanic acid and cyanogen by heating them with ammonia and ammonium chloride failed, probably because of the polymerization which these substances undergo on heating.

Pyrogenetic Decomposition of Salts of the Carbazylic Acids.—It will be recalled that when an alkali salt of a carboxylic acid is heated with sodium hydroxide, there is produced a hydrocarbon containing one less carbon atom than the parent carboxylic acid and an alkali carbonate.

The analogous reaction has been found to take place with the salts of the carbazylic acids when heated with sodium or potassium amide, the reaction proceeding in the case of sodium ammonobenzoate, for example, as follows

$$C_6H_5C(NH)NHNa + NaNH_2 = C_6H_6 + Na_2NCN + NH_3$$

There are formed a hydrocarbon and sodium cyanamide, the salt of one of the ammonocarbonic acids. This again bears out the striking relationship between the carbazylic and carboxylic acids.

Esters of the Carbazylic Acids.—A large number of compounds are known which are related to the carbazylic acids just as ordinary esters are related to the carboxylic acids. These compounds are of the types $RC(NR)NH_2$, $RC(NR)NHR$, $RC(NH)NR_2$ and $RC(NR)NR_2$ and are

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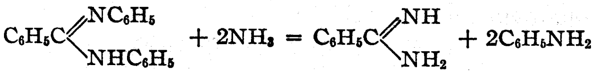
[7] Franklin and Kraus [*Am. Chem. J.*, 23, 305 (1900)] have shown that this substance exhibits acidic properties in liquid ammonia solution.

to be regarded as esters of the carbazylic acids. These esters can be prepared by reactions similar to those used in the preparation of aquo esters. For example, ethylbenzamidine, the ethyl ester of ammonobenzoic acid, has been prepared[8] by the action of ethyl iodide on benzamidine, the ammonobenzoic acid. This is analogous to the preparation of an aquo ester by the action of an alkyl halide on a carboxylic acid.

Ammonolysis of Esters of Carbazylic Acids.—Just as esters of the carboxylic acids can be hydrolyzed, so can the analogous process of ammonolysis be carried out with esters of the carbazylic acids. Niemann has ammonolyzed several of these esters. He has shown that diphenylbenzamidine, for instance, undergoes ammonolysis when heated in liquid ammonia solution in the presence of an acid, the products being the carbazylic acid, benzamidine and the ammono alcohol, aniline.



$$C_6H_5C\begin{cases}NC_6H_5\\NHC_6H_5\end{cases} + 2NH_3 = C_6H_5C\begin{cases}NH\\NH_2\end{cases} + 2C_6H_5NH_2$$

This reaction is exactly analogous to the hydrolysis of aquo esters.

Action of Ammonia on the Grignard Addition Product to a Nitrile.—The nitriles form addition products with the Grignard reagent, according to the equation

$$RCN + R'MgBr = RC(NMgBr)R'$$

Moureu and Mignonac[10] have shown that hydrolysis of the addition products at low temperatures gives rise to the ketimines, $R_2C{=}NH$. These compounds, generally speaking, are ammonia analogs of the ketones. However, they are either acids or alcohols at the same time, by virtue of the presence of a hydrogen atom in the imide group.

The writer has shown that ammonolysis of the addition products gives the same compounds.

$$(C_6H_5)_2C{=}NMgBr + NH_3 = (C_6H_5)_2C{=}NH + Mg(NH_2)Br$$

The reaction is analogous to the formation of ketones by the hydrolysis of the addition product of the Grignard reagent to the acid anhydrides.

Experimental

The preparation of nineteen salts of the carbazylic acids was carried out in Faraday tubes, following the manipulation developed in this Laboratory.[11] The reactions generally consisted in the action of a liquid ammonia solution of a metallic amide on a liquid ammonia solution of a nitrile, according to the equation

$$RCN + MNH_2 = RC(NH)NHM$$

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[8] Pinner and Klein, *Ber.*, 11, 7 (1878).

[9] Niemann, Master's "Thesis," Stanford University, 1926.

[10] Moureu and Mignonac, *Compt. rend.*, 156, 1790 (1900).

[11] Franklin, THIS JOURNAL, 27, 831 (1905); 35, 1460 (1913); *J. Phys. Chem.*, *15*, 609 (1911); 16,694 (1912); Fitzgerald, *ibid.*, 29, 1694 (1907).

The salts described in the table, with four exceptions, were prepared according to this general equation. In the notes following the table is given a description of the methods used in the preparation of these four salts, as well as observations of interest on several of the other salts. The metallic amide was prepared in every case by the reaction of the metal with ammonia, a spiral of iron wire being used as a catalyst. The salt in each case was washed several times by distilling fresh solvent onto it and decanting the wash liquor. Final drying was accomplished at room temperature in a vacuum. All the soluble salts were obtained beautifully crystallized and, in general, of sharply definite composition.

TABLE I

SALTS OF CARBAZYLIC ACIDS

Name	Formula	Solubility[a]	Metal, % Calcd.	Metal, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
Potassium ammonoacetate[b]	$CH_3C(NH)NHK$	ex. sol.	40.7	42.2	29.1	25.8
				42.0		24.8
Sodium ammonoacetate	$CH_3C(NH)NHNa$	ex. sol.	28.8	28.7	35.0	33.7
Potas. ammonopropionate	$C_2H_5C(NH)NHK$	m. sol.	35.5	35.4	25.4	24.9
Sodium ammonopropionate	$C_2H_5C(NH)NHNa$	m. sol.	24.5	24.3	29.7	27.9
Cal. ammonopropionate[c]	$[C_2H_5C(NH)NH]_2Ca$	insol.	21.9	25.9	..	..
Potas. ammono-n-butyrate	$C_3H_7C(NH)NHK$	m. sol.	31.5	31.7	22.6	21.9
Sodium ammono-n-butyrate	$C_3H_7C(NH)NHNa$	m. sol.	21.3	21.2	25.9	25.3
Potas. ammono-*n*-valerate	$C_4H_9C(NH)NHK$	m. sol.	28.3	28.5	20.2	19.9
Potas. ammono-*iso*-caproate	$C_5H_{11}C(NH)NHK$	m. sol.	25.7	26.0	18.4	18.2
Potas. ammonopalmitate	$C_{15}H_{31}C(NH)NHK$	insol.	13.4	12.9	9.6	7.9
Potas. ammonosuccinate	$(CH_2C(NH)NHK)_2$	insol.	41.1	41.7	..	..
Potas. ammonobenzoate[d]	$C_6H_5C(NH)NHK$	m. sol.	24.7	25.0	17.7	17.8
				24.5		17.6
Sodium ammonobenzoate	$C_6H_5C(NH)NHNa$	m. sol.	16.2	16.7	19.8	20.0
Silver ammonobenzoate[e]	$C_6H_5C(NH)NHAg$	insol.	47.6	47.0	12.3	15.5
Calcium ammonobenzoate[c]	$[C_6H_5C(NH)NH]_2Ca$	insol.	14.4	17.4	..	..
Cupric ammonobenzoate[f]	$[C_6H_5C(NH)NH]_2Cu$	insol.	21.1	23.5	18.6	15.2
Cuprous ammonobenzoate[g]	$C_6H_5C(NH)NHCu$	insol.	34.9	34.5	15.3	13.4
Potas. ammono-*p*-toluate	$CH_3C_6H_4C(NH)NHK$	m. sol.	22.7	22.0	16.3	16.2
Sod. dibenzenylimidoimide[h]	$(C_6H_5C{=}NH)_2NNa$	m. sol.	9.4	9.2	17.1	17.0

[a] Rough estimates of solubilities at room temperature are indicated: ex. sol. = extremely soluble; v. sol. = very soluble; m. sol. = moderately soluble; insol. = insoluble or very slightly soluble,

[b] This salt is extremely soluble and could be washed but once. The high analytical values are due to the presence of potassium amide in the sample.

[c] The high values for calcium on this salt and on calcium ammonobenzoate are explained on the basis of the presence of some unchanged calcium amide in the samples. Since both the calcium amide and the salt are insoluble, the reaction is slow and incomplete, even though the nitrile solutions are allowed to stand in contact with the calcium amide for some time.

[d] Benedict, Master's "Thesis," Stanford University, **1924,** first prepared this salt by the action of potassium amide on benzamidine and also upon benzonitrile. Pound: K, **23.9;** N, **18.1.** An attempt was made to prepare the dipotassium salt

by using an excess of two equivalents of potassium amide. The salt was found on analysis to be the monopotassium derivative. Found: K, 24.5; N, 17.6.

[e] Silver amide does not dissolve in either benzamidine or benzonitrile solution. This salt was prepared by the action of silver nitrate on potassium ammonobenzoate, according to the equation $C_6H_5C(NH)NHK + AgNO_3 = C_6H_5C(NH)NHAg + KNO_3$.

[f] The cupric salt was prepared by the action of a solution of $Cu(NO_3)_2 \cdot 4NH_3$ on potassium ammonobenzoate, $2C_6H_5C(NH)NHK + Cu(NO_3)_2 = [C_6H_5C(NH)NH]_2Cu + 2KNO_3$. The analysis of this salt indicates that it is contaminated with some of the cuprous salt.

[g] A quantity of the cupric salt contained in the wash leg of the tube was found to change gradually from a green to a white color. The analysis of this white salt showed it to be cuprous ammonobenzoate. The change from cupric to cuprous condition has also been noted in the case of cupric amide, Fitzgerald, THIS JOURNAL, 29, 657 (1907); Franklin, *ibid.*, 34, 1501 (1912).

[h] Benzonitrile is formed by the loss of a molecule of ammonia from benzamidine. It is possible for two molecules of benzamidine to lose a molecule of ammonia between them. The resulting compound would still be an ammonobenzoic acid. Pinner, *Ber.*, 11, 8 (1878), describes such a compound, dibenzenylimido-imide, $[C_6H_5C(NH)]_2NH$. Sodium amide reacts with this acid to give a salt. An attempt was made to prepare the potassium salt. Because of its high solubility, however, a sample sufficiently pure for analysis was not obtained.

Action of Potassium Amide on Hydrocyanic Acid.—A quantity of hydrocyanic acid, 0.52 g., was obtained in the following manner. A solution of equimolecular quantities of ammonium chloride and sodium cyanide contained in one leg of a reaction tube was evaporated to dryness. The resulting residue was heated to 40° while keeping the empty leg in a bath of liquid ammonia. Ammonium cyanide sublimed over, leaving the sodium chloride as a residue. The leg containing the residue was opened, the residue removed and 0.72 g. of potassium introduced Addition of potassium amide solution to the hydrocyanic acid solution caused the immediate formation of a crop of white crystals of potassium cyanide. Calculated for KCN: K, 60.0. Found: K, 60.8.

Action of Potassium Amide on Cyanogen.—A quantity of cyanogen was liquefied in one leg of a reaction tube. The addition of the potassium amide from 0.80 g. of potassium contained in the other leg produced a heavy white amorphous precipitate of potassium cyanide and potassium cyanamide. The presence of cyanide and cyanamide was demonstrated by the usual qualitative tests. The equation is $C_2N_2 + 3KNH_2 = K_2NCN + KCN + 2NH_3$.

Action of Potassium Hydroxide on Benzonitrile and Propionitrile.—In a straight tube, sealed at one end, were placed 1.31 g. of benzonitrile and 0.71 g. of potassium hydroxide which had been freshly fused and heated to redness to remove traces of water. Ammonia was distilled into the tube until it was about one-third full and the open end sealed off. The tube was heated for sixteen hours at 175°, following the procedure as described by Blair.[12] The solution, after cooling, deposited white flaky crystals of potassium benzamide. Calcd. for C_6H_5CONHK: K, 24.5. Found: K, 21.6.

In a similar manner, 1.39 g. of propionitrile and 1.40 g. of potssaium hydroxide were heated for twenty-four hours at 200°. The solution, upon cooling, contained a quantity of light, flaky crystals of potassium propionamide. Calcd. for C_2H_5CONHK: K, 35.2. Found: K, 35.8.

In both cases, the major portion of the hydroxide and nitrile remained unchanged after heating.

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[12] Blair, THIS JOURNAL, 48, 91 (1926).

Ammonation of Benzonitrile and Propionitrile.—A solution of 2.45 g. of benzonitrile and 1.32 g. of ammonium chloride was heated for sixteen hours at 200° in the same manner as stated above. The residue, after evaporation of the ammonia and drying in vacuum, was extracted with absolute alcohol. The alcohol solution contained a small quantity of benzamidine, which was identified by forming its insoluble picric acid salt, melting at 225°.

A solution of 1.89 g. of propionitrile and 1.85 g. of ammonium chloride was heated for twenty-four hours at 200°. The residue after evaporation of the ammonia was dried in a vacuum and extracted with absolute alcohol. The alcohol solution was found to contain a small quantity of propionamidine, which was identified through the formation of a double salt with platinic chloride.

Pyrogenetic Decomposition of Salts of Carbazylic Acids.—The potassium salts of ammonobenzoic acid, ammono-*iso*caproic acid, ammono-*n*-valeric acid, ammono-n-butyric acid, ammonopropionic acid and ammono-acetic acid were heated with potassium amide. In the case of the first three, a quantity of a volatile liquid was obtained upon which the molecular weights were determined by the Victor Meyer method. Values of 80.3, 73.3 and 63.4, respectively, were obtained, which correspond fairly closely to benzene, pentane and butane. The hydrocarbons produced by the decomposition of the last three salts, propane, ethane and methane, respectively, had such low boiling points that they could not be condensed readily. It is significant that a combustible gas was produced in each case.

However, in every case the presence of cyanamide in relatively large quantity was demonstrated by the formation of the characteristic yellow precipitate of silver cyanamide on addition of silver nitrate to an ammoniacal solution of the residue. The same reaction takes place when benzonitrile and sodium amide are heated together, benzene and sodium cyanamide being produced according to the equation $C_6H_5CN + 2NaNH_2 = C_6H_6 + Na_2NCN + NH_3$. Experimentally this was realized by sealing up equimolecular quantities of benzonitrile and sodium amide in straight tubes and heating for two hours at 250°.

Preparation of Benzamidine from Potassium Ammonobenzoate.—Benzamidine has been prepared from its potassium salt by treatment in alcohol solution with hydrogen chloride, $C_6H_5C(NH)NHK + 2HCl = C_6H_5C(NH)NH_2\cdot HCl + KCl$.

Potassium ammonobenzoate was prepared from 1.00 g. of benzonitrile and 0.30 g. of potassium in the usual way. The ammonia was allowed to evaporate, the salt was dried in a vacuum at room temperature and the dry salt then treated with absolute alcohol saturated with dry hydrogen chloride. The precipitate of potassium chloride was filtered off. Evaporation of the alcohol yielded 1.35 g. of a white solid This was shown to be benzamidine hydrochloride by its melting point. The yield obtained is 89% of the theoretical.

It was possible also to obtain benzamidine from potassium ammonobenzoate by carefully hydrolyzing this salt. However, the yield was always poor since the hydrolysis proceeds further than with the formation of benzamidine; potassium benzamide and ultimately potassium benzoate are formed.

Action of Ammonia on the Grignard Reagent Addition Product to Benzonitrile.—A quantity of the addition product of phenylmagnesium bromide to benzonitrile was placed in a reaction tube and, after sealing, ammonia was distilled in. The solid was extracted repeatedly with ammonia and the ammonia was then allowed to evaporate completely. There remained in the leg containing the washings a light brown oil. This oil was dissolved in ether and the solution saturated with dry hydrogen chloride. The white crystalline precipitate which formed was filtered off, washed once with ether and recrystallized from chloroform and ether. The analysis showed the compound to

be diphenyl ketimine hydrochloride. Calcd. for $C_{13}H_{12}NCl$: N, 6.4; Cl, 16.3. Found: N, 6.6; Cl, 18.2.

In conclusion, the writer wishes to express his appreciation to Dr. Franklin, under whose kind guidance the work presented here has been carried out.

Summary

1. It is shown in this paper that the amidines are to be regarded as the ammonia analogs of the carboxylic acids. The term carbazylic acid has been used to denote these acids.
2. The alkyl and aryl cyanides have been shown to be the anammonides of the carbazylic acids.
3. The preparation of a number of salts of the different carbazylic acids has been described.
4. The ammonation of the acid anammonides in the presence of an acid has been demonstrated.
5. The decomposition of the salts of the carbazylic acids, when heated with a metallic amide, proceeds with the formation of a hydrocarbon and an alkali salt of cyanamide.
6. The difference in behavior of hydrocyanic acid and cyanogen from that of other nitriles toward potassium amide in liquid ammonia solution has been noted and an explanation offered.

STANFORD UNIVERSITY, CALIFORNIA

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF UPSALA]

THE MOLECULAR WEIGHTS OF SERUM ALBUMIN AND OF SERUM GLOBULIN

BY THE SVEDBERG AND BERTIL SJÖGREN

RECEIVED JUNE 28, 1928 PUBLISHED DECEMBER 10, 1928

The two chief protein constituents of blood serum are serum albumin and serum globulin. Crystallized serum albumin was obtained as early as 1894,[1] while serum globulin crystals have not as yet been observed. The fact that serum albumin is easily crystallized has been taken as an indication of its homogeneity. Recently, however, the validity of this conclusion has been questioned by Sörensen,[2] who found that by fractional crystallization a series of protein samples with different solubilities could be obtained from serum albumin. The osmotic pressures of the various fractions were, however, the same. The question as to whether serum globulin is a simple protein or a mixture has been the object of much experi-

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[1] A. Gürber, *Würzburger Physiol.-med. Ges.*, 1894, 113; 1895, 26.

[2] S. P. L. Sörensen, "Proteins," The Fleischmann Company, New York, 1925, p. 40.

mental work and discussion. By the fractional precipitation of serum globulin it is possible to obtain protein samples differing in solubility and in chemical composition, the so-called euglobulins and pseudoglobulins; this fact has been taken as a proof of the complex nature of serum globulin.[3] Sörensen found somewhat higher osmotic pressures for the pseudoglobulin fractions than for the euglobulin fractions[4] and so did Adair.[5]

The molecular weights of serum albumin and of the serum globulin fractions have been calculated by Sörensen and by Adair from their osmotic pressure measurements. Sorensen gives 45,000 and Adair 62,000 for serum albumin. Sörensen's globulin fractions gave values from 140,000 (euglobulins) to 80,000 (pseudoglobuliis), while Adair found for euglobulin 174,000 and for pseudoglobulin fractions 150,000–130,000.

Cohn has made an attempt to estimate the molecular weights of these proteins from analytical data.[6] For serum albumin he arrives at the value 45,000, and for serum globulin he finds 27,000 as the minimal molecular weight, which value he multiplies by three in order to obtain a molecular weight of 81,000 in agreement with Sörensen's osmotic pressure determinations.

In view of the uncertainty involved in many of the analytical data used by Cohn in his calculations and the numerous and uncontrollable sources of error in osmotic measurements, it was thought advisable to undertake an investigation of the molecular weights of these important proteins by means of the centrifugal methods already used in this Laboratory for the determination of the molecular weights of hemoglobin,[7] egg albumin,* phycocyan,[9] phycoerythrin[g] and hemocyanin.[10]

Experimental

The protein material used in this investigation was prepared from horse blood. All determinations were carried out in buffer solutions at the isoelectric point, namely, at *P*H 4.8 for serum albumin and at 5.5 for serum globulin, where the stability of the proteins is greatest and all effects due to the presence of protein ions are at a minimum. A study of the *P*H limits within which these proteins are stable will be carried out later.

[3] (a) E. Marcus, *Z. physiol. Chem.*, 28,559 (1899); (b) E. Fuld and K. Spiro, *ibid.*, 31, 132 (1900); (c) E. P. Pick, *Hofmeisters Beitr.*, 1, 351, 393 (1901); (d) O. Porges and K. Spiro, *ibid,*, 3,277 (1902).

[4] Ref. 2, p. 52.

[5] G. S. Adair, *Scandinavian Arch. Physiol.*, 49, 76 (1926).

[6] (a) E. J. Cohn, J. L. Hendry and A. M. Prentiss, *J. Biol. Chem.*, 63, 721 (1925); (b) E J. Cohn, *Physiol. Reviews*, 5,349 (1925).

[7] (a) T. Svedberg and R Fåhraeus, THIS JOURNAL, 48,430 (1926); (b) T. Svedberg and J. B. Nichols, *ibid.*, 49,2920 (1927).

[8] T. Svedberg and J. B. Nichols, *ibid.*, 48,3081 (1926).

[9] T. Svedberg and N. B. Lewis, *ibid.*. 50,525 (1928).

[10] T. Svedberg and E. Chirnoaga, *ibid.*, 50,1399 (1928).

Preparation of Material.—Serum albumin was prepared in the following manner.[11] Horse serum free from hemoglobin and containing toluene as a preservative was mixed with an equal volume of a saturated ammonium sulfate solution. After standing for one day at 5°, the globulin precipitate was centrifuged off. To the solution was added slowly 0.1 *N* sulfuric acid half saturated with ammonium sulfate until a permanent cloudiness appeared. Toluene was added and the mixture was left to crystallize at room temperature. After a period of three days, the crystals were filtered off and washed with a weak solution of ammonium sulfate. The serum albumin thus obtained was recrystallized three times and for eight days dialyzed in collodion bags against flowing distilled water saturated with toluene at 0°. In order to remove the last traces of globulin it was finally electrodialyzed in a Pauli apparatus[12] for thirty-six hours at a current density of 0.6 mil. amp. per sq. cm. The concentration of the stock solution made up from this material (called in the following serum albumin I) was 0.76%.

Measurements with the ultracentrifuge showed that the protein of the above solution had been partly split into some non-centrifugible substance. We therefore prepared a second batch of serum albumin, working as quickly as possible. Only one process of crystallization was performed. The dialysis was continued for four days only and the electrodialysis for three days. A stock solution containing 2.80% of organic substance in acetate buffer at P_H 4.8 (0.02 *N* with regard to acetate ion) was made up (serum albumin II). The centrifuging experiments showed that this solution was much less decomposed.

During the work done on proteins in this Laboratory we have often had the opportunity to observe that an elaborate process of purification furnishes a material less homogeneous with regard to molecular weight than does a cruder but quicker method. The preparation of serum albumin is a typical example of this phenomenon. We have the impression that the living organisms always contain proteins of well defined molecular weights, but that many of these proteins are so unstable that they are often decomposed during the process of separation and purification.

Serum globulin was prepared in the following way.[13] The precipitate obtained after half saturating the serum with ammonium sulfate was washed with half saturated ammonium sulfate solution and dissolved in 10% sodium chloride solution, using toluene as a preservative. The protein was again precipitated by half saturating with ammonium sulfate, washed and dissolved as before. This process was repeated a third time, the washing being continued until the biuret reaction was negative. The precipitate was dissolved again in 10% sodium chloride solution and dialyzed against a phosphate buffer of P_H 5.5, 0.19 M in KH_2PO_4 and 0.009 M in Na_2HPO_4. The strength of this solution (serum globulin I) was 2.60%.

A second batch was made in the following way. The material was precipitated three times with ammonium sulfate, washed and dissolved in phosphate buffer and dialyzed against the same phosphate buffer until the outer liquid did not show the presence of sulfate and chloride. The stock solution had a strength of 3.25% (serum globulin II).

part of the serum globulin material was fractionated according to Sörensen[14] by means of ammonium sulfate. The centrifugal study of the different fractions

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[11] (a) Compare H. T. Krieger, "Ueber Darstellung krist. tierisch. Eiweissstoffe," Dissertation, Strassburg, 1899; (b) S. P. L Sorensen, *Medd. Carlsberg Lab.*, 12, 12 (1915).

[12] W. Pauli, Biochem. Z., 152, 355 (1924).

[13] Compare G. Kauder, *Arch. exptl. Pathol.*, 22, 411 *(1886).*

[14] Ref. 2, p. 44.

showed that a rapid decomposition of the protein took place during the process of fractionation, more and more non-centrifugible material being formed.

Specific Volume.—The partial specific volume was determined pycnometrically at 19.5'. The amount of protein in solution was found by means of the following methods: (a) heating the solution until coagulation occurred, filtering and washing in a Gooch crucible and drying to constant weight at 105°; (b) drying at 105° to constant weight and subtracting the amount of salt in the sample as known from the composition of the buffer. The two methods gave consistent results.

No change of specific volume with concentration was observed for the range 0.75–3.0%. As mean value we obtained for serum albumin **0.748** and for serum globulin **0.745.** These figures are equal within the limits of experimental error. It is worth noticing that according to previous determinations in this Laboratory[7,8,9] the values for egg albumin, hemoglobin, phycocyan and phycoerythrin are almost identical with the value found for serum albumin and serum globulin. These six proteins are, therefore, probably built up according to a plan common to all of them. On the other hand hemocyanin from *Helix*[10] and from *Limulus*[15] have a specific volume of **0.735** near their isoelectric points.

Light Absorption.—Serum albumin as well as serum globulin absorb only in the short-waved ultraviolet part of the spectrum. The measurements were carried out by means of a Judd-Lewis spectrophotometer in 20 mm. cells for solutions of concentration **0.20, 0.10** and **0.05%.** The toluene dissolved in the solutions and serving as a preservative was removed by bubbling moist nitrogen through them before measuring the light absorption. The specific extinction coefficient $\epsilon/c = 1/d \log I_0/I$, where c is the concentration in %, I_0 the intensity of the light beam after passing a layer of solvent d cm. thick and I the intensity after passing the same thickness of solution, is plotted against wave length in Fig. **1.** The absorption curve of serum albumin (A) has a maximum at **278** μμ and **a** minimum at 250 μμ; the corresponding values for serum globulin, curve (B), are **285** μμ and **255** μμ. The positions of the maxima and minima are identical within the limits of error. The values of the extinction coefficients are, however, much higher for serum globulin than for serum albumin. This is probably due to the high tryptophane content of serum globulin compared with that of serum albumin.

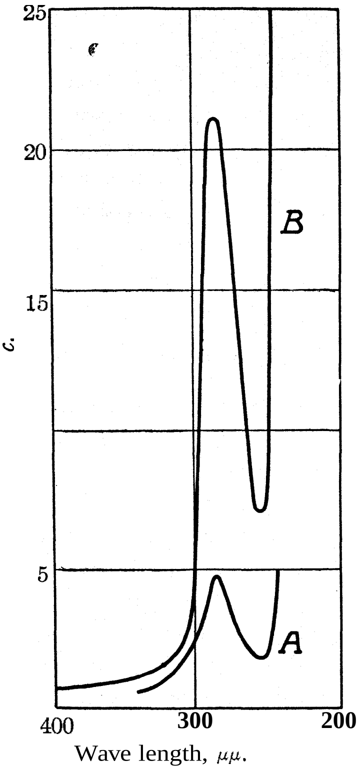

Fig. 1.

The centrifuging experiments have shown that in dilute solutions serum albumin is partly transformed into a non-centrifugible substance. In order to check the influence of this decomposition upon the light absorption some measurements were also made in a **2.80%** solution using a 1-mm. absorption cell. Only a slight decrease in light absorption was observed, indicating that the specific extinction coefficient is almost the same for serum albumin and the decomposition products in question.

Unpublished determinations by Dr. F. F. Hepoth.

Determination of the Molecular Weight

A. Sedimentation Velocity Method.[16]—Because of the more detailed information with regard to uniformity of molecular species and variation of diffusion and molecular weight with concentration which the sedimentation velocity method furnishes, this procedure was first applied.

The molecular weight is given by the relation

$$M = \frac{RTs}{D(1 - V\rho)}$$

where R is the gas constant, T the absolute temperature, s the specific sedimentation velocity or $1/\omega^2 x \cdot dx/dt$, 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.

The specific sedimentation velocity and the diffusion constant were calculated from the photographic records as described in previous papers. The values were all reduced to 20° by means of the relations $s_1/s_2 = \eta_2/\eta_1$ and $D_1/D_2 = T_1/T_2 \cdot \eta_2/\eta_1$, where η is the viscosity of the solution.

A few changes in the apparatus were made in order to improve the experimental conditions. Thus a new oil cooler was inserted in the oil circulation system so that the temperature of the oil entering the turbines could be lowered from 25 to 15°. This caused a drop of temperature in the cell from about 30 to about 25°. When working with such unstable proteins as serum albumin and serum globulin, it is of great importance to keep the temperature of the cell as low as possible. Cells of three different thicknesses were used, namely, 2, 6 and 12 mm., in order to obtain suitable light extinction for solutions of various concentrations. The middle or sector plate of the cells previously made of glass was replaced by an ebonite plate. The quartz plates were cemented to the ebonite plate and the steel collar surrounding the plates by means of a cement composed of 2 parts of shellac and 1 part of pine tar heated together at 125° for five hours. These new cells endured the enormous strain in the centrifuge much better than the old ones.

The height of column of solution in the cells was 12 to 14 mm. The speed was chosen as high as possible, namely, around 42,000 r.p.m. corresponding to a centrifugal force about 100,000 times the force of gravity. The protein solutions used in the centrifuging experiments were made up from the stock solution by dilution with buffer immediately before each run and the dissolved toluene was removed by bubbling moist nitrogen through it.

As source of light a vertical quartz mercury lamp with a ground quartz plate as a diffuser was used. Chlorine and bromine quartz filters isolated a suitable range of wave length below 290 μμ, and a quartz water filter re-

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[16] (a) T. Svedberg, *Z. physik. Chem.*, 127, 51 (1927); (b) T. Svedberg and J. B. Nichols, THIS JOURNAL, 49, 2920 (1927).

moved the infra-red radiations. The photographs were taken on Imperial Process plates by means of a quartz lens of 100.5 cm. focal length. Metol-hydroquinone developer was used; the time of development was one minute,

TABLE I

SERUM ALBUMIN I, SEDIMENTATION VELOCITY RUN

Concentration, 0.12%; electrolyte-free solution; $V = 0.748$; $p = 1.000$; length of column of solution, 0.90 cm.; thickness of column, 1.20 cm.; speed, 42,100 r.p.m. (ω = 1403.3~); source of light, mercury lamp, light filters, chlorine and bromine. aperture of objective, F: 36; plates, Imperial Process; time of exposure, 30 sec.; metol-hydroquinone developer; time of development, 1 min.

Sedimentation

Time interval, hours	T	Ax per half hour, cm.	Mean x, cm.	Centrif. force, ω^2x	$s_{20°}$, cm./sec. per cm./sec.^{2}
1.5–2.0	298.8	0.090	5.29	10.38×10^7	4.25×10^{-13}
2.0–2.5	298.9	.090	5.38	10.45×10^7	4.18×10^{-13}
2.5–3.0	299.0	.100	5.46	10.61×10^7	4.56×10^{-13}

Diffusion

Time of diffusion. min.	T	Mean[a] z, cm.	$D_{20°}$, cm.^{2}/sec.
65	298.6	0.060	8.75 X 10^{-7}
95	298.8	.080	10.58×10^{-7}
125	298.9	.105	13.82 X 10^{-7}
155	299.0	.120	14.19 X 10^{-7}

Mixture of different molecules; 43% non-centrifugible substance.

[a] "Mean z" is the mean of the distances from $c = 25$ to $c = 50$ and from $c = 50$ to $c = 75$, the concentration in the unchanged part of the solution being taken as 100 (compare THIS JOURNAL, 49, 2922 (1927)).

The data of a run with the material "serum albumin I" are given in Table I. The distinct drift in the values of the diffusion constant with time indicates the presence of molecules or particles of various sizes. Pure buffer was not formed in the top part of the cell during centrifuging as usual. The light absorption indicated that about 43% of the organic matter was not centrifugible under the present experimental conditions. The material "serum albumin I," therefore, does not represent a pure protein but rather a mixture of molecules of different weight, some of them being so small that they were not influenced by the enormous centrifugal field applied.

In Tables II and III are given the results of two typical runs with the material "serum albumin II." In this case there is no drift in the diffusion constant with time. Pure buffer was formed in the top part of the cell when solutions of concentrations 1.25 to 0.75% were centrifuged. In more dilute solutions (0.50 and 0.25%), however, pure buffer was not formed. The concentration of the non-centrifugible substance increased with the dilution. The fact that there is no drift in the diffusion constant shows that the material "serum albumin II" contains protein molecules of the same weight and shape. The serum albumin is therefore to be regarded as homogeneous with regard to molecular weight. The determinations also show that in dilute solution the serum albumin molecule breaks up into small units. The molecular weight of the centrifugible

TABLE II

SERUM ALBUMIN II, SEDIMENTATION VELOCITY RUN

Concn., 0.50%; acetate buffer, P_H 4.8 (0.02 M in total acetate); V = 0.748; p = 1.000; length of col. of soln., 1.10 cm.; thickness of col., 0.60 cm.; speed, 40,000 r.p.m. (w = 1333π); source of light, mercury lamp; light filters, chlorine and bromine; aperture of lens F: 36; plates, Imperial Process; exposure, 60 sec.; metol-hydroquinone developer, 1 min. Not centrifuged to pure buffer.

Sedimentation

Time interval, hours	T	Δx per half hour, cm.	Mean x, cm.	Centrif. force, $\omega^2 x$	$s_{20°}$, cm./sec. per cm./sec ^{2}
1.0–1.5	299.6	0.080	5.01	8.79×10^{7}	4.35×10^{-13}
1.5–2.0	299.7	.085	5.09	8.93×10^{7}	4.54×10^{-13}
2 0–2.5	299.8	.080	5.18	9.08×10^{7}	4.19×10^{-13}
2 5–3.0	299.9	.080	5.26	9.22×10^{7}	4.12×10^{-13}
3.0–3.5	299.9	.080	5.34	9.36×10^{7}	4.06×10^{-13}
3.5–40	299.9	.080	5.42	9.50×10^{7}	4.00×10^{-13}
				Mean	4.21×10^{-13}

Diffusion

Time of diff., min.	T	Mean z, cm.	$D_{20°}$, cm.^{2}/sec.
67.5	299.5	0.050	5.71×10^{-7}
97.5	299.6	.063	6.26×10^{-7}
127.5	299.8	.073	6.40×10^{-7}
157 5	299.9	.080	6.21×10^{-7}
187 5	299.9	.088	6.31×10^{-7}
217.5	299.9	.095	6.34×10^{-7}
		Mean	6.20×10^{-7}

Molecular weight = 65,000; 14% non-centrifugible substance.

TABLE III

SERUM ALBUMIN II, SEDIMENTATION VELOCITY RUN

Concn., 1.25%; buffer, V and ρ as in Table II; length of col., 1.43 cm.; thickness of col., 0.20 cm.; speed, 40,100 r.p.m. (ω = 1367π); exposure, 40 sec.; optical and photographic conditions as in Table 11.—Centrifuged to pure buffer.

Sedimentation

Time interval, hours	T	Δx per half hour, cm.	Mean x, cm.	Centrif. force, $\omega^2 x$	$s_{20°}$, cm./sec. per cm./sec.^{2}
1.0–1.5	299.6	0.060	..	....	....
1.5–2.0	299.8	.070	4.72	8.32×10^{7}	4.01×10^{-13}
2.0–2.5	299.9	.065	4.80	8.46×10^{7}	3.64×10^{-13}
2.5–3.0	300.0	.075	4.88	8.61×10^{7}	4.12×10^{-13}
3.0–3.5	300.0	.080	4.96	8.74×10^{7}	4.33×10^{-13}
3.5–4.0	300.0	.090	5.05	8.89×10^{7}	4.79×10^{-13}
				Mean	4.18×10^{-13}

TABLE III (Concluded)

Diffusion

Time of diffusion, min.	T	Mean z, cm.	$D_{20°}$, cm.²/sec.
73.5	299.4	0.053	5.92×10^{-7}
103 5	299.7	.065	$6\ 27 \times 10^{-7}$
133.5	299.3	.070	5.61×10^{-7}
163.5	300.0	.080	5.96×10^{-7}
193.5	300.0	.090	6.38×10^{-7}
223 5	300.0	.093	5.90×10^{-7}
			Mean 6.01×10^{-7}

Molecular weight = 67,200; centrifuged to pure buffer.

part was found to be the same in concentrated solutions where no decomposition had taken place as in the very dilute (0.25%) solutions where

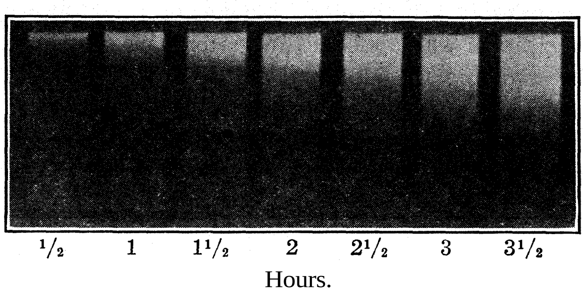

Fig. 2.

about 29% of the protein was decomposed. This shows that the decomposition leads immediately to very small molecules without giving rise to any appreciable amount of intermediate products. The behavior of the material "serum albumin I" indicates that the elaborate purification used in that case has caused a rather complicated decomposition and aggregation process to take place, the result being a less pure material than when a cruder and quicker purification method was used (Material II).

The photographs from which the data of Table II have been derived are reproduced in Fig. 2. The corre-

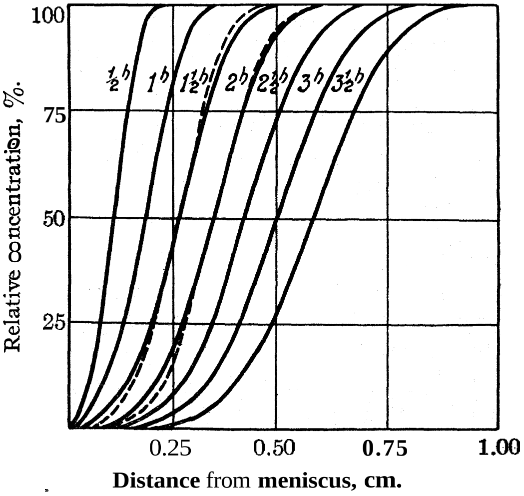

Fig. 3.

sponding concentration curves, corrected for the sector shape of the cell and the variation of centrifugal force with distance from the center of rotation,[16] are given in Fig. 3. The dotted curves for one and one-half and tow hours represent the theoretical diffusion curves of a substance of only one molecular species if subjected to the same experimental conditions. The deviation from the experimentally determined variation of concentration is within the limits of experimental error.

In order to ascertain whether the formation of the non-centrifugible substance in the dilute serum albumin solutions is a reversible or an irreversible process, the following experiment was performed. A 0.25% solution was precipitated by saturating with ammonium sulfate. A measurement of the light absorption of the liquid from which the precipitate had been filtered off showed that all the albumin and its decomposition products had really been completely salted out. The biuret reaction was also negative. The precipitate was dissolved in water, the solution was dialyzed and electrodialyzed and the albumin studied in the ultracentrifuge at a concentration of 1.1% in an acetate buffer of PH 4.8, as usual. The protein this time sedimented with normal molecular weight, leaving pure buffer in the top part of the cell, showing that the breaking up of the serum albumin in dilute solution is a reversible process.

TABLE IV

SERUM ALBUMIN II, SUMMARY OF SEDIMENTATION VELOCITY MEASUREMENTS

Concn., g. per 100 cc.	Mean speed, r.p.m.	$s_{20°}$, cm./sec. per cm./sec.^{2}	$D_{20°}$, cm.^{2}/sec.	Mol. wt.
1.25	40.100	4.18×10^{-13}	6.01×10^{-7}	67,200
1.00	42,100	4.48×10^{-13}	6.35×10^{-7}	68,200
0.75	41,600	4.00×10^{-13}	5.97×10^{-7}	65,000
0.50	40,000	4.21×10^{-13}	6.20×10^{-7}	65,600
0.25	39,900	4.18×10^{-13}	5.97×10^{-7}	67,700
	Mean	4.21×10^{-13} Mean	6.10×10^{-7} Mean	66,740

The results of all the sedimentation velocity runs with serum albumin are summarized in Table IV. The mean value of the molecular weight is 66,740 ± 2000.

In Tables V and VI are given the results of two typical runs with serum globulin (Material I and II, respectively). The photographs and the concentration curves corresponding to the data of Table V are reproduced in Figs. 4 and 5. No drift in the diffusion constant occurs and pure buffer is formed in the top part of the cell at all concentrations studied (1.00 to 0.12%). It is therefore obvious that serum globulin is a homogeneous substance with regard to molecular weight. The results of all sedimentation velocity runs with serum globulin are given in Table VII. The mean value of the molecular weight is 104,400 ± 3000.

As already mentioned under "Preparation of Material" an attempt was

TABLE V

SERUM GLOBULIN I, SEDIMENTATION VELOCITY RUN

Concn., 0.72%; phosphate buffer, P_H 5.5 (0.19 M in KH_2PO_4 and 0.009 M in Na_2HPO_4); V = 0.745; p = 1.018; length of col., 1.33 cm.; thickness of col., 0.20 cm.; speed, 41,400 r.p.m. ($\omega = 1380\pi$); exposure, 40 sec.; optical and photographic conditions as in Table I.

Sedimentation

Time interval, min.	T	Δx per 20 min., cm.	Mean x, cm.	Centrif. force, $\omega^2 x$	$s_{20°}$, cm./sec. per cm./sec.^{2}
20–40	298.4	0.060	4.72	8.83×10^7	5.01×10^{-13}
40–60	298.5	.075	4.79	900x107	6.11×10^{-13}
60–80	298.7	.070	4.86	9.13×10^7	5.61×10^{-13}
80–100	298.9	.065	4.93	9.26×10^7	5.12×10^{-13}
100–120	299.0	.065	4.99	$9\ 38 \times 10^7$	5.02×10^{-13}
120–140	299.1	.075	5 06	9.50×10^7	5.71×10^{-13}
140–160	299.1	.075	5.13	9.69×10^7	5.60×10^{-13}
160–180	299.1	.075	5.21	9.83×10^7	5.52×10^{-13}
					Mean 5.46×10^{-13}

Diffusion

Time of diff. min.	T	Mean z, cm.	$D_{20°}$, cm.^{2}/sec.
32	298.3	0.040	7.95×10^{-7}
52	298.5	.040	4.87×10^{-7}
72	298.6	.045	4.41×10^{-7}
92	298.8	.055	5.17×10^{-7}
112	299.1	.060	5.02×10^{-7}
132	299.1	.067	5.31 × 10-7
152	299.1	.068	4.75 × 10-7
172	299.1	.072	4.71 × 10-7
		Mean	5.27×10^{-7}

Molecular weight = 104,500.

TABLE VI

SERUM GLOBULIN II, SEDIMENTATION VELOCITY RUN

Concn., 0.75%; buffer, V and p as in Table V; length of col., 1.45 cm.; thickness of col., 0.20 cm.; speed, 41,700 r.p.m. ($\omega = 1390\pi$); exposure, 30 sec.; optical and photographic conditions as in Table I.

Sedimentation

Time interval, min.	T	Ax per 20 min. cm.	Mean x, cm.	Centrif. force, $\omega^2 x$	$s_{20°}$, cm./sec. per cm./sec.^{2}
20-40	296.0	...	..	....	....
40-60	296.3	0.060	4.64	8.85×10^7	5.23×10^{-13}
60-80	296.5	.070	4.71	8.97×10^7	5.99×10^{-13}
80-100	296 6	.065	4.77	9.10×10^7	5.48×10^{-13}
100-120	296.7	.070	4.84	9.23×10^7	5.80×10^{-12}
120-140	296.8	.070	4.91	9.36×10^7	5.70×10^{-13}
140-160	296 9	.078	4.98	9.50×10^7	6.24×10^{-13}
160-180	296.9	.077	5.06	9.65×10^7	6.07×10^{-13}
					Mean 5.79×10^{-13}

TABLE VI (*Concluded*)

Diffusion

Time of diff., min.	T	Mean z, cm.	D_{20° cm.^{2}/sec.
25	295.7	0.030	6.12×10^{-7}
45	296.3	.040	5.97×10^{-7}
65	296.5	.048	5.90×10^{-7}
85	296.5	.055	5.93×10^{-7}
105	296.7	.058	5.31×10^{-7}
125	296.8	.060	4.76×10^{-7}
145	296.9	.065	4.81×10^{-7}
165	296.9	.070	4.90×10^{-7}
			Mean 5.46×10^{-7}

Molecular weight = 106,800.

TABLE VII

SERUM GLOBULIN, SUMMARY OF SEDIMENTATION VELOCITY MEASUREMENTS

Subs.	Concn., g. per 100 cc.	Mean speed, r.p.m.	s_{20°, cm./sec. per cm./sec.^{2}	D_{20° cm.^{2}/sec.	Mol. wt.
Ser. glob. II	1.00	42,000	5.50×10^{-13}	5.37×10^{-7}	103,400
Ser. glob. II	0.75	41,700	5.79×10^{-13}	5.46×10^{-7}	106,800
Ser. glob. I	.72	41,400	5.46×10^{-13}	5.27×10^{-7}	104,500
Ser. glob. I	.53	41,900	5.54×10^{-13}	5.49×10^{-7}	101,800
Ser. glob. I	.12	41,400	6.01×10^{-13}	5.45×10^{-7}	105,700
			Mean 5.66×10^{-13}	Mean 5.41×10^{-7}	Mean 104,400

made to study the "euglobulins" and "pseudoglobulins" obtained by fractionating serum globulin with ammonium sulfate. It was found, however, that the process of fractionation causes decomposition of the globulin, more and more non-centrifugible substance appearing during the course of the operations. From our experiences, therefore, it seems possible that the so-called pseudoglobulins are just artificial products representing mixtures of undecomposed serum globulin and decomposition products generated by the fractionating process. This important question will be dealt with fully in a subsequent communication.

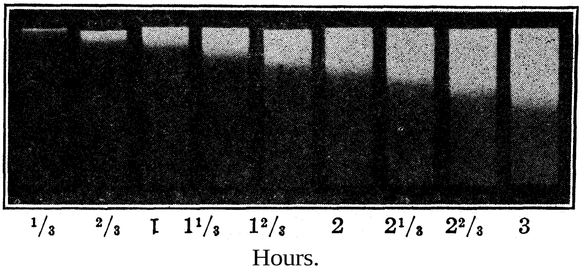

Fig. 4.

B. Sedimentation **Equilibrium Method.**[7a,8,17]—The molecular weight is given by the relation

$$M = \frac{2RT \ln (c_2/c_1)}{(1 - V\rho)\, \omega^2(x_2^2 - x_1^2)}$$

c_1 and c_2 are the concentrations at the distances x_1 and x_2 from the center of rotation and the other symbols have the same significance as previously.

Because of the decomposition of serum albumin observed in the sedimentation velocity experiments, this protein was only studied in relatively high concentration using a 2 mm. cell. On the other hand, serum globulin, which was found to be stable also in dilute solution, was investigated at lower concentrations by means of a cell 8 mm. in thickness.

The source of light, the light filters and the lens were similar to those used in the sedimentation velocity runs. The same plates and the same developer were used. Pictures were taken with three different times of exposure in order to obtain suitable photographic densities for the various concentrations. Changes in the intensity of the lamp were corrected for by having another cell of the centrifuge filled with a solution of potassium chromate of suitable strength and photographing this cell at the same time as the cell filled with the protein solution.

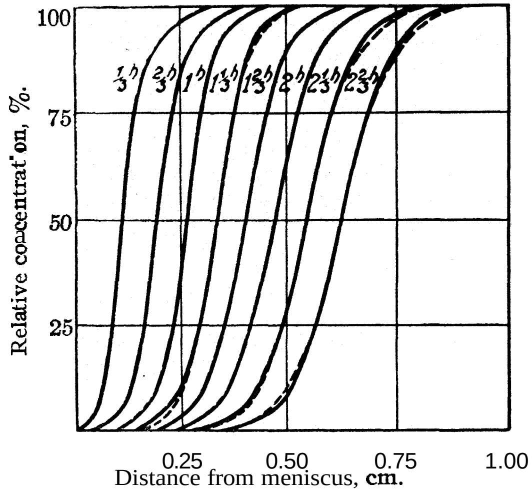

Fig. 5.

TABLE VIII

SERUM ALBUMIN II, SEDIMENTATION EQUILIBRIUM RUN

Concn., 1.00%; acetate **buffer,** P_H 4.8 (0.02 M in total acetate); $V = 0.748$; $\rho = 1.000$; $T = 293.2$; length of col. of soln., 0.50 cm.; thickness of col., 0.20 cm.; dist. of outer end of sol. from axis of rotation, 4.73 cm.; speed, 8200 r.p.m. ($\omega = 273.3\pi$); optical and photographic conditions similar to those in Table I; aperture of lens, F: 30; time of exposure 1, 2 and 4 min.; exposures made after 36, 40 and 44 hours of centrifuging.

Distances, cm. x_2	x_1	Mean concn., % c_2	c_1	No. of exposures	Mol. wt.
4.63	4.58	1.300	1.154	11	68,000
4.58	4.53	1.154	1.022	11	69,600
4.53	4.48	1.022	0.909	10	68,600
4.48	4.43	0.909	.810	10	67,700
4.43	4.38	.810	.724	10	67,200
4.38	4.33	.724	.645	10	69,100
				Mean	68,400

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[17] Svedberg, Z. *physik.* Chem., **121,** 65 (1926).

TABLE IX

SERUM GLOBULIN II, SEDIMENTATION EQUILIBRIUM RUN

Concn., 0.15%; phosphate buffer, PH 5.5 (0.19 M in KH_2PO_4 and 0.009 M in Na_2HPO_4); V = 0.745; ρ = 1.018; T = 291; length of col., 0.50 cm.; thickness of col., 0.80 cm.; speed, 6920 r.p.m. (ω = 230.7~); times of exposure, 20, 40 and 60 sec.; exposures made after 38, 44 and 48 hours of centrifuging; other data as in Table VIII.

Distances, cm. x_2	x_1	Mean concn., % c_2	c_1	No. of exposures	Mol. wt.
4.68	4.63	0.215	0.189	2	105,600
4.63	4.58	.189	.167	10	102,500
4.58	4.53	.167	.147	10	106,800
4.53	4.48	.147	.130	10	104,100
4.48	4.43	.130	.116	10	105,000
4.43	4.38	.116	.104	7	101,800
4.38	4.33	.104	.093	2	97,900
				Mean	103.400

Details of a run with serum albumin (Material II) are given in Table VIII. A typical serum globulin run is shown in Table IX (Material II). The results of all the sedimentation equilibrium runs are summarized in Table X.

TABLE X

SUMMARY OF SEDIMENTATION EQUILIBRIUM MEASUREMENTS

Subs.	Concn. at start, %	Mean speed, r.p.m.	Mol. wt.
Serum albumin II	0.92	8540	67,900
Serum albumin II	1.00	8200	68,400
Serum globulin I	0.10	7000	102,900
Serum globulin I	.15	6900	103,100
Serum globulin II	.15	6920	103,400
	Mean for serum albumin		68,150
	Mean for serum globulin		103,100

The values of the molecular weight calculated from measurements at different distances from the center of rotation were identical within the limits of error as demonstrated by Tables VIII and IX. The study of serum albumin and serum globulin by means of the sedimentation equilibrium method, therefore, confirms the result arrived at by means of the sedimentation velocity method, namely, that these proteins are to be regarded as homogeneous with regard to molecular weight. The mean value of the molecular weight found by the equilibrium method is 68,150 ± 2000 for serum albumin and 103,100 ± 3000 for serum globulin. These figures are identical within the limits of error with those furnished by the velocity method.

Discussion of Results

The measurements described in this paper have shown that serum albumin and serum globulin isolated from horse blood by means of a rapid process of purification must be regarded as two proteins homogeneous with regard to molecular weight. The value for serum albumin is 67,500 ± 2000 and that for serum globulin 103,800 ± 3000. This is rather surprising when compared with the results of earlier investigations of these proteins. As already mentioned, Sorensen found that serum albumin could be divided into a series of fractions possessing widely different solubilities.[2] His figure for the molecular weight calculated from osmotic measurements was 45,000, which is about 33% lower than our value. The fact brought to light by our experiments that serum albumin is a very unstable protein easily decomposed during the process of purification and always partly decomposed in dilute solutions seems to indicate that the discrepancy might be explained by assuming that Sorensen's carefully purified albumin had undergone partial decomposition. An abnormally high osmotic pressure would probably have been the result of such a change. Adair's serum albumin, which showed an osmotic pressure corresponding to a molecular weight of 62,000, seems to have been less decomposed. The different solubilities found by Sorensen in his different serum albumin fractions could be interpreted by assuming that serum albumin, although homogeneous with regard to molecular weight, is a mixture of two or more proteins of different chemical properties. The simplest explanation, however, seems to be that the differences in solubility are caused by the presence in the fractions of varying amounts of decomposition or aggregation products.

The fact that serum globulin was found to be homogeneous with regard to molecular weight is perhaps still more surprising than the behavior of serum albumin. Most of the previous work on this protein seemed to indicate that serum globulin was to be regarded as a rather complicated mixture of euglobulins and pseudoglobulins. Our fractionation experiments controlled by measurements in the ultracentrifuge, although only of a preliminary nature, have shown, however, that this protein also is liable to break up during the usual process of fractionation. It seems, therefore, probable that the so-called euglobulins and pseudoglobulins do not exist in the blood but are to be regarded as artificial products.

In a previous communication attention was drawn to the fact that the molecular weights of hemoglobin, phycocyan and phycoerythrin as determined by the centrifugal methods were all very nearly simple multiples of the molecular weight of egg albumin.[9] It is of considerable interest to note that the molecular weight of serum albumin is now found to be almost exactly two times the molecular weight of egg albumin, while the molecular weight of serum globulin is three times the weight of egg albumin. Thus we now have six proteins of widely different origin obeying this rule of simple multiples. Perhaps of equal importance is the information that there exist proteins possessing widely different chemical and physical properties but having approximately the same molecular weight. We now know two such pairs, hemoglobin and serum albumin on the one hand and phycocyan and serum globulin on the other. The detailed discussion of these regularities will be reserved for a subsequent communication.

Summary

1. The centrifugal sedimentation velocity and sedimentation equilibrium methods have been applied to the study of the molecular weights of serum albumin and serum globulin in buffer solutions at their isoelectric points, using various protein concentrations.

2. The serum albumin was found to have a molecular weight of 67,500 ± 2000 and the serum globulin 103,800 ± 3000, both being independent of concentration.

3. It was found that within the limits of experimental error both these proteins are homogeneous with regard to molecular weight and that they therefore may represent pure chemical individuals.

4. It was found that both these proteins, but especially the serum albumin, are rather unstable substances easily decomposed during the process of purification. Serum albumin is always partly, although reversibly, decomposed in dilute solution. These facts seem to afford an explanation for the discrepancies between the results of various investigators working on the proteins of the serum.

5. It was pointed out that the molecular weights of serum albumin and serum globulin are, like the molecular weights of hemoglobin, phycocyan and phycoerythrin, very nearly simple multiples of that of egg albumin.

6. It was pointed out that these new molecular weight determinations show that there exist proteins of different chemical composition and widely different properties but possessing very nearly the same molecular weight. Hemoglobin and serum albumin with molecular weights near 68,000 and phycocyan and serum globulin with molecular weights near 105,000 are two such pairs.

UPSALA, SWEDEN

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF FORDHAM UNIVERSITY]

THE ACTION OF PYRIDINE AS A CATALYST IN PERKIN'S SYNTHESIS OF CINNAMIC ACID

BY GEORGE BACHARACH AND FRANCIS BROGAN

RECEIVED JULY 16, 1928 PUBLISHED DECEMBER 10, 1928

Our search for a catalyst to enhance the velocity of the reaction in Perkin's synthesis of cinnamic acid led us to study the action of pyridine on the usual mixture of benzaldehyde, sodium acetate and acetic anhydride.

Twenty grams of freshly distilled benzaldehyde was mixed with 30 g. of redistilled acetic anhydride and 10 g. of anhydrous sodium acetate. To this, S drops of pyridine was added. The mixture was heated in a first experiment for four hours on an air-bath, a reflux condenser being used. After this, water was added (1200 cc.) and an excess of benzaldehyde distilled off by steam; 5 cc. of benzaldehyde was recovered. Concentrated hydrochloric acid was now added until the mass became acid to Congo Red. We were able then to observe a rapid precipitation of the cinnamic acid, which was filtered off by suction and dried. The yield was 18.8 g. or 67.1% of the theoretical. The acid needs no further purification, its melting point being 132'.

In a second experiment, conducted in the same way as before and using the same proportions, we continued the period of digestion for six hours and obtained 23.2 g. of cinnamic acid or 83% of the theoretical. The melting point was again 132°.

In a third experiment, the digestion was continued for a period of eight hours, everything else being equal. The result was a yield of 23.8 g. or 85% of the theoretical; melting point, 132.5'.

In each of these two latter experiments we naturally recovered a correspondingly lower amount of unchanged benzaldehyde. We have also performed experiments with a period of digestion of ten hours, but the yields were the same as in the eight-hour experiment. We can, therefore, consider the yield of the eight-hour experiment as the highest obtainable in this reaction. Furthermore, we have also conducted experiments with amounts of pyridine as large as 2 cc. but the results were the same as above.

It should be noted that the cinnamic acid thus obtained is pure and needs no further recrystallization with charcoal with its inevitable loss of material.

The following table shows a comparison of yields obtained with pyridine as a catalyst and those obtained without pyridine.[1]

The yields reported in the literature are usually given as between 15 and 20 g. with the proportions used in the above experiments, that is,

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[1] These latter experiments were performed with the collaboration of Mr. P. Conroy.

TABLE I

COMPARISON OF YIELDS

Hours of digestion	Without pyridine Actual yield, g.	% of the theoretical	With pyridine Actual yield, g.	% of the theoretical
4	10.3	36.7	18.8	67.1
6	15.00	53.6	23.2	83
8	17.00	60.7	23.8	85

between 53.6 and 70% of the theoretical; furthermore, after a digestion period of eight hours, the yield is similar to the one obtained in four hours when pyridine is used. When the digestion is continued for eight hours in the experiment with pyridine, the yield becomes 85% of the theoretical and considering also that no charcoaling is necessary, we may say that we have here a decided improvement.

Summary

A substantially increased yield (up to 85%) of cinnamic acid in the Perkin synthesis has been produced by using pyridine as a catalyst at the rate of 8 drops for 20 g. of benzaldehyde, the time of reaction being eight hours. Additional pyridine and longer heating do not increase the yield. The product is obtained in very pure condition.

NEW YORK CITY

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

SOME SIDE REACTIONS IN THE PREPARATION OF ALKYLMAGNESIUM HALIDES

BY HENRY GILMAN AND ROBERT E. FOTHERGILL

RECEIVED JULY 20, 1928 PUBLISHED DECEMBER 10, 1928

Introduction

In connection with studies concerned with the analysis of gases evolved in Grignard reactions it is necessary to know the nature and extent of gas evolution *during the preparation* of several typical organomagnesium halides. The present paper discusses some results obtained in the preparation of methyl-, ethyl- and n-butylmagnesium halides.

It has long been known that in addition to the formation of RMgX compound in the reaction between RX compound and magnesium in ether, the following side reaction occurs

$$2RX + Mg \longrightarrow R{\cdot}R + MgX_2 \qquad (1)$$

Until recently this side reaction was supposed to increase markedly with the weight of the R-group and its greater branching (particularly with tertiary groups), so that with a hexyl or octyl group the extent of Reaction 1 equaled or exceeded the yield of RMgX compound.[1] Even in the

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[1] Grignard, *Ann. chim. phys.*, [7] 24,433 (1901).

preparation of benzylmagnesium chloride the yield of dibenzyl has equaled 30%;[1] and in the reaction between allyl bromide and magnesium it has long been thought impossible to prepare allylmagnesium bromide because of the quantitative formation of di-allyl.[2] As a consequence, practically all reactions involving "allylmagnesium bromide" have been carried out in accordance with Barbier's original procedure: namely, allyl bromide and the other reactant have been added to magnesium in ether so that the allylmagnesium bromide is brought into reaction simultaneously with its formation.

However, studies in this Laboratory have shown that under suitable conditions excellent yields of Grignard reagents are generally obtainable,[3] and that Reaction 1 takes place to but a minor extent in most cases. In particular it has been possible to prepare *tert.*-butylmagnesium chloride in satisfactory yields (70%),[4] and to prepare allylmagnesium bromide directly and in excellent yields (over 90%).[2] There is little doubt but that the improved methods of Gilman and Zoellner[4] and Gilman and McGlumphy[2] will make it possible to obtain satisfactory yields with other RX compounds where the halogen is very highly active and, therefore, favorable to Reaction 1 at the expense of RMgX compound. Two such RX compounds are benzohydryl chloride, $(C_6H_5)_2CHCl$, and cinnamyl chloride.[5] The most recent[6] reaction between benzohydryl chloride and magnesium gave an extraordinarily large quantity of coupling product (Reaction 1), namely, 95.5% of tetraphenylethane.

The formation of R·R compound as illustrated in Reaction 1 has been variously interpreted. In addition to the usual Wiirtz–Fittig reaction, some have proposed Reaction 2

$$RMgX + RX \longrightarrow R{\cdot}R + MgX_2 \qquad (2)$$

Some splendid studies by Fuson[7] show that under certain conditions the coupling reaction is best interpreted as follows

$$2RX + 2R'MgX \longrightarrow R{\cdot}R + R'{\cdot}R' + 2MgX_2 \qquad (3)$$

In Fuson's articles there is a review of related work by Späth,[8] Gomberg

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[2] Gilman and McGlumphy, Bull. *soc. chim.*, **43** (1928).

[3] Gilman and McCracken, THIS JOURNAL, 45, 2462 (1923); and Rec. trav. *chim.*, 46, 463 (1927). Completed studies by E. A. Zoellner have shown that it is possible to get distinctly superior yields to those reported by Gilman and McCracken. Marvel and coworkers have recently determined the yields of some Grignard reagents prepared in di-*n*-butyl ether (THIS JOURNAL, 50, 2810 (1928)).

[4] Gilman and Zoellner, THIS *JOURNAL*, 50, 425 (1928); also, Puntambeker and Zoellner, "Organic Syntheses," 8, 104 (1928).

[5] Gilman and Harris, *ibid.*, 49, 1825 (1927).

[6] Gilman and Kirby, *ibid.*, 48, 1733 (1926).

[7] Fuson, *ibid.*, **48**, 830, 2681, 2937 (1926).

[8] Spath, *Monatsh.*, 34, 1965 (1913).

and Cone,[9] Schmidlin and Massini,[10] Schmidlin,[11] Gomberg and Kamm,[12] Binaghi and Oddo[13] and Binaghi.[14]

We are inclined to agree with Gomberg and Bachmann[15] that the R·R compound results, at least in part, as a consequence of the initial formation of free radicals.

$$2RX + Mg \longrightarrow 2R- + MgX_2 \qquad (4)$$
$$2R- \longrightarrow R{\cdot}R \qquad (5)$$
$$2R- \longrightarrow R(+H) + R(-H) \qquad (6)$$

The free radicals so formed may then combine with the magnesium halide (MgX) of Gomberg and Bachmann[15] to give the RMgX compound; or with itself to give the R·R compound according to Reaction 5; or it may disproportionate, and if it is an alkyl group the products of such disproportionation would be a saturated and an olefinic hydrocarbon. Admittedly there is no convincing experimental proof as yet for the preliminary formation of such free radicals.[16] We are nevertheless led to such an opinion, first, because of the formation of small quantities of di-*p*-tolyl in the preparation of benzylmagnesium chloride, and, second, because of the disproportionation evidenced by the evolution of saturated and olefinic hydrocarbons, see Reaction 6 in the preparation of alkylmagnesium halides. The formation of free radicals from the Grignard reagent in reactions of it after it has been prepared has been suggested by several.[8,17]

The side reactions leading to the formation of R·R, R(+H) and R(−H) are undoubtedly the chief reactions when the oxygen, carbon dioxide and moisture of the atmosphere are excluded. Some other side reactions that can take place to a minor extent when the Grignard reagent is prepared in an inert atmosphere like nitrogen or hydrogen are due to contaminations of the ether (dissolved oxygen and water, and peroxides[18]) and the

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[9] Gomberg and Cone, Ber., 39,1463 (1906).

[10] Schmidlin and Massini, ibid., 42,2384 (1909).

[11] Schmidlin, *ibid.*, 43, 1141 (1910).

[12] Gomberg and Kamm, THIS JOURNAL, 39,2009 (1917).

[13] Binaghi and Oddo, *Gazz. chim.* ital., [II] 51,330 (1921).

[14] Binaghi, *ibid.*, 53, 879 (1923).

[15] Gomberg and Bachmann, THIS JOURNAL, 49, 236 (1927). A review of related theories of the activation of magnesium for the Grignard reaction is given on pages 255–256 of this reference.

[16] A preliminary report indicating the capture of these free radicals by preparing organomagnesium halides in the presence of (1) olefins, like ethylene, (2) other free radicals like triphenylmethyl and diphenyl nitrogen and (3) hydrogen was read by Gilman, Pothergill. Kirby and McGlumphy at the September. 1928, meeting held at Swampscott.

[17] Bachmann and Clarke, THIS JOURNAL, 49, 2089 (1927); Blicke, *ibid.*, 48, 738 (1926); 49, 2843 (1927); Rheinboldt and Kirberg, J. *prakt.* Chem., 118, *1* (1928); Gilman and Fothergill, THIS JOURNAL, 50, 867 (1928).

[18] Unless the ether is of an extreme degree of purity it contains small amounts of ether peroxide. See Gilman and Wood, THIS JOURNAL, 48,806 (1926), and Gilman and Adams, *ibid.*, **47**, 2816 (1925).

splitting[19] of the ether by the RMgX compound or by MgX_2 and MgX formed as by-products in the preparation of the Grignard reagent. We assume here that the RX compound and magnesium are pure.

The reactions already considered are not the only ones that take place, because minute quantities of hydrogen were detected in some preparations.

Related studies have been made by Jolibois,[20] Job, Reich and Dubien,[21] Chelinzev,[22] Chavanne and DeGraef,[23] Leroide,[24] Bouveault,[25] Madelung and Volker,[26] Grignard,[1] and Gilman and Zoellner.[4]

Experimental Part

The alkylmagnesium halides were prepared in the customary manner, essentially after the general procedure followed by Gilman and McCracken[3] in determining the yields of some typical Grignard reagents. The apparatus used in the experiments with 0.2 and 0.5 mole of reagents consisted of a 150-cc. wide-necked flask having a tight-fitting rubber stopper provided with a small dropping funnel, a 6-inch condenser and a mechanical stirrer with a mercury seal. The condenser outlet was connected, through a drying tube filled with calcium chloride, to a 2-liter eudiometer containing water. A small crystal of iodine was used as a catalyst in each experiment. The preparations were carried out in carefully dried apparatus and after the alkyl halide had been added the solution was refluxed for at least one hour to expel dissolved gases.

The gas evolved was analyzed by standard procedures. Diethyl ether vapor was removed by absorption in water; unsaturated gases were removed by bromine water followed by washing with 30% potassium hydroxide; carbon dioxide by 30% potassium hydroxide; oxygen by alkaline pyrogallate; hydrogen by palladium black at 100°; and the saturated hydrocarbons were analyzed by combustion with oxygen in an explosion pipet. Check analyses were obtained with aliquots from a given experiment. Some inherent errors in such gas analyses were minimized by uniformity of procedure and by corrections for dissolved gases. The quantities of gas obtained in the several runs were too small to permit of careful fractionation by the use of liquid air. In a few cases the volume of hydrogen measured was close to the experimental error. However, from Table I it is evident that the volume of hydrogen in other cases is unquestionably beyond any experimental error. The total gas collected was the volume obtained after the removal of ether and includes the air displaced by the gas. In order to have a basis for comparison with earlier studies, all yields are expressed as percentages of alkyl halide used.

Two Mole Experiments. **(a)** Methyl Iodide.—This large run was carried out in a

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[19] Such splitting of diethyl ether takes place, if at all, to a negligible extent under ordinary conditions. However, methylmagnesium iodide will split di-n-butyl ether to an appreciable extent if, during its preparation, the solution is allowed to become too warm.

[20] Jolibois, *Compt. rend.*, 155,213 (1912); 156,712 (1913).

[21] Job, Reich and Dubien, *Bull. soc. chim.*, 37, 976 (1925).

[22] Chelinzev, *J. Russ. Phys.-Chem. Soc.*, 36, 549 (1904); *J. Chem. Soc.*, *86*, 641 (1904).

[23] Chavanne and DeGraef, *Bull. soc. chim. Belg.*, 33,366 (1924).

[24] Leroide, Ann. *chim.*, 16, 354 (1921).

[25] Bouveault, *Compt. rend.*, 138,1108 (1904).

[26] Madelung and Volker, *J. prakt. Chem.*, **115,** 24 (1927).

500-cc. three-necked flask in order positively to identify the olefin by the preparation of a derivative. The dilute solution of bromine in carbon tetrachloride that was used to absorb the olefin was carefully fractionated and the ethylene bromide was characterized

TABLE I

GASES OBTAINED IN THE PREPARATION OF SOME ALKYLMAGNESIUM HALIDES

Alkyl halide	Moles	Olefin	Yield, %	Hydrogen %	Saturated Hydrocarbons R·H	Yield, %	R·R	Yield, %
CH_3I	0.25	Ethylene	0.43		Methane	2.35	Ethane	1.34
CH_3I[a]	.5	Ethylene	.69	0.0324	Methane	1.82	Ethane	1.87
CH_3I[b]	.2	Ethylene	4.76[b]	.0	Methane	4.84	Ethane	1.16
CH_3I[c]	.2	Ethylene	0.14	.0104	Methane	2.12	Ethane	0.24
C_2H_5Br	.2	Ethylene	.12	...	Ethane	1.53	Butane	.577
C_2H_5Br	.2	Ethylene	.118	...	Ethane	1.46	Butane	.497
C_2H_5Br[d]	.2	Ethylene	.116[d]	.0112	Ethane	0.753	Butane	.0
n-C_4H_9Br[e]	.5	a-Butylene	.823	.0	Butane	1.505	.....	...
n-C_4H_9Br[e]	.2	α-Butylene	.308	.0	Butane	1.16	.....	...

[a] The methyl iodide was added rapidly in this experiment in order to increase the volume of evolved gas. However, the addition was so rapid that part of the methyl iodide was vaporized and collected in the eudiometer; 42% of unused magnesium was recovered. The total volume of gas collected was 535.1 cc., of which 7.24% was ethylene, 0.34% hydrogen, 36 5% methane and 18 93% ethane. The yields given in the table are based on the total quantity of methyl iodide used.

[b] In this experiment 130 cc. of di-n-butyl ether was used as the solvent and after the addition of halide over a thirty-minute period, the mixture was refluxed for one hour. The total gas collected was 561 cc., of which 19.03% was unsaturated, 38.7% was methane and 4.64% was ethane. The high yield of unsaturated gas is probably due to a splitting reaction of the butyl ether by methylmagnesium iodide. This finds confirmation in other studies on the Zerewitinoff analysis, where it has been shown that gases are evolved when the methylmagnesium iodide solution in butyl ether is heated to 140–150°. Ethylmagnesium bromide is stable at 175° in boiling cymene.

[c] In this experiment, 130 cc. of di-n-butyl ether was again used as the solvent. However, the reaction flask was cooled below 70° during the addition of methyl iodide and when all of the iodide had been added the reaction mixture was stirred at 70° for two hours. The total gas evolved was 269.1 cc. and the percentage of hydrogen determined in this case was too near the experimental error to warrant its serious consideration as one of the evolved gases.

[d] One hundred and thirty cc. of di-n-butyl ether was used as the solvent in this experiment and after adding the ethyl bromide the mixture was stirred and heated at 70° for 2.25 hours.

[e] In the analysis of the saturated hydrocarbons in the two *n*-butylmagnesium bromide experiments, the contraction after explosion of a sample was always slightly greater than that calculated for the quantity of butane present as based on the volume of carbon dioxide formed. This corresponds with values obtained by Fuson[7] in the analysis of ethane by the same method. If free radicals are formed (see Discussion of Results) then according to Taylor [*Proc.* Am. Phil. *Soc.*, 65, 90 (1926)] and Bates and Taylor [THIS JOURNAL, 49, 2439 (1927)] such free radicals may under some conditions add to the ethylenic compounds (see Ref. 16) to give hydrocarbons of higher molecular weight. It is apparent that such mixtures of higher hydrocarbons would affect the gas analysis. If disproportionation is the true explanation for the formation of R(+H) and R(— H) compounds, then the excess of R(+H) compound is to be expected in view of traces of moisture and ether peroxide[18] in the already carefully prepared ether.

by the formation of ethylene di-*p*-tolylsulfone prepared from sodium *p*-toluenesulfinate. A mixed melting-point determination with an authentic specimen showed no depresssion. Only a part of the gas evolved was collected and it had the following composition: **31.0%** methane, **12.1%** ethane, **0.417%** ethylene and **0.326%** hydrogen.

(b) *n*-Butyl Bromide.—The gases evolved in a 2-mole run were first passed into a dilute solution of bromine in carbon tetrachloride and almost all dissolved in this solution. From this solution there was obtained **1640** cc. of gas of which 65.13% was butane and **4.0** g. of α-butylene bromide, which agreed in b. p., density and refractive index with the compound reported in the literature.

Gases Evolved on the Hydrolysis of Methylmagnesium Iodide

The analysis of **409.6** cc. of gas evolved from the dil. sulfuric acid hydrolysis of an ether solution of methylmagnesium iodide showed 77.8% methane, **0.515%** ethylene and a negligible quantity (0.095%) of hydrogen. The analysis of **393.9** cc. of gas evolved from the hydrolysis of methylmagnesium iodide prepared in di-n-butyl ether showed **69.3%** methane, 2.6% ethylene and 0.285% hydrogen. The higher percentages of ethylene and hydrogen in the experiment where di-n-butyl ether was used as a solvent are probably due, in part, to the collection of the gases over water which had previously been saturated with ethylene and hydrogen. In the diethyl ether experiment, the gas was collected over fresh water.

The gas explosion values of the saturated hydrocarbons obtained in these two experiments did not entirely agree for methane. The combustions gave a greater contraction than that required for the methane present as based on the volume of carbon dioxide formed.

Discussion of Results

Entirely apart from the future consideration of the evolved gases on the possibility of the initial formation of free radicals and their disproportionation,[16] the results have a direct bearing on some problems concerned with the Grignard reagent. First, the extent of gas evolution accounts, in part, for the 90% and greater yields of most RMgX compounds.[2,3,27] Second, one of the five methods investigated by Gilman, Wilkinson, Fishel and Meyers[28] for the quantitative estimation of Grignard reagents was a gas analysis based on the following reaction

$$\text{RMgX} + \text{HOH} \longrightarrow \text{RH} + \text{Mg(OH)X} \qquad (7)$$

Ob iously, in any determinations carried out without refluxing the solution to expel dissolved gases before hydrolysis, the results of the gas analysis would be too high. Also, the gases evolved on hydrolysis (see Experimental Part) show that Reaction 1 is not the only one that takes place.

Third, the Zerewitinoff[29] method for the estimation of active hydrogen

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[27] Gilman and Meyers, THIS JOURNAL, **45,159 (1923).**

[28] Gilman, Wilkinson, Fishel and Meyers, *ibid.*, **45,150 (1923);** Gilman and Meyers, Rec. trav. chim., **45, 314 (1926);** Job and Reich, *Bull. soc. chim.*, **33, 1414 (1923);** Job, Reich and Dubien, *ibid.*, **37,976 (1925).**

[29] In one of the most recent studies on this method, Kohler, Stone and Fuson [THIS JOURNAL, **49,** 3181 (1927)] have described an ingenious, workable and accurate method for determining simultaneously the amount of gas evolved and the amount of reagent consumed in reactions of methylmagnesium iodide.

is affected not only by the gases evolved during the preparation of the Grignard reagent but also by the gases evolved when a compound having an active hydrogen is treated with an RMgX compound. The danger of dissolved gases formed during the preparation of the Grignard reagent in solutions like amyl and butyl ether is slight if the customary procedure of heating to remove excess methyl iodide is followed, but active hydrogen determinations with diethyl ether as a solvent may introduce larger errors because of the low boiling point of this ether.[30] The gas measured in a Zerewitinoff analysis where methylmagnesium iodide, for example, is used may not be pure methane, for if the disproportionation of free radicals should be the true explanation for the formation of olefins on hydrolysis of RMgX compounds, then it is reasonable to assume that free radicals are formed transitorily in all decompositions with active hydrogen compounds.

Fourth, the mixture of gases obtained on the hydrolysis of Grignard reagents shows that this reaction cannot be used directly for the preparation of pure hydrocarbons and related derivatives. This, however, is not peculiar to this method for it is quite probable that no method of preparation of hydrocarbons will give pure compounds without some subsequent rectification. With the Grignard reaction, the extent of such impurities is not large.

Fifth, many reactions involving reduction by the Grignard reagent are accompanied by the evolution of olefins. Allowances should be made, therefore, for any olefins formed during the preparation of RMgX compounds or as a result of subsequent treatment with active hydrogen compounds.

The evolution of ethylene and hydrogen in the preparation of methylmagnesium iodide indicates that the methyl radical undergoes secondary reactions in a manner contrary to the predictions of some. Of course, it is possible that these gases may owe their formation to other reactions like that involving the direct removal of hydrogen iodide.

$$2CH_3I + 2Mg \longrightarrow CH_2{=}CH_2 + 2MgHI \qquad (8)$$

If this were the case, and if no disproportionation took place, one would expect equal volumes of ethylene and hydrogen. The nearest approach to this in the results so far obtained is in the 2-mole run with methylmagnesium iodide where the percentage of ethylene was 0.417, and that of hydrogen, 0.326. The hydrogen evolved on hydrolysis may be due to a reaction between magnesious bromide and water.

Both the nature of the gases and the extent of their formation appear to vary with the solvent.

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[30] References to this method are contained in an article by **Gilman** and **Fothergiil,** THIS JOURNAL, 49,2815 (1927).

Summary

A study has been made of the gases formed during the preparation and in the hydrolysis of some alkylmagnesium halides. From the nature of these gases it appears that the free radicals that are probably formed prior to the formation of organomagnesium halides undergo disproportionation and coupling to varying degrees.

AMES, IOWA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

THE SYNTHESIS OF MESOXALATES BY INTERACTION OF NITROGEN TETROXIDE WITH ESTERS OF MALONIC ACID[1]

BY ELIZABETH GILMAN[2] AND TREAT B. JOHNSON

RECEIVED JULY 24, 1928 PUBLISHED DECEMBER 10, 1928

Only a few examples of organic compounds are known in which two hydroxyl groups appear to exist in stable union with a single carbon atom. What influence such linkages have on physiological activity is not well understood. Although the physiological action of chloral hydrate is not definitely linked with the property of hydrate formation, and while the effect of this drug is regarded as due to the organic radical containing chlorine, yet the prevalence of activity among hydrated constructions of the type which we are investigating (alloxan, for example) leads the writers to suppose that mesoxalates may be of pharmacological interest. As far as we have been able to ascertain, mesoxalates have never been investigated physiologically. They are admirably suited to intravenous injection. The diethyl ester is soluble in its own weight of water and it has been our experience that even the esters of higher molecular weight are surprisingly soluble in water. Diethyl mesoxalate is also a valuable reagent for synthetic work and any method that can be devised for preparing it more easily and cheaply will undoubtedly find important applications.

Bouveault and Wahl,[3] in 1903, provided the basis for the present method of preparing mesoxalates when they succeeded in obtaining diethyl mesoxalate from diethyl isonitrosomalonate by the action of oxides of nitrogen generated from sodium nitrate and nitrosyl-sulfuric acid. The principal oxide generated in this manner is nitrogen tetroxide (N_2O_4). They made their isonitrosomalonate from diethyl malonate in alcoholic sodium ethylate solution by interaction with methyl nitrite. Treatment with an ex-

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[1] Constructed from a dissertation presented by Elizabeth Gilman in June, 1927, to the Faculty of the Graduate School of Yale University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Holder of the Alice Freeman Palmer Fellowship of Wellesley College in 1926–27.

[3] Bouveault and Wahl, Compt. rend., 137,196 (1903).

cess of nitrogen tetroxide at 0° then led to the formation of the mesoxalates, as expressed by the following equation

$$2ON\cdot CH(COOC_2H_5)_2 + N_2O_4 \longrightarrow OC(COOC_2H_5)_2 + O_2NCH(COOC_2H_5)_2$$

These same investigators later prepared ethyl diketobutyrate from ethyl acetoacetate by action of nitrous oxide (N_2O_3) in acetic anhydride solution and mention the fact that either N_2O_3 or N_2O_4 will give the desired ketone.[4] Schmidt[5] applied this latter procedure for the preparation of diethyl mesoxalate, and later Curtiss[6] utilized the Schmidt reaction, using no solvent, and reported a yield of 95% of the theoretical. Several investigators who have followed the directions of Curtiss for the preparation of diethyl mesoxalate have not been able to obtain the yield reported by him.[7] The latest work on this preparation is that of Dox,[8] who followed the Curtiss procedure with the exception that his nitrous oxide was dried over calcium chloride before being brought into reaction with diethyl malonate. He quotes yields of diethyl mesoxalate corresponding to 74–75% of the theoretical.

We are now able to report new data contributing to our knowledge of the methods applicable for the synthesis of mesoxalates. In the study of the reactivity of nitrogen tetroxide toward organic combinations, now in progress in this Laboratory,[9] we have investigated the action of this oxide on diethyl malonate and find that the reaction can be so well controlled as to be productive of a nearly quantitative yield of the mesoxalate. A detailed account of the technique of our modified method of preparation is given in the Experimental Part of this paper. Empirically this reaction may be represented as below, but it was our experience that an excess of the oxide is necessary in order to obtain a maximum yield of the mesoxalate.

$$N_2O_4 + CH_2(COOC_2H_5)_2 \longrightarrow OC(COOC_2H_5)_2 + H_2O + 2NO$$

In order to ascertain whether the reaction between nitrogen tetroxide and diethyl malonate is a general one and applicable to other esters of malonic acid we selected the following three representatives for further research: di-β-chloro-ethyl malonate, di-β-bromo-ethyl malonate and di-β-diethylamino-ethyl malonate. Of these only the chlorine compound has hitherto been described in the literature, and indeed our knowledge of any malonic ester derivatives of this type is very limited.

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[4] Bouveault and Wahl, *Compt. rend.*, 138, 1221 (1904).

[5] Schmidt, *ibid.*, 140, 1400 (1905).

[6] Curtiss, *Am. Chem. J.*, 35, 477 (1906); THIS JOURNAL, 33, 962 (1911).

[7] A. Meyer, *Bull. soc. chim.*, [4] 9, 423 (1911); Lemaire, *Rec. trav. chim.*, 29, 22 (1910).

[8] Dox, "Organic Syntheses," John Wiley and Sons, New York City, 4, 27 (1925).

[9] In the development of a new synthetical method for the preparation of alkaloids of the ephedrine type, we have made a new application of the reactivity of N_2O_4 in preparing one of our intermediate products utilized in the process. This work will be described in a future publication (T. B. J.).

Theoretically these ester combinations would yield three new esters of mesoxalic acid of immediate pharmacological interest if found reactive toward nitrogen tetroxide in the same manner as diethyl malonate. This is particularly true of the amino ester $(C_2H_5)_2NCH_2CH_2OOCCH_2COOCH_2CH_2N(C_2H_5)_2$ and the corresponding mesoxalate, both of which contain part of the molecular structure functioning in the well-known local anesthetic, novocaine. In consequence of this structural relationship aliphatic combinations of this type should possess intrinsic interest pharmacologically.

When subjected to the action of nitrogen tetroxide these three malonic esters presented individual problems. Di-β-chloro-ethyl malonate behaved almost exactly like diethyl malonate and gave consistently a 90% yield of the corresponding mesoxalate. Di-β-bromo-ethyl malonate was more sluggish in its reactivity toward nitrogen tetroxide. This ester was likewise more unstable and could not be heated to its boiling point at atmospheric pressure without decomposition. Conditions were found, however, under which good yields of di-β-bromo-ethyl mesoxalate could be obtained. Di-p-diethylamino-ethyl malonate presented many difficulties when treated with nitrogen tetroxide, behaving individually when allowed to interact with the oxide, and thus far we have not succeeded in isolating the corresponding pure mesoxalate. The free ester and the hydrochloride react with the oxide giving unstable oils which cannot be purified by distillation. The free base decolorizes three equivalents of nitrogen tetroxide while the hydrochloride reacts with only one, so that the amino groups apparently do not interact when protected by hydrochloric acid. It seems probable that the insoluble and unstable oil obtained in the case of the hydrochloride represents an intermediate formed by interaction of nitrogen tetroxide with the methylene carbon atom.

Pharmacological Report

Pharmacological experiments of a preliminary nature have thus far been carried out on three of these compounds by Professor Henry G. Barbour of the University of Louisville, Louisville, Kentucky, and the effects thus far reported to us are recorded below.

Diethyl Mesoxalate.—This ester has no hypnotic action but shows marked stimulative effects on respiration and blood pressure which last about thirty and ten minutes, respectively, and can be repeated. It can be injected intravenously into dogs and the fatal dose for mice is 0.3 g. per kilo.

Di-β-chloro-ethyl Mesoxalate.—The same tendency to produce sympathetic stimulation of the circulation is shown by this chlorine derivative accompanied by other effects suggestive of choline or eserine, that is, salivation and tremors. It is far more toxic than the diethyl mesoxalate, and increases the percentage of blood sugar.

Di-β-diethylamino-ethyl Malonate.—This ester is especially interesting. It is much less toxic than the two preceding esters and has a very definite, long-continued effect on the total metabolism which is stimulating. Both heat and blood sugar outputs are very noticeably increased for quite an extended period of time. It has little effect on blood pressure and respiration and does not show marked anesthetic properties.

The series of compounds under investigation is unusually interesting from a physiological standpoint, and offers many possibilities for future research. The effects thus far recorded were entirely unexpected, but are exceedingly interesting and somewhat extraordinary.

Experimental Part

Preparation of Diethyl Mesoxalate by the Action of Nitrogen Tetroxide on Diethyl Malonate.—Nitrogen tetroxide was supplied for our research in a large bomb, and an all-glass apparatus was constructed for drying the gas over phosphorus pentoxide, condensing it at 0°, and weighing the condensate. No attempt was made to purify the gas from traces of nitrogen trioxide since either oxide produces the desired reaction. Units of about 25 g. of purified diethyl malonate were used for most of the experiments, cooled to 0°, and the calculated quantitities of nitrogen tetroxide added in the liquid state. All reagents were protected from moisture during the time of reaction. The yield was calculated in percentage of the theoretical weight of the crystalline hydrate of diethyl mesoxalate obtained, in accordance with the equation $N_2O_4 + CH_2(COOC_2H_5)_2 = 2NO + H_2O + CO(COOC_2H_5)_2$.

The reaction between nitrogen tetroxide and diethyl malonate was found to proceed slowly at low temperatures. Temperatures above the boiling point of nitrogen tetroxide did not prove beneficial, since much of the oxide was lost by evaporation, and a smaller amount of nitrogen tetroxide, if allowed to interact a longer time at low temperatures, accomplished quite as complete a reaction. Slightly more than the theoretical quantity of nitrogen tetroxide required by the above equation was found desirable, but no more than a quantity equal in weight to that of the malonic ester was used.

In applying reactions with nitrogen tetroxide, ether, acetic anhydride, and carbon tetrachloride were incorporated as solvents but the best results were obtained when the last solvent was used. It was found, however, that this was unnecessary and all solvents were finally abandoned except for the purpose of rinsing, when carbon tetrachloride was employed.

In one experiment phosphorus pentoxide was introduced into the reaction mixture in the hope that the presence of this dehydrating agent would facilitate the desired reaction. A most surprising result was obtained in the quantitative recovery of unaltered malonic ester. This result led us to search for an alkaline catalyst which could be introduced without producing side reactions, and metallic sodium was found to serve this purpose. A small piece of sodium introduced into a mixture of anhydrous malonic ester and liquid nitrogen tetroxide at 0° appeared to undergo no reaction, and when withdrawn at the end of three hours had suffered practically no loss in weight. At the end of the reaction period, the precaution was taken of pouring the reaction mixture upon phosphorus pentoxide in order to insure removal of any trace of alkali. The use of sodium was found to increase the yield of mesoxalate quite appreciably and our adopted procedure for preparing the mesoxalate was as follows.

Twenty-five grams of diethyl malonate was mixed with an equal weight of liquid nitrogen tetroxide at $-5°$ and a freshly cut piece of sodium weighing one gram was introduced. The mixture was maintained at $-5°$ for three hours with frequent shaking and protecting, as usual, from moisture by a calcium chloride tube. The sodium, apparently, did not enter into reaction and when removed at the end of three hours still weighed one gram. The reaction mixture was allowed to stand for two days at room temperature and was then poured into a flask containing phosphorus pentoxide and heated gently to the boiling point of the carbon tetrachloride which had been added as rinsings. It was then decanted into a Claisen flask, the pentoxide residue well rinsed with carbon tetrachloride and the rinsings added to the main lot. Heat was applied at ordinary pressure, when the decomposition of the oil took place in steps. The main distillate boiled almost entirely between 103 and 105° at 19 mm. representing 85% of the theoretical amount of anhydrous mesoxalate expected. The calculated amount of water converted it quantitatively into its crystalline hydrate. The residue in the distilling flask contained crystals of the hydrated mesoxalate and no indication of any other reaction product was observed. The hydrate when recrystallized from chloroform melted at 57". The total yield, including the mesoxalate isolated from both residue and water distillate, was 90% of the theoretical.

The nature of the gas evolved in the above reaction was also studied. During the first two hours of reaction at 30° all of the gas evolved was collected over a 10% solution of alkali, all the air in the system having been previously displaced by carbon dioxide. No brown color developed as usual over the solution and 600 cc. of a colorless gas was collected which was very soluble in ferrous sulfate solution and produced brown fumes when exposed to air. Thus, during the first stages of the reaction, the principal gas evolved was nitric oxide.

Preparation of Some Substituted Ethyl Malonates

Di-β-chloro-ethyl Malonate, $CH_2(COOCH_2CH_2Cl)_2$.—This ester has been prepared according to another method by George Bennett,[10] and its boiling point is given as 164° at 15 mm. We prepared it by esterifying malonic acid with ethylene chlorohydrin, using hydrogen chloride as a catalyst. Two hundred grams of ethylene chlorohydrin was added to 50 g. of diethyl malonate and 50 g. of sodium sulfate (anhydrous). Dry hydrogen chloride was passed into the suspension to saturation and the

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[10] G. M. Bennett, *J. Chem. Soc.,* **127**, 1277 (1925).

mixture heated at 60° for three hours. It was then cooled, filtered, and excess of hydrochloric acid and ethylene chlorohydrin removed by heating under diminished pressure. The heavy oil remaining behind was washed with sodium bicarbonate solution until neutral and finally with pure water. After drying over anhydrous sodium sulfate it was distilled at 24 mm. and 90 g. of a colorless oil boiling at 178–182° was obtained. This represented a yield of **82%** of the theoretical. On redistillation the oil had a boiling point of 143–144° at 4 mm. The ester is a heavy oil, insoluble in water and soluble in the ordinary organic solvents.

Anal. Calcd. for $C_7H_{10}O_4Cl_2$: Cl, 30.96. Found: Cl, 30.90.

Di-p-bromo-ethyl Malonate, $CH_2(COOCH_2CH_2Br)_2$.—This ester was prepared in a manner exactly analogous to the procedure used for the di-β-chloro ester, using ethylene bromohydrin and malonic acid. The yield of crude di-β-bromo-ethyl malonate was 84% of the theoretical, but it was found to contain considerable quantities of ethylene bromohydrin, which is insoluble in water and cannot be removed by washing with water as in the case of the chloro ester. The pure ester was obtained by fractional distillation as a heavy, colorless oil boiling at 153° at 1 mm. It decomposes if low pressures are not employed in its distillation and tends to turn dark on standing for long periods. It is soluble in all organic solvents, especially carbon tetrachloride and chloroform, and is very insoluble in water.

Anal. Calcd. for $C_7H_{10}O_4Br_2$: Br, 50.28. Found: Br, 49.7.

Di-p-diethylamino-ethyl Malonate, $CH_2(COOCH_2CH_2N(C_2H_5)_2)_2$.—We first attempted to prepare this ester by the action of diethylamine on di-β-chloro-ethyl malonate. Experiments were conducted at atmospheric pressure under a reflux, in bomb tubes at 110°, and also at room temperature under pressure, but in all cases the reaction was incomplete and none of the desired ester was obtained.

The procedure applied successfully for the preparation of this ester was the reaction of malonyl chloride on diethylamino-ethyl alcohol, and we operated as follows.

Forty-eight grams of β-diethylamino-ethyl alcohol was dissolved in 500 cc. of dry chloroform and hydrogen chloride gas passed into the solution until it was just acid to methyl red. After cooling, 28 g. of malonyl chloride dissolved in an equal volume of chloroform was added slowly through a dropping funnel. The reaction mixture was refluxed for three hours. Dry potassium carbonate was then added to the boiling mixture until it showed a neutral reaction, when it was filtered. The excess of chloroform was distilled off and on cooling the solution became solid with crystalline material. Purification was accomplished by trituration with acetone, when 55 g. of the reaction product was obtained, melting between 120 and 140° with decomposition. Two recrystallizations from absolute alcohol and acetone yielded 25 g. of a pink powder melting at 152–154° with decomposition. This was identified as the hydrochloride of the desired ester.

The free base, $CH_2(COOCH_2CH_2N(C_2H_5)_2)_2$, was prepared from its hydrochloride by digesting the salt in anhydrous chloroform with dry sodium bicarbonate and sodium sulfate. Ten grams of di-0-diethylamino-ethyl malonate dihydrochloride (m. p. 153–154°) was dissolved in chloroform, an excess of sodium bicarbonate and sodium sulfate added and the mixture refluxed for ten to fifteen minutes. After standing for two days, it was filtered and the chloroform distilled off, giving an orange oil with a pungent odor. This was dissolved in anhydrous ether, filtered to free it from traces of hydrochloride and the oil distilled under diminished pressure. The product distilled at 163° (4.5 mm.). and yielded quantitatively the original hydrochloride when treated with hydrogen chloride gas. The ester is soluble in all common organic solvents and also appears to be completely soluble in water, producing a strongly basic solution.

The dihydrochloride of di-β-diethylamino-ethyl malonate is a colorless powder soluble in alcohol and chloroform, insoluble in ether, and very difficultly soluble in acetone. It deposits in opaque clusters from absolute alcohol and will dissolve in its own weight of this solvent at the boiling point. It is extremely soluble in water, producing a neutral solution, and the amino ester cannot be recovered from water by adding alkali and extracting the free base without considerable hydrolysis. It takes up water whenever exposed to moist air for any considerable length of time. When pure it melts at 154° with decomposition.

Anal. Calcd. for $C_{15}H_{32}O_4N_2Cl_2$: Cl, 18.9; N, 7.47. Found: Cl, 18.93; N, 7.72.

Action of Nitrogen Tetroxide on the above Malonates

Preparation of **Di-β-chloro-ethyl** Mesoxalate, $CO(COOCH_2CH_2Cl)_2$.—Thirty grams of di-β-chloro-ethyl malonate was mixed with 44 g. of liquid nitrogen tetroxide at −5° and a small piece of sodium added. After removing the sodium at the end of three hours, the mixture was allowed to stand for two to three days at room temperature and was then poured upon phosphorus pentoxide, heated at atmospheric pressure and finally distilled. Twenty-nine grams of a yellow oil boiling at 155–160° (6 mm.) was obtained, representing a yield of 90%. After redistillation this gave a fraction boiling at 148° at 3 mm. The ester is a greenish-yellow oil with a pungent odor similar to that of anhydrous diethyl mesoxalate. It is soluble in the common organic solvents and combines with a molecular equivalent of water with evolution of heat and almost complete decolorization. The hydrate formed is an oil and could not be induced to crystallize even when cooled to 25'. Further addition of water is accompanied by a yellow color which disappears again as the dilution is increased. The ester is apparently soluble in water in all proportions.

Anal. Calcd. for $C_7H_8O_5Cl_2$: Cl, 29.18. Found: Cl, 29.07.

Preparation of **Di-β-bromo-ethyl** Mesoxalate, $CO(COOCH_2CH_2Br)_2$.—Eight grams of di-β-bromo-ethyl malonate was mixed with 10 g. of liquid nitrogen tetroxide and a piece of metallic sodium added at −5°. The sodium was allowed to remain in the solution for twelve hours at 0° and then removed. After standing for two days at room temperature, the reaction mixture was dissolved in chloroform, phosphorus pentoxide added, and excess nitrogen tetroxide boiled off. The yellow solution was then heated to remove chloroform, whereupon decomposition set in with evolution of oxides of nitrogen. As soon as the oil assumed a yellow color, heating was discontinued and the product distilled at 1 mm. pressure. We obtained 6 g. of a yellow oil boiling at 158–159". This ester interacted with water with evolution of heat and almost complete decolorization but did not crystallize on cooling to 0°. It is soluble in an excess of water. On redistillation after removing water with phosphorus pentoxide, the anhydrous oil had a boiling point of 155° at 0.8 mm.

Anal. Calcd. for $C_7H_8O_5Br_2$: Br, 48.17. Found: Br, 48.16.

Action of Nitrogen Tetroxide on **Di-β-diethylamino-ethyl Malonate.**—The reaction between nitrogen tetroxide and the above ester proved to be explosively violent. Liquid nitrogen tetroxide could not be introduced and gaseous nitrogen tetroxide could be passed in only slowly at low temperatures. Three equivalents of nitrogen tetroxide were completely decolorized before any green color was imparted to the solution and an orange oil insoluble in carbon tetrachloride collected on the surface of the solution. The dihydrochloride of the malonic ester in question produced a much less vigorous reaction with nitrogen tetroxide and only one equivalent was decolorized, but an insoluble orange oil collected as before on the surface. None of the desired mesoxalate was isolated from either reaction. The reaction product decomposed violently upon gentle heating. A great many factors combine to make this preparation difficult; the amino malonic ester employed is peculiarly sensitive to hydrolysis, the alkyl amino groups are apparently attacked in anhydrous solution by nitrogen tetroxide, the avidity of the methylene carbon atom for nitrogen tetroxide is apparently increased and no satisfactory method of decomposing the intermediate to yield mesoxalate has thus far been discovered.

Summary

1. An improved method for preparing diethyl mesoxalate has been described. It involves the action of nitrogen tetroxide on diethyl malonate.

2. Two new mesoxalates prepared by application of this nitrogen tetroxide reaction are: di-β-chloro-ethyl mesoxalate and di-β-bromo-ethyl mesoxalate.

3. Di-0-diethylamino-ethyl malonate has been prepared for the first time.

4. The pharmacology of these new ester combinations is being investigated.

NEW HAVEN, CONNECTICUT

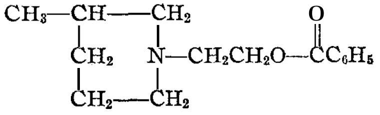
[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

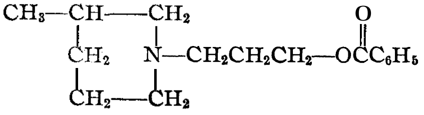
PIPERIDINE DERIVATIVES. VI. 3-METHYLPIPERIDINO-ALKYL BENZOATES[1]

BY J. R. THAYER AND S. M. McELVAIN

RECEIVED AUGUST 3, 1928 PUBLISHED DECEMBER 10, 1928

In a previous communication[2] a number of substituted and unsubstituted piperidino-alkyl benzoates were described together with a brief report on their pharmacological behavior. Of these compounds it was noted that those containing an alkyl group substituted in the piperidine nucleus possessed the greatest local anesthetic efficiency. It seemed, therefore, advisable to ascertain the effect of variations in the alkylene group on the pharmacological properties of the type of compound represented by 3-methylpiperidino-ethyl and propyl benzoates (I and II).


I


II

In the previous work it was found that the number of carbon atoms in the alkylene group that joins the nitrogen to the oxygen was quite important. In I where there are two carbon atoms in this alkylene group,

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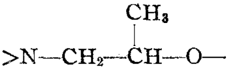
[1] This paper is an abstract of a portion of the thesis submitted by J. R. Thayer to the Graduate School of the University of Wisconsin in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry.

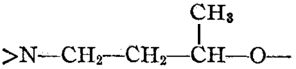
[2] McElvain, THIS JOURNAL, 49,2835 (1927).

the compound was found to have no local anesthetic action on mucous membranes, while in II the presence of the third carbon atom caused the compound to show appreciable anesthetic action on mucous membranes.[3] The work reported in this paper is concerned with the preparation and attempted preparation of a number of 3-methylpiperidino-alkyl benzoates in which the alkylene group between the nitrogen and the oxygen (Types I and II) contains one or more substituent methyl groups.

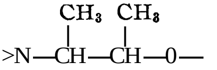
The structures which were considered and whose syntheses were attempted may be represented as follows



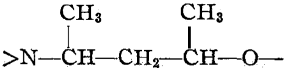
$$>\mathrm{N-CH_2-}\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{C}}}\mathrm{H-O-}\quad\text{(III)}$$



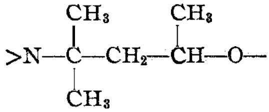
$$>\mathrm{N-CH_2-CH_2-}\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{C}}}\mathrm{H-O-}\quad\text{(IV)}$$



$$>\mathrm{N-}\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{C}}}\mathrm{H-}\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{C}}}\mathrm{H-O-}\quad\text{(V)}$$

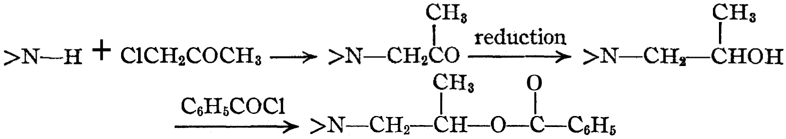


$$>\mathrm{N-}\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{C}}}\mathrm{H-CH_2-}\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{C}}}\mathrm{H-O-}\quad\text{(VI)}$$



$$>\mathrm{N-}\underset{\mathrm{CH_3}}{\underset{|}{\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{C}}}}}\mathrm{-CH_2-}\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{C}}}\mathrm{H-O-}\quad\text{(VII)}$$

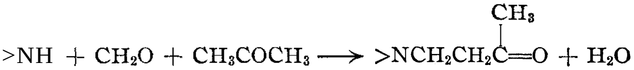
Of the above types only III and IV were successfully synthesized. The former (III) was prepared by a series of reactions which may be indicated thus (>NH in all succeeding formulas = 3-methylpiperidine)



$$>\mathrm{N-H} + \mathrm{ClCH_2COCH_3} \longrightarrow\ >\mathrm{N-CH_2}\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{C}}}\mathrm{O} \xrightarrow{\text{reduction}}\ >\mathrm{N-CH_2-}\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{C}}}\mathrm{HOH}$$

$$\xrightarrow{\mathrm{C_6H_5COCl}}\ >\mathrm{N-CH_2-}\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{C}}}\mathrm{H-O-}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{-C_6H_5}$$

The desired structure (IV) was prepared by a method which has been developed by Mannich and his coworkers[4] for the synthesis of 1,3-keto bases. This synthesis involves a reaction between a secondary amine, paraformaldehyde and acetone. Using 3-methylpiperidine as the secondary amine, this reaction may be indicated as follows



$$>\mathrm{NH} + \mathrm{CH_2O} + \mathrm{CH_3COCH_3} \longrightarrow\ >\mathrm{NCH_2CH_2}\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{C}}}\mathrm{=O} + \mathrm{H_2O}$$

The catalytic reduction of this keto amine yielded the corresponding alcohol, which was converted into Structure IV by benzoylation with benzoyl chloride.

The preparation of V and VI was attempted by condensing α,β-dimethyl-β-bromo-ethyl benzoate and α,γ-dimethyl-γ-chloropropyl benzoate with 3-methylpiperidine just as I and II were prepared by the condensation of chloro-ethyl and chloropropyl benzoates with the secondary amine. The α,β-dimethyl-β-bromo-ethyl benzoate was prepared by the action

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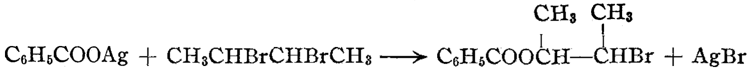
[3] Ref. 2, p. 2839.

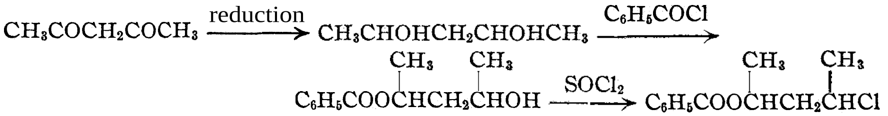
[4] Mannich and others, Arch. *Pharm.*, 255,261 (1917); 265,589 (1927).

of 2,3-dibromobutane on silver benzoate, thus



$$\mathrm{C_6H_5COOAg + CH_3CHBrCHBrCH_3 \longrightarrow C_6H_5COO\overset{\overset{CH_3}{|}}{C}H—\overset{\overset{CH_3}{|}}{C}HBr + AgBr}$$

α,γ-dimethyl-γ-chloropropyl benzoate was prepared from acetylacetone by the following reactions

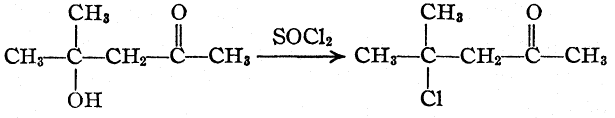


$$\mathrm{CH_3COCH_2COCH_3 \xrightarrow{\text{reduction}} CH_3CHOHCH_2CHOHCH_3 \xrightarrow{C_6H_5COCl}}$$

$$\mathrm{C_6H_5COO\overset{\overset{CH_3}{|}}{C}HCH_2\overset{\overset{CH_3}{|}}{C}HOH \xrightarrow{SOCl_2} C_6H_5COO\overset{\overset{CH_3}{|}}{C}HCH_2\overset{\overset{CH_3}{|}}{C}HCl}$$

In the preparation of I and II it was found that one mole of β-chloroethyl benzoate or γ-chloropropyl benzoate reacted smoothly in twenty to thirty minutes at 100° with 2 moles of 3-methylpiperidine to give one mole of the tertiary amine (3-methylpiperidino-ethyl (or propyl) benzoate) and one mole of 3-methylpiperidine hydrochloride. In the case of α,β-dimethyl-β-bromo-ethyl benzoate and α,γ-dimethyl-γ-chloropropyl benzoate, no such reaction was found to take place. Under the conditions (thirty minutes at 100°) which caused complete reaction when the halogen was attached to a primary carbon atom, practically no reaction was obtained with the compounds having the halogen attached to a secondary carbon atom. The extent of reaction was judged in all cases by the amount of 3-methylpiperidine hydrochloride that was precipitated when the reaction mixture was diluted with ether. It was found in the cases of the secondary halogen compounds that if the reaction mixture was heated for twelve to fifteen hours at 100° or three to four hours at 130° and then cooled and diluted with ether, a fairly complete recovery of one mole of 3-methylpiperidine hydrochloride (or hydrobromide) could be made. But the ether solution contained no tertiary amine, for when it was treated with dry hydrogen chloride only 3-methylpiperidine hydrochloride precipitated. The total recovery of the secondary amine salt practically corresponded to the secondary amine that was originally a part of the reaction mixture. From these results it is apparent that the tendency of secondary halogen esters of this type is to lose a molecule of halogen acid when they are treated with a secondary amine rather than to form a tertiary amine.

The attempted synthesis of the compound containing Structure VII started with diacetone alcohol, which on treatment with thionyl chloride was converted into 2-methyl-2-chloropentanone-4.



$$\mathrm{CH_3—\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}—CH_2—\overset{\overset{O}{\|}}{C}—CH_3 \xrightarrow{SOCl_2} CH_3—\underset{\underset{Cl}{|}}{\overset{\overset{CH_3}{|}}{C}}—CH_2—\overset{\overset{O}{\|}}{C}—CH_3}$$

Should this chloro ketone react with 3-methylpiperidine to give a tertiary amine, then reduction of the ketone and benzoylation of the resulting alcohol would give the desired structure (VII). After the experience with the secondary halogen esters it was not expected that the 2-methyl-2-chloropentanone-4 would react with the secondary amine to give the tertiary amine, but the reaction was tried in order to ascertain what the behavior of such a tertiary halogen compound would be. It was found that this chloro ketone reacted with the secondary amine at room temperature and after about twelve hours approximately one-half of the secondary amine was precipitated as the hydrochloride when the reaction mixture was diluted with ether. The ether solution when treated with dry hydrogen chloride yielded only 3-methylpiperidine hydrochloride. These results indicate that halogen attached to secondary and tertiary carbon atoms in compounds of the type studied here do not react with secondary amines to give tertiary amines, but rather lose a molecule of halogen acid to form, presumably, an unsaturated compound.

Experimental

1-(3-Methylpiperidino)-propanone-2 Hydrochloride.—Ten g. (1 mole) of freshly distilled chloro-acetone, dissolved in 200 cc. of ether, was treated with 20 g. (2 moles) of **3-methylpiperidine,** dissolved in 200 cc. of ether. A precipitate of 3-methylpiperidine hydrochloride appeared immediately. The mixture was allowed to stand with occasional shaking for about one hour and then the precipitated amine hydrochloride was filtered off. Dry hydrogen chloride was then passed into the filtrate until the precipitation of the keto base was complete. The hydrochloride of the keto base could not be obtained crystalline at this point so the free base was liberated with 40% sodium hydroxide and extracted with ether. After removal of the ether the product was distilled under diminished pressure. Thirteen *g.* of a product boiling at 101–102° (18 mm.) was obtained. This free base was then dissolved in ether and reprecipitated as the hydrochloride. On recrystallization it melted at 162–163°.

Anal. Subs., 0.2031, 0.1889: AgCl, 0.1511, 0.1406. Calcd. for $C_9H_{18}ONCl$: Cl, 18.51. Found: 18.40, 18.42.

1-(3-Methylpiperidino)-propanol-2 Hydrochloride.—A solution of 15.5 g. of 1-(3-methylpiperidino)-propanone hydrochloride in 75 cc. of alcohol was reduced catalytically using 0.3 g. of Adams' platinum-oxide platinum black catalyst. The reduction was complete in three and one-half to four hours. The catalyst was removed from the reduced solution and the alcohol evaporated off under diminished pressure. The residue was treated with 40% sodium hydroxide and extracted with three 100-cc. portions of ether. The ether solution was dried over anhydrous sodium sulfate, after which the solvent was removed and the amine distilled under diminished pressure. The amino alcohol boiled at 98–100° (18 mm.); yield, 9 *g.* It was converted into the hydrochloride by precipitation from ethereal solution with hydrogen chloride and analyzed in this form. The hydrochloride melted at 184–185°.

Anal. Subs., 0.1633, 0.2710; AgCl, 0.1220, 0.2020. Calcd. for $C_9H_{20}ONCl$: Cl, 18.32. Found: 18.47, 18.43.

α-Methyl-β-(3-methylpiperidino)-ethyl Benzoate Hydrochloride (III).—The residue obtained after the evaporation of the solvent from the reduction of 1-(3-methylpiperidino)-propanone hydrochloride was benzoylated by heating with benzoyl chloride at 150–160° for twenty to thirty minutes. The acylation proceeded normally and the amino ester hydrochloride was isolated by diluting the reaction mixture with ether.

After several recrystallizations from an alcohol–ether mixture the product melted at 165–166°; yield, 5 g.

Anal. Subs., 0.2370, 0.1982: AgCl, 0.1165, 0.0980. Calcd. for $C_{16}H_{24}O_2NCl$: Cl, 11.92. Found: 12.16, 12.23.

1-(3-Methylpiperidino)-butanone-3 Hydrochloride.—A mixture of 13.5 g. of 3-methylpiperidine hydrochloride, 3.6 g. of paraformaldehyde, 30 cc. of acetone and 5 cc. of absolute alcohol was heated on a water-bath until the paraformaldehyde went into solution. This required three to four hours. The reaction mixture was then diluted with 100 cc. of dry ether and allowed to stand in an ice box until crystallized. This precipitated keto amine hydrochloride after recrystallization from an alcohol–ether mixture melted at 151–152°; yield, 12 g.

Anal. Subs., 0.1980, 0.2061: AgCl, 0.1378, 0.1431. Calcd. for $C_{10}H_{20}ONCl$: Cl, 17.25. Found: 17.22, 17.18.

α-Methyl-γ-(3-methylpiperidino)-propyl Benzoate **Hydrochloride (IV)**.—A solution of 7 g. of 1-(3-methylpiperidino)-butanone-3 hydrochloride in 50 cc. of alcohol was reduced catalytically with Adams' platinum–oxide platinum black catalyst. The reduction was complete in one to two hours with the absorption of the theoretical amount of hydrogen. The catalyst was filtered off from the reduced solution and the alcohol removed from the filtrate under diminished pressure. The residue was benzoylated with benzoyl chloride as described above for α-methyl-β-(3-methylpiperidino)-ethyl benzoate hydrochloride. The amino ester hydrochloride after recrystallization melted at 178–180°; the yield was 3.5 g.

Anal. Subs., 0.1441, 0.1659: AgCl, 0.0666, 0.0781. Calcd. for $C_{17}H_{26}O_2NCl$: Cl, 11.38. Found: 11.42, 11.64.

α,β-Dimethyl-β-bromo-ethyl Benzoate.—To 216 g. (1 mole) of β-butylene bromide (Eastman) dissolved in 200 cc. of toluene, was added 114 g. (0.5 mole) of silver benzoate. The mixture was stirred and refluxed for six hours. After this period of heating another 114 g. of silver benzoate was added and the mixture refluxed for an additional six hours. The reaction mixture was then filtered to remove the insoluble silver salts and the precipitate washed with 100 cc. of toluene. The filtrate was shaken with 10% sodium hydroxide to remove any benzoic acid that was present and then distilled under diminished pressure. Eighty g. (31%) of a product that boiled at 139–141° (4 mm.) was obtained. In spite of the apparent purity of the compound it failed to show the correct halogen content upon analysis by the Carius method. The analysis showed 20.5–21.0% of bromine, whereas the theoretical amount for the bromo ester is 31.10%. On redistillation of the product through a 15-cm. fractionating column, it boiled at 140–141 (4 mm.), but the analysis of the product so obtained gave practically the same results as indicated above. The only explanation of these low analyses that seems possible is that a small amount of the dibenzoate was present in the bromo ester and that the two could not be completely separated by fractional distillation.

α,γ-Dimethyl-γ-chloropropyl Benzoate.—Acetylacetone was reduced catalytically with Adams' platinum–oxide platinum black catalyst to pentane-diol-2,4, which was isolated in 60% yield. This diol has previously been prepared by the action of methyl magnesium iodide on aldol[5] and by the reduction of pentane-01-4-one-2 with sodium amalgam.[6] Twenty-six g. (0.25 mole) of this glycol was heated at 110–120° and to this was added slowly from a dropping funnel 35 g. (0.25 mole) of benzoyl chloride. The mixture was kept at this temperature for about half an hour after all the benzoyl chloride had been added. The reaction mixture was then cooled, 60 g. of thionyl

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[5] Franke and Kohn, *Ber.*, 37,4730 (1904).

[6] Poray-Coschitz, *Chem. Centr.*, [I]1327 (1904).

chloride added, and the resulting solution heated for about half an hour under a reflux on a water-bath. Water was then added to decompose the excess of thionyl chloride and the chlorobenzoate was extracted with ether and dried over calcium chloride. After the removal of the solvent the chloro ester was distilled under diminished pressure. There was obtained 18–20 g. of product, b. p. 134–135° (2 mm.); n_D^{20}, 1.5074; d_{20}^{20}, 1.1008.

Anal. Subs., 0.4813, 0.4749: AgCl, 0.3031, 0.2981. Calcd. for $C_{12}H_{15}O_2Cl$: Cl, 15.65. Found: 15.58, 15.53.

Reaction of **α,β-Dimethyl-β-bromo-ethyl** Benzoate **and α,γ-Dimethyl-γ-chloro-**propyl Benzoate with **3-Methylpiperidine.**—A mixture of 0.1 mole of 3-methylpiperidine and 0.05 mole of the halogen ester was heated on a steam cone for thirty minutes. At the end of this time the mixture was cooled and diluted with ether in order to precipitate any of the 3-methylpiperidine hydrohalide that would have been formed had any reaction taken place. There was no indication of reaction during this period of heating. The time of heating was extended to four hours and dilution with ether showed that some reaction had taken place, but it was not nearly complete. After twelve hours of heating at 100°, however, approximately half of the 3-methylpiperidine originally used was precipitated by ether as the hydrobromide, showing that the reaction had been completed. The ether solution after the removal of the secondary amine hydrobromide was treated with dry hydrogen chloride. A precipitate was obtained which proved to be 3-methylpiperidine hydrochloride. The combined hydrobromide and hydrochloride obtained was practically equivalent to the total amount of 3-methylpiperidine started with. There was no qualitative difference in the behavior of α,β-dimethyl-β-bromo-ethyl benzoate and α,γ-dimethyl-γ-chloropropyl benzoate toward the secondary amine.

2-Chloro-2-methylpentanone-4.—To a solution of 58 g. of diacetone alcohol in 100 cc. of ether was added 60 g. of thionyl chloride and the mixture was refluxed for thirty minutes. Water was then added to decompose the unreacted thionyl chloride and the ether solution of the chloro-ketone dried over anhydrous sodium sulfate. The ether was distilled off and the chloro-ketone distilled under diminished pressure. The product boiled at 50–52° (14 mm.) and the yield was 50 g. (74%). When first distilled it was a colorless oil, but it began to darken almost immediately on standing. After standing for three to four hours, there was sufficient hydrogen chloride evolved to cause noticeable fumes when the bottle containing the product was unstoppered. The chloro-ketone was washed with dilute sodium carbonate solution, dried with calcium chloride, redistilled and immediately weighed out for analyses. A chlorine content of 23.05% was found, whereas the theoretical is 26.39%. On account of its instability no other physical constants of the chloro-ketone were determined.

Reaction of **2-Chloro-2-methylpentanone-4** with **3-Methylpiperidine.**—To a solution of 6.8 g. (0.05 mole) of the chloro-ketone in 100 cc. of ether was added 10 g. (0.1 mole) of 3-methylpiperidine and the mixture allowed to stand at room temperature. Precipitation of 3-methylpiperidine hydrochloride began at once and after twelve hours' standing the reaction mixture was filtered. Approximately one-half of the secondary amine was recovered as the hydrochloride. The filtrate was treated with dry hydrogen chloride and the precipitate was 3-methylpiperidine hydrochloride, which together with that obtained by the first filtration of the reaction mixture corresponded to practically all of the 3-methylpiperidine that was originally put into the reaction.

Pharmacological Report

α-Methyl-β-(3-methylpiperidino)-ethyl benzoate hydrochloride (III) and α-methyl-γ-(3-methylpiperidino)-propyl benzoate hydrochloride (IV)

are being studied pharmacologically by Mr. Charles L. Rose of the Lilly Research Laboratories, Eli Lilly and Company, Indianapolis, Indiana. A brief report of a portion of this work is given in the table below. For comparison the corresponding values for β-(3-methylpiperidino)-ethyl benzoate hydrochloride (I), γ-(3-methylpiperidino)-propyl benzoate hydrochloride (II), cocaine and procaine are included. The anesthetic efficiencies were determined in the usual way by the application of a 2% solution of the anesthetic to the rabbits cornea and noting the duration of anesthesia. The toxicities were determined by subcutaneous injection into white mice and also by intravenous injection into white rats.

TABLE I

PHARMACOLOGICAL DATA

	Av. duration of compound anes., min.	Subcutaneous toxicity to white mice (mg./kg.)			Intravenous toxicity to white rats (mg./kg.)		
		M. T. D.	M. L. D.	No. of mice used	M. T. D.	M. L. D.	No. of rats used
I	0	3000	3500	29	25	30	11
II	11	450	500	7	20	25	9
III	2.5	2000	2500	30	20	25	14
IV	28	250	300	40	12.5	15	10
Cocaine	29.0	200	250	18	15	17.5	12
Procaine	0	900	1000	17	45	50	10

Discussion of the Pharmacological Data

A comparison of compounds I and I1 with III and IV shows that the introduction of a methyl group in the alkylene group that separates the oxygen and nitrogen in these substances causes a considerable change in their pharmacological behavior. The compounds (III and IV) containing the methyl substituted alkylene group have distinctly higher anesthetic effect and higher toxicities than the corresponding compounds (I and II) in which the alkylene group is unsubstituted. Compound IV has practically the same pharmacological properties as cocaine. It may be of interest to note that in compounds II and III where there are the same number of carbon atoms in the alkylene groups, the straight chain compound (II) appears to be the most efficientanesthetic.

Summary

1. α-Methyl-β-(3-methylpiperidino)-ethyl benzoate and a-methyl-γ-(3-methylpiperidino)-propyl benzoate have been prepared as the hydrochlorides. They have been found to have higher anesthetic efficiencies and higher toxicities than the corresponding compounds in which the alkylene group between the oxygen and nitrogen is unsubstituted.

2. It has been found that certain halogen compounds in which the halogen is attached to a secondary or tertiary carbon atom do not react

with a secondary amine to give a tertiary amine, but undergo an internal loss of halogen acid to form, presumably, an unsaturated compound.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE UNIVERSITY CHEMICAL LABORATORIES. CAMBRIDGE. ENGLAND]

A PRELIMINARY EXAMINATION OF ROTENONE AND SOME OF ITS DEGRADATION PRODUCTS

BY GORDON MITCHELL WRIGHT

RECEIVED AUGUST 11, 1928 PUBLISHED DECEMBER 10, 1928

For many years considerable interest has been taken in a number of tropical plants, extracts of which have been used as fish and arrow poisons. More recently there has been a commercial development of these plants as sources of insecticides, and in this connection the root of *Derris elliptica Benth.* or *Tuba* has been widely used. On the agricultural side considerable attention has been given to the properties of *Derris* and it seemed of interest to obtain some light on the chemical structure and properties of the toxic principle.

A toxic principle from the root was first isolated as an amorphous substance by Greshoff,[1] who assigned it the name "Derrid." This worker showed that derrid did not contain nitrogen and was not a glucoside. Wray[2] also appears to have isolated the same substance, though he assigned to it the name "Tubain."

Derrid was also obtained by van Sillevoldt[3] as an amorphous powder, m. p. 73°, with an empirical formula $C_{33}H_{30}O_{10}$. It was suggested that it contained three mexthoxyl groups and two hydroxyl groups, although benzoylation or acetylation failed. Further, "anhydroderrid," yellow needles, m. p. 210–214°, of formula $C_{33}H_{28}O_9$, was obtained. A crystalline substance, m. p. 158°, from the roots of *Derris elliptica Benth.* was obtained by Lenz,[4] who gave it the name "Derrin." Takeo Ishikawa[5] isolated *a* toxic substance, m. p. 163.5°, from the same source and assigned to it the name "tubotoxin" and the empirical formula $C_{18}H_{18}O_5$. The work of the previous author was extended by Kariyone and Atsumi,[6] who confirmed the above formula. This compound, which in alcoholic solution reduced Fehling's solution, formed a phenylhydrazone, $C_{18}H_{18}O_5{=}N\cdot NHC_6H_5$, m. p. 255°, and a monoxime, $C_{18}H_{18}O_5{=}NOH$, m. p. 245°. It was suggested that a diacetyl derivative, m. p. 125–155°, was obtained but

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[1] Greshoff, *Ber.*, **23**, **3538** (1890).

[2] Wray, *Pharm. J.*, [3] **23**, (1892).

[3] van Sillevoldt, *Arch. Pharm.*, **237**, 595 (1899).

[4] Lenz, *ibid.*, **249**, 298 (1911).

[5] Takeo Ishikawa, *Japan* Med. *Lit.*, *1*, 7 (1916).

[6] Kariyone and Atsumi, *J. Pharm. Soc. Japan*, **491**, 6 (1923)

the analyses did not bear this out. A methoxyl estimation showed the presence of 1.5 methoxyl groups in the molecule. Further work by Kariyone, Kimura and Kondo[7] showed that tubotoxin in hot alcoholic solution added on a molecule of hydrogen chloride (needles, m. p. 194°) and a molecule of hydrogen bromide (needles, m. p. 185°). Tubotoxin, whose formula in conformity with more recent work had been altered to $C_{19}H_{18}O_5$, on reduction in presence of palladium and barium sulfate, yielded dihydrotubotoxin, $C_{19}H_{20}O_5$, m. p. 216°, which was confirmed by the preparation of an oxime. When warmed with alcoholic potash at water-bath temperature, tubotoxin yielded "tubaic acid," $C_9H_{10}O_3$, m. p. 129°, which decolorized bromine and potassium permanganate solutions, and formed a methyl ester, m. p. 54°, and a mono-acetyl derivative, m. p. 133°. This acid may be reduced under the same conditions as tubotoxin to give dihydrotubaic acid, m. p. 166°, which was also obtained by the fission of dihydrotubotoxin with alcoholic potash. The methyl ester of this acid melts at 79° and the acetyl derivative at 169°.

In a later communication Kariyone and Kondo[8] revised the formula of tubaic acid to $C_{12}H_{12}O_4$ and stated that this acid is isomeric with "rotenic acid," m. p. 182°, obtained by the fusion of tubotoxin with potash, and which yielded an acetyl derivative, m. p. 154°.

Contemporaneous with Kariyone and his collaborators, Takei[9] was also examining the same toxic substance from *Derris elliptica Benth.* He found that this principle was identical with rotenone isolated by Kazuo Nagai[10] from *Derris chinensis Benth.* Takei[9] had shown that rotenone had the formula $C_{19}H_{18}O_5$, which was supported by an examination of the phenylhydrazone, m. p. 254°. He found that rotenone contained 1.5 OCH_3 groups; was converted into isorotenone by concentrated sulfuric acid; was degraded into an acid, $C_{10}H_{10}O_3$, m. p. 129°, which reacted with bromine; and on fusion with potash was transformed into rotenic acid, $C_9H_{10}O_3$ (or $C_6H_6O_2$). Further, the acid $C_9H_{10}O_3$ (m. p. 182°) yielded a mononitro derivative (m. p. 168°) and from its reaction with ferric chloride he suggested that it was a dimethyl-o-hydroxybenzoic acid.

On treating rotenone at 150° with acetic anhydride in acetic acid, or with chromic anhydride in acetic acid at 50°, a compound of empirical formula $C_{18}H_{16}O_5$ (m. p. 233°) was obtained. On oxidation of rotenone with chromic anhydride in acetic acid at a higher temperature, a compound of empirical formula $C_{17}H_{14}O_5$ (m. p. 298°) was produced to which he assigned the name "rotenonone." The heating of rotenonone with fused potash yielded rotenic acid.

[7] Kariyone, Kimura and Kondo, J. *Pharm. Soc. Japan,* **514, 1049** (1924).

[8] Kariyone and Kondo, *ibid.,* **518, 376 (1925).**

[9] (a) Takei, Bull. *Inst. Phys. Chem. Research Japan,* **2, 485 (1923)**; (b) *Biochem. Z.,* **157, 1 (1925).**

[10] Kazuo Nagai, J. *Chem. Soc. Tokyo,* **23, 740 (1902).**

In a later communication Takei[11] revised almost completely his original paper. Rotenone was now assigned the formula $C_{23}H_{22}O_6$ and this formula was confirmed by analysis of the phenylhydrazone, the oxime, the addition product with hydrogen chloride and a re-examination of isorotenone and its oxime. At the same time rotenic acid was given the formula $C_{12}H_{12}O_4$ and was further confirmed by acetylation and preparation of a dimethyl derivative and its nitration product.

It was found on gradually raising the temperature of rotenic acid to 210° and then to 300° two products were obtained: a phenol, $C_{11}H_{12}O_2$ (m. p. 42°), and an alkali-insoluble substance (m. p. 136°) of probable formula $C_{22}H_{22}O_4$. The phenol was characterized by the preparation of a *p*-tolylsulfonyl derivative and of a methyl ether.

In 1925, and therefore previous to the publication by Takei,[11] the discrepancies between the results of the various investigators had been noticed, and it was decided to reopen the problem in an attempt to establish a formula and a partial structure for the same principle of *Derris elliptica Benth.* In view of the drastic revision to which Takei[11] has subjected his previous work,[9b] it seems necessary to obtain independent confirmatory evidence. It has now been shown that the composition of rotenone is best expressed by the molecular formula $C_{23}H_{22}O_6$ and that it forms an oxime, $C_{23}H_{22}O_5{=}NOH$, a phenylhydrazone, $C_{23}H_{22}O_5{=}N{\cdot}NHC_6H_5$, and an addition product with hydrogen chloride, $C_{23}H_{22}O_6{\cdot}HCl$. Further proof is afforded by the preparation of the hydrobromide of rotenone and the oxime of the hydrochloride. The formation of isorotenone, its oxime and its phenylhydrazone has been established, again confirming the work of Takei.[11]

On oxidation of rotenone with chromic anhydride in acetic acid under conditions described by Takei,[9b] a substance having the same analysis and melting point was obtained, agreeing with a revised formula $C_{21}H_{18}O_6$.

The action of alcoholic potash yielded an acid $C_{12}H_{12}O_4$ (m. p. 129°)[8] which is presumably identical with $C_{10}H_{10}O_3$ described by Takei.[9b] Rotenic acid, which was obtained by the fusion of rotenone with potash, has been shown to have the formula $C_{12}H_{12}O_4$.[8,11] The formula of this acid has been further confirmed by the preparation of a mononitro derivative and a methyl ester. Rotenic acid on heating at about 210° until evolution of carbon dioxide had ceased yielded a compound $C_{23}H_{22}O_5$ (m. p. 103°).

Experimental

Rotenone (m. p. 163°) was prepared by extracting the powdered root with ether and crystallization of the product, which separated on cooling from carbon tetrachloride and then alcohol.

Anal. Calcd. for $C_{23}H_{22}O_6$: C, 70.05; H, 5.6; OCH_3, 15.7; mol. wt., 394. Found:

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[11] Takei, *Ber.*, 61, 1003 (1928).

C, 69.6, 69.5, 69.7; H, 5.85, 5.6, 5.9; OCH_3, 15.0, 15.1; mol. wt. in $C_2H_4Br_2$: 403, 376, 381; in $CHBr_3$, 386.

Rotenone-oxime.—A mixture of 5 g. of rotenone, 3.7 g. of hydroxylamine hydrochloride and 4.2 g. of fused sodium acetate dissolved in 80 cc. of absolute ethyl alcohol was refluxed for three to four hours. The hot solution was filtered and the crystals which separated from the filtrate on cooling were filtered, washed with water and on repeated recrystallization from methyl alcohol formed colorless needles, m. p. 252°.

And. Calcd. for $C_{23}H_{22}O_5$=NOH: C, 67.5, H, 5.6; N, 3.4. Found: C, 67.9, 67.4, 67.75; H, 5.3, 5.65, 5.85; N, 3.4, 3.5, 3.45.

Rotenone phenylhydrazone was prepared by refluxing for five hours a mixture of 5 g. of rotenone, 7.5 g. of phenylhydrazine hydrochloride and 4.2 g. of fused sodium acetate dissolved in 50 cc. of absolute alcohol. The solid product which separated was filtered, washed with water and on crystallization from alcohol yielded fine yellow needles, m. p. 245°.

Anal. Calcd. for $C_{23}H_{22}O_5$ = $NNHC_6H_5$: C, 71.9; H, 5.8; N, 5.8. Pound: C, 71.6; H, 5.7; IS, 6.0.

Rotenone hydrochloride was best prepared in the cold by dissolving with shaking 2 g. of rotenone in 100 cc. of glacial acetic acid saturated with hydrogen chloride and leaving for two to three days. The greenish-yellow solution, on addition of water, precipitated a solid which after filtering, drying and recrystallizing from alcohol had a m. p. of 197°. On concentration of the alcoholic mother liquors, in addition to a further quantity of rotenone hydrochloride, there was obtained a very small quantity of a solid forming yellow crystals from alcohol (m. p. 255°) containing chlorine.

Anal. Calcd. for $C_{23}H_{22}O_6 \cdot HCl$: C, 64.1; H, 5.35; Cl, 8.25; OCH_3, 14.4; mol. wt., 430.5. Found: C, 64.2, 63.95, 64.5; H, 5.35, 5.3, 5.5; Cl, 8.1, 7.95; OCH_3, 14.1; mol wt., 442.

The **oxime** of rotenone hydrochloride was obtained by refluxing a mixture of 5 g. of rotenone hydrochloride, 3.7 g. of hydroxylamine hydrochloride and 4.2 g. of fused sodium acetate, dissolved in 100 cc. of absolute alcohol, for six hours. The hot solution after filtering deposited crystals which gave on repeated crystallization from alcohol colorless needles, m. p. 239° (with decomposition).

Anal. Calcd. for $C_{23}H_{22}O_5$=$NOH \cdot HCl$: C, 61.95; H, 5.4; Cl, 7.95; OCH_3, 13.9. Found: C, 62.65, 62.60; H, 5.45, 5.60; Cl, 7.95; OCH_3, 14.0.

Rotenone hydrobromide was prepared in a manner similar to rotenone hydrochloride using glacial acetic acid saturated with hydrogen bromide. In this case the product separated from solution and after twenty-four hours was filtered off; it crystallized from methyl alcohol in long white needles, m. p. 190".

Anal. Calcd. for $C_{23}H_{22}O_6 \cdot HBr$: C, 58.1; H, 4.85; Br, 16.85. Found: C, 57.7, 58.1; H, 4.85.4.95; Br, 16.75.

Isorotenone was obtained by the gradual addition of 30 cc. of concentrated sulfuric acid to 5 g. of rotenone in 40 cc. of glacial acetic acid. After addition was complete the red solution was poured into ice water; the solid which was precipitated was crystallized from alcohol in small needles, m. p. 184°.

Anal. Calcd. for $C_{23}H_{22}O_6$: C, 70.05; H, 5.6. Found: C, 69.5; H, 5.65.

Isorotenone phenylhydrazone, which was prepared in the same manner as rotenone phenylhydrazone, on crystallization from alcohol formed fine yellow needles, m. p. 230°.

Anal. Calcd. for $C_{23}H_{22}O_5=NNHC_6H_5$: C, 71.9; H, 5.8; N, 5.8. Found: C, 71.95. 71.43; H, 5.73, 5.5; N, 5.85, 6.05.

No appreciable action takes place on passing hydrogen chloride into a hot alcoholic solution of isorotenone for fourteen hours nor had concentrated sulfuric acid any action on rotenone hydrochloride.

Rotenonone was obtained by the slow addition of a solution of 10 g. of chromic anhydride in glacial acetic acid to a hot acetic acid solution of 5 g. of rotenone. On crystallization of the product from acetic acid, yellow needles were obtained, m. p. 300°.

Anal. Calcd. for $C_{21}H_{18}O_6$: C, 68.85; H, 4.9. Found: C, 68.7; H, 5.3.

Rotenic acid, obtained by the fusion of rotenone with potash, crystallized from benzene in white needles, m. p 183°.

Anal. Calcd. for $C_{12}H_{12}O_4$: C, 65.45; H, 5.45; equiv., 220. Found: C, 65.4; H, 5.35; equiv., 220,226.

A Zeisel determination for the methoxyl group gave a negative result.

Methyl Ester of Rotenic Acid.—A solution of 1 g. of rotenic acid in ether was treated with an ethereal solution of diazomethane prepared from 3 cc. of nitrosomethylurethan and allowed to stand at ordinary temperature for three days. On evaporating the ether, an oil was obtained which went solid after washing with dilute sodium carbonate and water. On crystallization from methyl alcohol, colorless prisms (m. p. 39–40°) were obtained. This ester may also be prepared by the action of methyl iodide on the silver salt of rotenic acid.

Anal. Calcd. for $C_{12}H_{11}O_4CH_3$: C, 66.65; H, 6.0. Found: C, 66.15, 66.7; H, 5.6, 5.8.

Nitrorotenic acid was obtained by the careful addition of 2 cc. of a 10% solution of nitric acid (sp. gr. 1.42) in glacial acetic acid to 0.5 g. of $C_{12}H_{12}O_4$ dissolved in 15 cc. of glacial acetic acid. The solution was warmed gently for a few minutes and left overnight. On addition of water a yellow solid was precipitated which crystallized from alcohol and water in yellow needles, m. p. 187°.

Anal. Calcd. for $C_{12}H_{11}O_4NO_2$: N, 5.3. Found: N, 5.2, 5.1.

Action of Heat on Rotenic Acid.—Two g. of rotenic acid was heated between 216 and 225° until evolution of carbon dioxide had ceased. The oily residue was washed with dilute caustic soda and the residual white solid crystallized from methyl alcohol; it formed small, white crystals (m. p. 104°). In alcoholic solution it gave a green color with ferric chloride.

Anal. Calcd. for $C_{23}H_{22}O_5$: C, 73.0; H, 5.8; mol. wt., 378. Found: C, 73.0, 73.4; H, 5.9, 6.15; mol. wt., 396, 405.

The alkaline filtrate on acidification gave a substance of phenolic character which could not be obtained in a pure state.

Tubaic acid, which was prepared by the action of alcoholic potash on rotenone. yielded colorless needles on crystallization from water, m. p. 128–129°.

Anal. Calcd. for $C_{12}H_{12}O_4$: C, 65.45; H, 5.45; equiv., 220. Found: C, 65.55 65.5; H, 5.45, 5.65; equiv., 221.

No methoxyl grouping was found to be present.

The author wishes to thank Messrs. Guthrie and Co., Ltd., East India merchants, London, and the Agricultural Department F. M. S. for the gift of a considerable amount of the Derris used in the above work.

Summary

1. Rotenone has been shown to have the formula $C_{23}H_{22}O_6$ and to form a monoxime and a phenylhydrazone. It adds on one molecule of hydrochloric acid or hydrobromic acid.

2. Isorotenone is formed by the action of sulfuric acid on rotenone, and yields a phenylhydrazone.

3. Rotenic acid, which is obtained by the fusion of rotenone with potash, has the formula $C_{12}H_{12}O_4$. It yields a monomethyl ester and a mononitro derivative.

Cambridge, England

[Contribution from the Chemistry Department of the University of Nebraska]

THE ACTION OF ALKYL CHLOROCARBONATES ON STIBANILIC ACID[1]

By Cliff S. Hamilton and R. E. Etzelmiller

Received August 15, 1928 Published December 10, 1928

Studies in the field of organic antimonials have been carried out in connection with investigations of protozoal diseases because in some of these diseases the antimonials appear to be of greater value than the arsenicals.

It was the object of this investigation to prepare some of the carbalkoxy derivatives of p-aminostibinic acid and to study some of their properties. Methyl, ethyl, propyl, *iso*propyl, butyl, *iso*butyl, β-chloro-ethyl and y-chloropropyl chlorocarbonates were condensed with p-stibanilic acid. Only one of the products, *p*-carbethoxyaminophenylstibinic acid was found reported in the literature.[2]

Two general methods, with various modifications, have been used for the preparation of *p*-aminophenylstibinic acid or p-stibanilic acid from *p*-aminoacetanilide; the first, by diazotization of *p*-aminoacetanilide and subsequent addition to alkaline antimony trioxide;[3] the second, by formation of the double salt in acid solution[4] and its addition to a solution of sodium hydroxide.[5] In both cases the acetyl group was removed by hydrolysis with a 5% solution of sodium hydroxide.

In this study both of the above methods were tried in the preparation of p-stibanilic acid with about equal results. With either method several difficulties were encountered. Not only was the material hard to handle mechanically but the yields were low. In the method finally adopted *p*-amino-acetanilide was diazotized and slowly added to an alkaline solution of antimony trioxide containing a little glycerol. The foam which forms was kept down by vigorous stirring and by regulating the

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[1] Some of the compounds described in this paper are being studied pharmacologically under the direction of Dr. A. S. Loevenhart, Department of Pharmacology, University of Wisconsin.

[2] Brachmachari, *Indian* J. Med. *Research, 10, 508* (1922).

[3] German patent 254,421 (1911).

[4] May and Gray, *J. Chem. Soc.,* 3174 (1926).

[5] Dunning and Reid, This Journal, 48,2959 (1926); 49,2869 (1927).

addition of the diazonium solution. At the conclusion of the reaction, the crude *p*-acetylaminophenylstibinic acid was precipitated with dilute acetic acid, hydrolyzed with a solution of sodium hydroxide and the crude stibanilic acid precipitated with dilute acetic acid. The derivatives prepared from this crude acid always analyzed too high in antimony content and it was found necessary to purify the acid before making the chlorocarbonate derivatives.

The several carbamates were prepared by dissolving the purified stibanilic acid in a slight excess of N sodium carbonate solution and adding slowly a slight excess of the chlorocarbonate. Their sodium salts separated out from the sodium carbonate solution and were converted to the free acids by use of hydrochloric acid. These carbamates were almost colorless powders insoluble in benzene, water or dilute acids. Concentrated hydrochloric acid changed them into a tarry oil. They showed but slight solubility in dilute sodium hydroxide solution, their solubility decreasing with an increase in their carbon content.

When 4-carbo-β-chloro-ethoxy- and 4-carbo-γ-chloropropoxyamino-phenylstibinic acids were heated with four equivalents of aqueous alkali, β- and γ-phenylstibino-alkylamino alcohols, respectively, were obtained as illustrated by the formation of the β-compound.

$$H_2O_3SbC_6H_4NH_2 \longrightarrow H_2O_3SbC_6H_4NHCOOCH_2CH_2Cl \longrightarrow H_2O_3SbC_6H_4\underbrace{NCOOCH_2CH_2} \longrightarrow H_2O_3SbC_6H_4NHCH_2CH_2OH$$

No attempt was made to isolate the substituted oxazolidone shown in the above formulation but it was no doubt formed as an intermediate product.

Experimental

p-Aminophenylstibinic Acid (**p-Stibanilic** Acid), $NH_2C_6H_4SbO_3H_2$.—Ninety grams of *p*-amino-acetanilide was added to 600 cc. of boiling water and decolorized with charcoal. One hundred and forty-four cubic centimeters of concentrated hydrochloric acid was then added and the solution cooled to 0–5°, when white crystals of the hydrochloride separated out. This mixture was diazotized with a solution of 42 g. of sodium nitrite in 250 cc. of water. The nitrite solution was introduced through a capillary tube at the bottom of the beaker, with mechanical stirring. The diazotized solution was then slowly added through a capillary tube to a jar containing a cold alkaline solution of antimony trioxide, prepared by dissolving 150 g. of antimony trichloride or 80 g. of antimony trioxide in a small amount of warm concentrated hydrochloric acid and 200 cc. of glycerol and adding this solution to just sufficient 5 N sodium hydroxide to dissolve the oxide that forms, followed by dilution with ice and water to eight liters. By regulating the addition of the diazonium solution and by vigorously stirring the mixture, a heavy foam which tends to form was prevented. During the addition of the diazonium solution the antimony trioxide was kept in solution by adding 10% sodium hydroxide solution from time to time as needed. When the reaction was complete the mixture was almost neutralized with hydrochloric acid and saturated with carbon dioxide to precipitate the unchanged antimony trioxide and tarry products. Before filtering the mixture was heated to 75° to coagulate the precipitated products; otherwise the finely divided particles clogged the filter paper and a considerable time was required to filter. After filtering the *p*-acetylaminophenylstibinic acid was precipitated from the warm solution with dilute acetic acid and filtered. The acetyl group was removed by hydrolysis during one hour, in 1 liter of 5% sodium hydroxide solution at 90°. The crude acid was precipitated with acetic acid. The yields varied from 35 to 50%.

Purification of **Stibanilic** Acid.—Purification was accomplished by adding the moist crude acid, in small portions, to ice-cold, concentrated hydrochloric acid and stirring into a paste. After standing for a short time, the tetrachloride thus formed was filtered, washed with cold, concentrated hydrochloric acid and dissolved in just the required amount of 10% sodium hydroxide. This solution was warmed to 90°, decolorized with charcoal and the stibanilic acid precipitated with dilute acetic acid. To obtain a pure product consistently the process as outlined above was repeated. Yields of the purified acid were low and varied from 8 to 15% based on the crude acid.

Preparation of **Alkyl** and **Chloro-alkyl Chlorocarbonates.**—Following the method of Rose[6] these were prepared from the corresponding alcohols and phosgene at 0°.

Carbo-alkoxy-aminophenylstibinic Acids.—Purified *p*-stibanilic acid was dissolved in a slight excess of N sodium carbonate solution. To this solution a slight excess of the alkyl or chloro-alkyl chlorocarbonate was added, drop by drop, the reaction mixture frequently being shaken. The sodium salt of the carbo-alkoxy-aminophenylstibinic acid soon began to separate but the reaction mixture was allowed to stand overnight. The sodium salt was filtered off and suspended for a time in N hydrochloric acid to convert it into the free acid. The carbo-alkoxyaminophenylstibinic acid was washed with 2 N hydrochloric acid, to insure complete removal of any unchanged *p*-stibanilic acid, and then with water. When dried over sulfuric acid in a vacuum an almost colorless powder was obtained.

TABLE I

YIELDS AND ANALYTICAL DATA

4-Carbo-( )-aminophenylstibinic acid	Yield, %	Analysis			
		Subs., g.	0.0559*N* I_2, cc.	Sb, % Calcd.	Sb, % Found
Methoxy, $CH_3OCONHC_6H_4SbO_3H_2$	73	0.1582	17.40	37.83	37.45
Ethoxy, $C_2H_5OCONHC_6H_4SbO_3H_2$	85	.1790	19.10	36.25	36.33
Propoxy, $CH_3CH_2CH_2OCONHC_6H_4SbO_3H_2$	87	.1573	15.93	34.80	34.48
Isopropoxy, $(CH_3)_2CHOCONHC_6H_4SbO_3H_2$	89	.1602	16.47	34.80	35.01
Butoxy, $CH_3CH_2CH_2CH_2OCONHC_6H_4SbO_3H_2$	70	.1577	15.46	33.46	33.38
*Iso*butoxy, $(CH_3)_2CHCH_2OCONHC_6H_4SbO_3H_2$	85	.1616	15.97	33.46	33.66
β-Chloro-ethoxy, $ClCH_2CH_2OCONHC_6H_4SbO_3H_2$	Good	.1576	16.02	32.88	34.61
γ-Chloropropoxy, $ClCH_2(CH_2)_2OCONHC_6H_4SbO_3H_2$	Good	.1579	14.68	31.68	31.66

***p*-Stibino-phenylamino** Alcohols.—One molecular equivalent of the 4-carbo-β-chloro-ethoxy- or 4-carbo-γ-chloropropoxy-aminophenylstibinic acid was suspended in 4 molecular equivalents of a 5% aqueous solution of sodium hydroxide and heated on a water-bath at 70–75°, with occasional stirring, for about thirty minutes. The gummy material which first formed soon dissolved, leaving a small residue of dark-colored material. Dilute acetic acid was then added until a precipitate just began to form. The mixture was decolorized with a small amount of charcoal, filtered and the amino alcohol precipitated with dilute acetic acid. The product was washed with a small amount of water and dried in a vacuum over sulfuric acid.

The amino alcohols thus produced were almost colorless powders, readily soluble in dilute alkali and soluble in hydrochloric acid.

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[6] Rose, *Ann.*, 205, 229 (1880).

Table II

Yields and Analytical Data

p-Aminophenylstibinic acid	%	Analysis Subs., g.	0.0606 N I_2, cc.	Sb, % Calcd.	Found
β-Hydroxy-ethyl-, $HOC_2H_4NHC_6H_4SbO_3H_2$	25	0.1592	17.28	39.55	40.05
γ-Hydroxypropyl-, $HOC_3H_6NHC_6H_4SbO_3H_2$	25	.1608	17.22	37.83	39.51

Determination of Yields.—Since *p*-stibanilic acid decomposes quite rapidly when dried, a weighed sample could not be used in making the derivatives and the yield directly calculated. The amount of acid used was determined by analyzing a 5-cc. aliquot taken with a pipet from the sodium carbonate solution used in the preparation of the derivatives, and from the amount of antimony in this sample the amount of stibanilic acid in the known volume of solution was determined.

Analytical

Different methods were tried for the analysis of these compounds and only fair agreement was obtained. A modification of the iodimetric method of Ewins[7] for arsenic was finally adopted.

A mixture of 0.2 g. of the substance, 10 g. of potassium sulfate and 0.2 to 0.3 g. of starch in a Kjeldahl flask was treated with 20 cc. of concentrated sulfuric acid and heated until colorless. At first a small flame was used, but after half an hour a much hotter one was applied. The clear solution was cooled, diluted with 100 cc. of water and made just alkaline with 10 N sodium hydroxide. In order to dissolve any precipitated oxide, tartaric acid was then added until the solution was faintly acid. To the cooled solution, solid sodium bicarbonate was added in excess, the solution diluted to 350 cc. and titrated with *N*/20 iodine solution using starch as the indicator. The iodine solution was standardized each time with a weighed sample of antimony trioxide using the above procedure. The pure antimony trioxide used for this standardization was prepared by precipitating it from a boiling solution of tartar emetic (1 part to 10 parts of water) with ammonium hydroxide. After boiling for a time the trioxide was filtered and carefully washed.[8]

Summary

1. Methyl, ethyl, propyl, isopropy., butyl, *iso*butyl, β-chloro-ethyl and y-chloropropylchlorocarbonates have been condensed with stibanilic acid and the products isolated and identified (Table I).

2. The dried products were almost colorless powders, insoluble in water, dilute acids, benzene or ether. The methyl, ethyl and β-chloro-ethyl derivatives were slightly soluble in very dilute sodium hydroxide or carbonate solutions; the others were relatively insoluble. All were soluble in alcohol.

3. Two stibinophenylamino alcohols have been prepared (Table II).

Evanston, Illinois

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[7] Ewins, J. Chem. *Soc.*, 109, 1356 (1916).

[8] L. Vanino, "Praparative Chemie," Vol. II, Ferdinand Enke, Stuttgart, p. 195.

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 37]

THE CONSTITUTION OF FLAX CELLULOSE

BY GEORGE W. RIGBY[1]

RECEIVED AUGUST 16, 1928 PUBLISHED DECEMBER 10, 1928

A convenient hypothesis employed for many years by those investigating natural carbohydrates has been to assume cellulose to be a definite compound common to all plants. Cotton, however, containing relatively large percentages of easily purified cellulose, has been accepted quite generally as the source of material to be used as a "standard cellulose." The properties of the cellulose obtained from cotton have been determined with considerable accuracy and these properties have been assumed, in turn, for "cellulose" derived from other sources.

Although there is considerable evidence to justify the assumption that cellulose is a definite compound universally present in plant tissues, as yet no proof has been offered and many contradictory statements are found as to the properties of cellulose when isolated from various sources. In an attempt to aid in clarifying some of the confusion in regard to the universal occurrence of one cellulose and in order to afford a sound basis for the future investigations of the cell walls of the flax fiber,[1a] it was thought worth while to undertake the present research.

Throughout the present investigation each step has been duplicated with both flax and cotton cellulose, thus affording an accurate check on the results and a dependable basis of comparison for the cellulose derived from both sources.

Before proceeding to a discussion of the results of the present investigation, it is well to recall the outstanding researches which have a direct bearing on the present question. No work, however, has been done on the *Constitution of Flax Cellulose.*

As early as 1819 Braconnot[2] prepared glucose from fully bleached linen by the action of sulfuric acid. Blondeau de Caroles[3] isolated a compound to which he ascribed the formula $C_{18}H_{36}O_{18}(SO_3)_2BaO{\cdot}2H_2O$ which, incidentally, corresponds to a compound of a trisaccharide and H_2SO_4. H. Fehling[4] claimed isolation of a compound $C_{90}H_{180}O_{90}(SO_3)_2BaO$, which would correspond to 15 glucose residues. It has been a common observation[5] that mineral acids effect a weakening of linen cloth, with the forma-

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[1] From the thesis of George W. Rigby presented in partial fulfilment of the requirements for the degree of Master of Science, 1928.

[1a] As for example, those of A. E. Cashmore, J. *Chem. Soc.*, 718 (1927).

[2] H. Braconnot, Ann. *chim. phys.*, [2] 12, 172 (1819).

[3] Blondeau de Caroles, *Ann.*, 52,412 (1844).

[4] H. Fehling, *ibid.*, 53, 134–136 (1845).

[5] J. Kolb, *Bull. Mulhouse*, 38, 922 (1868); A. Girard, *Compt. rend.*, 81, 1105–1108 (1875); *Ann. chim. phys.*, 24,337–384 (1881); *Bull. soc. d'encourg.*. [3] 9,176–198 (1882).

tion of "hydrocellulose" in the same way that these acids affect cotton. H. de Mosenthal[6] has shown the "recovered" cellulose obtained by denitration of cellulose nitrate obtained from wood, ramie, flax and cotton to have approximately the index of refraction n_D, 1.5310. The specific heat[7] of linen is given as 0.321 and of cotton as 0.319, while the rotation of a copper–ammonium solution of the cellulose obtained from both sources is identical at $(\alpha)^{20}_{D} = 1000°$.[8] Furthermore, Schwalbe ("Die Chemie der Cellulose") has found highly purified flax cellulose and highly purified cotton cellulose to have practically no reducing properties.

Experimental

In order to secure the purest possible flax cellulose it was found entirely satisfactory to employ the general procedure recommended by the American Chemical Society for use with cotton.[9]

Flax fibers (obtained through courtesy of the Stevens Linen Works of Boston and of the Miles Linen Company of Salem, Oregon) were procured which previously had been retted, scutched and hackled. These fibers were thoroughly combed to remove all adhering woody tissue. At this stage the fibers showed a moisture content of 8%, which, however, is roughly proportional to the relative humidity. Analysis showed an ash content of 0.78% and an amount of wax extractable with hot petroleum ether of 1.65%, after which ethyl ether extracted 0.67% of wax. The same samples extracted with alcohol were found to contain 1.45% of a substance having the odor of burned sugar. (All of the alcohol extract was soluble in dilute alkali.) By the Cross and Bevan method 80.1% of cellulose was found.

About 200 g. of the thoroughly combed flax was placed in *a* large container filled with 1% Ivory soap solution on a steam table. The soap solution was changed daily and the fibers were thoroughly washed before being placed in a new solution. The preliminary soap treatment was deemed complete when, after being in contact with the fibers for a day, the solution remained colorless and the fibers themselves were leached to a very light yellow color. The washed and air-dried material showed: moisture, 7 to 8%; ash, 0.13%; petroleum ether extract, 1.28%; ethyl ether extract, 0.32%; alcohol extract, 0.84%; cellulose (Cross and Bevan), 90 to 95%.

In order to remove all extraneous material before the final purification, the soap-leached fibers were treated directly with 10% sodium hydroxide

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[6] H. de Mosenthal, J. *Soc. Chem. Ind.*, 26, 447 (1907).

[7] O. Dietz, *Wachbt. papier fabr.*, 43, 3119 (1912).

[8] A. Levallois, *Compt.* rend., 99, 1122 (1884); *ibid.*, 100, 456 (1885); K. Hess and E. Messmer, Ber., 55, 2432 (1922).

[9] Report of Committee of the American Chemical Society, J. Ind. Eng. *Chem.*, 15, 748 (1923).

and gaseous chlorine, as in the Cross and Bevan method for estimating cellulose. Bleaching was best effected by using 100-g. samples and continuing the bleach for fifteen-minute intervals, followed by washing and treatment with sodium bisulfite, the process being repeated until a perfectly white, homogeneous material was obtained. The air dry fibers were then subjected to extraction in a Soxhlet apparatus with ethyl ether for eighteen hours, followed by a similar treatment with ethyl alcohol.

Final purification was effected in an apparatus exactly similar to that recommended for making "standard cellulose," the alkali treatment being continued for as much as a week without interruption.[9] In the case of flax the chlorine bleach was found necessary since experiments performed without bleaching, as recommended by Corey and Grey,[10] did not give a homogeneous product. In passing it is significant to note, however, that fibers purified without bleaching yielded cellobiose octa-acetate in spite of their obvious impurity. This result is striking since L. E. Wise[11] has claimed the formation of cellobiose octa-acetate from wood pulp to be an indication of the identity of wood cellulose and cotton. Furthermore, J. C. Irvine[12] points out that with esparto-cellulose "in no case was cellobiose octa-acetate obtained from material which had not been fully exhausted with alkali."

Purified flax cellulose was perfectly white, soft and very lustrous. All of the original long bast fibers were disintegrated into short lengths due to removal of the intercellular matter. The pure flax cellulose was entirely a hexose cellulose, since distillation with 12% hydrochloric acid and subsequent calculation of the phloroglucide by Kröber's tables gave only 1.13% of pentosans, while purified cotton gave 0.95% calculated as pentosans. The pure cotton showed a moisture content of 4.0% when dried at 100° to a constant weight and also when dried over phosphorus pentoxide, while flax cellulose under similar conditious showed **3.5%** moisture. Halides, sulfur, phosphorus and nitrogen were definitely absent, The ash content in both cases was negligible.

Having obtained a highly purified flax cellulose and a generous supply of purified cotton (furnished by the Eastman Kodak Company, copper reduction value 0.001, ash content 0.0001%, a-cellulose 99%), the next problem was to compare the structure of **flax** cellulose with that of cotton cellulose. This was accomplished first by the method of methylation.

The method adopted was essentially the same as was used by Denham.[13] In no case was copper-ammonium used to remove lower methylated derivatives. The first four methylations were made using 30% aqueous

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[10] A. B. Corey and H. L. Grey, *Ind. Eng. Chem.*, 16,853, 1130 (1924).

[11] L. E. Wise and others, J. *Ind. Eng. Chem.*, **15,** 711–713, 815–818 (1923)

[12] Irvine and Hirst, J. *Chem. Soc.*, *125,* 15 (1924).

[13] W. S. Denham, J. *Chem. Soc.*, **119,** 77 (1921); *W.* S. Denham and H. Woodhouse, *ibid.*, 111,244 (1917).

sodium hydroxide and in the later treatments 30% methyl alcoholic potassium hydroxide was used. After three methylations the methoxy content, as determined in a modified Pregl semi-micro methoxy determination outfit, showed 23.6% of methoxy groups. After the fifth treatment, analysis showed 41.1% of methoxy groups. In all treatments the methyl sulfate was dissolved in ether before adding.

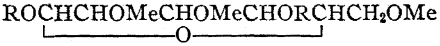
After 18 treatments the methoxy content had risen to 44.7% and continued methylation up to 26 treatments failed to exceed this maximum. The theoretical for trimethylcellulose is 45.6%—this figure, however, having never been reached by any investigator because of experimental difficulties.

Simultaneous hydrolysis and condensation of the methylated cellulose with methyl alcohol in a sealed tube, using 1% hydrochloric acid in methyl alcohol according to the directions of Irvine,[14] gave a clear liquid from which was obtained a golden-yellow sirup of n_D, 1.4632. Since this index of refraction was comparatively low, the sirup was thought to be a mixture of trimethyl- and dimethylglucose. Fractional distillation under 0.003 mm. pressure yielded a perfectly clear and colorless sirup which was collected in three fractions. The first fraction failed to show any tetramethylmethylglucose. This derivative would have been evident by a depression of the index of refraction and an elevation of the methoxy content. The constants obtained for the first and second fractions are compared, for convenience, with the accepted constants for 2,3,6-trimethylmethylglucose in the following tabulation:

Found (first and second fraction) n_D, 1.4592; $(\alpha)^{23}_D$, 67.1° for c = 0.669; MeO, 51.6%.
Accepted constants n_D, 1.4583; $(\alpha)^{20}_D$, 66.1° for c = 1.34; MeO, 52.6%.

The third fraction was found to be a mixture of 2,3,6-trimethylmethylglucose and of the dimethyl derivative. No 2,3,5-trimethylmethylglucose was found.

The conclusion is therefore drawn that completely methylated cotton and flax cellulose yield only 2,3,6-trimethylglucose on hydrolysis



$$\underbrace{\mathrm{ROCHCHOMeCHOMeCHORCH}}_{\mathrm{O}}\mathrm{CH_2OMe}$$

The formation of only 2,3,6-trimethylglucose from both cotton and flax cellulose indicated a similarity between the two, but reveals nothing of the size of the molecule. Furthermore, starch has been found to yield only 2,3,6-trimethylglucose, hence the next step was to prepare cellobiose octa-acetate from both cotton and flax and compare the yields.

As early as 1901, Skraup and König[15] noted that filter paper, from which they prepared cellobiose octa-acetate, consisted of a mixture of cotton and linen fibers. This result indicates that the presence of linen fibers did

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[14] J. C. Irvine and E. L. Hirst, J. *Chem. Soc.*, 123, 518 (1923).

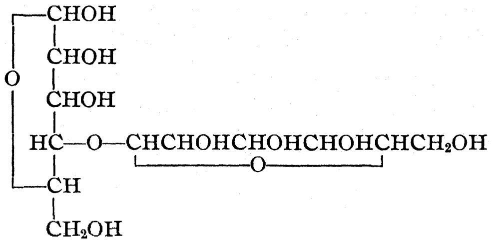
[15] Z. H. Skraup and J. König, *Monatsh.*, 22, 1011–1036 (1901).

not hinder the formation of cellobiose octa-acetate, but does not necessarily show that cellobiose octa-acetate was actually prepared from flax. In the present investigation the work of Skraup and Konig was, therefore, repeated, using highly purified flax cellulose.

Cellobiose octa-acetate was prepared from flax cellulose both according to the directions of Skraup and König[16] and after the method of Haworth and Hirst.[17]

Five grams of flax cellulose yielded, after four recrystallizations from hot 95% alcohol, two grams of cellobiose octa-acetate. This yield is exactly comparable with that obtained from pure cotton under parallel conditions.

Eighteen successive crystallizations from 95% alcohol yielded a material, m. p. 233.9' (corr.), showing no depression when mixed with an authentic sample prepared from cotton. In chloroform solution the rotation was found to be $(\alpha)^{23}_{D} + 40.9°$ for $c = 5.452$ and $(\alpha)^{23}_{D} + 41.4"$ for $c = 7.834$ in chloroform. C. S. Hudson[18] reports $(\alpha)^{20}_{D} + 41.95°$ for $c = 9.87$ and $(\alpha)^{20}_{D}$, + 40.87' for $c = 5.85$ in chloroform. As further identification the acetate was saponified in the cold with alcoholic sodium hydroxide and the phenylosazone of the liberated cellobiose prepared, m. p. 207–208°. Schliemann[19] gives 208–211° (corr.) as the melting point. Thus the cellobiose residues may be considered as integral parts of the flax cellulose molecule, as surely as of the cotton cellulose molecule.



Finally it was found that the flax cellulose molecule must contain at least three glucose residues. The method adopted was graded acetolysis after the directions of Irvine.[20] There was obtained by this method at the end of 168 hours a mixture of acetates of a trisaccharide and of an anhydro-trisaccharide, just as in the case of cotton after 100 hours. Six recrystallizations produced by dissolving the acetate in alcohol and precipitating with water yielded a material showing $(\alpha)^{23}_{D} +19.6°$ for $c = 10.608$ and $(\alpha)^{23}_{D} +19.2°$ for $c = 1.721$ in chloroform. Irvine reports $(\alpha)^{20}_{D} +19.4°$ for $c = 2.58$ in chloroform solution. The acetate

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[16] H. Skraup and J. Konig, *Ber.*, 34, 1115–1118 (1901).

[17] W. N. Haworth and E. L. Hirst, *J. Chem. Soc.*, *119*, 197 (1921).

[18] C. S. Hudson and J. M. Johnson, THIS JOURNAL, 37, 1276 (1915).

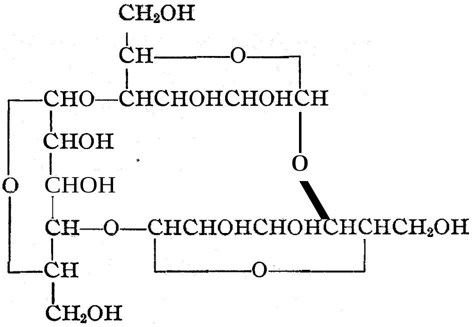
[19] W. Schliemann, *Ann.*, 378, 366–381 (1910).

[20] J. C. Irvine and G. J. Robertson, *J. Chem. Soc.*, 128, 1496 (1926).

is very soluble in cold 95% alcohol. Cellulose triacetate gives $(\alpha)^{20}_{D}$ $-22.3'$ with $c = 0.8092$ in chloroform solution and is insoluble in hot 95% alcohol. Cellobiose octa-acetate a-form is soluble in hot alcohol, but insoluble in the cold and gives a specific rotation of $(\alpha)^{20}_{D}$ $+41°$. The β-form is more soluble in cold alcohol, but has $(\alpha)^{22}_{D}$ $-14.48'$ for $c = 10.88$ and m. p. 202°.

The above described acetates were also obtained by fractional crystallization of the alcohol mother liquor from preparations of cellobiose octa-acetate, after the method of Bertrand and Benoist.[21] Parallel experiments using pure cotton completed the evidence that graded acetolysis yielded the same product from both cotton and flax cellulose.

Hence the unit structure for both cotton and flax cellulose, to the best of our present knowledge, may be represented by an anhydro-trisaccharide formula as proposed by Irvine.



Summary

From the above reported results the following general conclusions are proposed:

1. Flax bast fibers consist of cells composed of pure cellulose and an intercellular material containing a furfural-yielding constituent.

2. The glucose residues in flax cellulose are joined together in positions one and four by glucoside linkages, as are those in cotton.

3. Cellobiose is obtained from flax cellulose in yields equivalent to those from cotton. This assures that at least two glucose residues are combined in the cellulose and suggests that probably at least three are combined in a unit from which the cellulose molecule is constructed—as proposed by J. C. Irvine.

4. Acetates of a trisaccharide and of an anhydro-trisaccharide may be obtained from flax cellulose. This supports the proposed anhydro-trisaccharide unit formula.

5. The above submitted results point to the chemical identity of cotton

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[21] G. Bertrand and S. Benoist, *Compt. rend.*, 177, **85-87 (1923)**; *ibid.*, **176**, 1583–1587 **(1923)**.

and flax cellulose, without reference to the relative states of polymerization.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION PROM THE CHEMICAL RESEARCH LABORATORIES OF SHARP AND DOHME]

CATALYTIC REDUCTION OF NITRILES AND OXIMES

BY WALTER H. HARTUNG

RECEIVED AUGUST 30, 1928 PUBLISHED DECEMBER 10, 1928

In a study undertaken in this Laboratory it became desirable to reduce oximes and nitriles catalytically to pure primary amines. A review of the available literature showed that a large amount of research has been done on this type of reduction but that invariably a mixture of primary and secondary bases was obtained, with the latter often predominating.

Benzonitrile and benzaldoxime when reduced by gaseous hydrogen with palladium or nickel catalysts gave mixtures of benzylamine, dibenzylamine and ammonia.[1] From α- and β-naphthonitriles, phenylacetonitrile and β-phenylpropionitrile, Rupe and his coworkers obtained mixtures of the corresponding primary and secondary amines with ammonia. From acetaldoxime and propionaldoxime triethyl- and tripropylamines, respectively, and ammonia were obtained, while from benzophenone-oxime Paal and Gerum isolated a 57% yield of primary amine. Mignonac[2] obtained ketimines from the oximes of cyclohexanone, acetophenone and propiophenone. Braun, Blessing and Zobel,[3] by reducing nitriles in various non-aqueous solvents, found that they obtained both primary and secondary amines, the amount of each depending on the concentration and on the nature of the solvent. Vavon and Berton[4] report that cyclic ketoximes reduced with platinum from hydroxylamines.

Rosenmund and Pfankuch[5] were the first to forestall the formation of secondary amine by using the acetate of the oxime and an acetic acid solution of the nitrile. Thus benzaldoxime acetate gave a 91% yield and benzonitrile an 80% yield of benzylamine, benzylcyanide gave a 73% yield of phenylethyl amine, while *p*-hydroxybenzylcyanide again formed secondary amine.

Hence it appears that except for the methods of Rosenmund and Pfankuch and Carothers and Jones,[6] there is no known general procedure for

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[1] (a) Paal and Gerum, *Ber.*, 42, 1553 (1908); (b) Rupe and Beckerer, *Helv. Chim. Acta*, 6, 880 (1923); (c) Rupe and Glenz. *ibid.*, 5, 937 (1922); (d) Rupe and Hodel, *ibid.*, 6, 865 (1923); (e) Gulewitsch, *Ber.*, 57, 1645 (1924).

[2] Mignonac, *Compt. rend.*. 170, 936 (1920).

[3] Braun, Blessing and Zobel, *Ber.*, 56, 1988 (1923).

[4] Vavon and Berton, *Bull. soc. chim.*, 37, 296 (1925).

[5] Rosenmund and Pfankuch. *Ber.*. 56, 2258 (1923).

[6] Carothers and Jones, THIS JOURNAL, 47, 3051 (1925), using platinum catalyst in acetic anhydride solvent, reduced several nitriles to the corresponding primary amines,

the catalytic hydrogenation or reduction of nitriles and oximes to the corresponding pure primary amines.

An investigation in this Laboratory shows that it is possible to reduce benzonitrile and benzaldoxime to primary amine without contamination from the secondary base, by carrying out the reduction with palladinized charcoal in a solution of absolute alcohol containing hydrogen chloride, the base being isolated as the salt. Benzonitrile with one equivalent, or more, of hydrogen chloride was reduced very smoothly to benzylamine hydrochloride. Benzaldoxime yielded similar results when three equivalents of hydrogen chloride were used, whereas with one equivalent a mixture of the salts of the primary and secondary bases was obtained. When no acid was present both the nitrile and oxime formed benzylamine, dibenzylamine and ammonia, as previous investigators have found.

Mandelonitrile was also reduced under similar conditions. The product, however, was not phenylethanolamine, as one might expect, but phenylethylamine, for the alcoholic hydroxyl was also reduced; this happened even when the reaction was stopped on the absorption of sufficient hydrogen to reduce theoretically only the nitrile group; but the yield of primary amine salt was very low, 52% of the theoretical, and a non-basic by-product was formed which was not identified. Much better yields of phenylethylamine hydrochloride were obtained by starting with the benzoic and acetic acid esters of mandelonitrile. Esterification of the hydroxyl group did not protect it, for both the benzoate and acetate resulted in good yields of phenylethylamine hydrochloride. A similar reduction of the hydroxyl group, also catalytically, is recorded by Rosenmund and Schindler,[7] who obtained phenylethylacetic acid and substituted phenylethylacetic acids from mandelic and substituted mandelic acids where the hydroxyl group had been esterified.

An attempt to reduce benzonitrile in a solution of dibutyl ether without hydrogen chloride was a failure for only about a tenth of the hydrogen calculated for the complete reduction was absorbed. That the catalyst had not become poisoned was demonstrated by the fact that it subsequently reduced benzonitrile in absolute alcoholic solution. An attempt to reduce mandelonitrile acetate in benzene solution also resulted in failure.

Procedure and Apparatus

The reduction was carried out by shaking the substance to be reduced in an atmosphere of hydrogen delivered from a graduated cylinder under a pressure of approximately 30 inches of water.

The oxime or nitrile was dissolved in the proper amount of absolute alcohol and placed along with the catalyst in the reaction flask. The

isolating them as their acetyl derivatives, from which the free amine could be obtained by subsequent hydrolysis.

[7] Rosenmund and Schindler, *Arch. Pharm.*, **266**, 281 (1928).

reaction flask was connected to the hydrogen delivery train by means of a ground-glass joint held together with rubber bands caught over small projecting glass hooks. The only rubber connection throughout the whole apparatus was that joining the hydrogen tank to the delivery tube. The air was removed by evacuating the apparatus, filling with hydrogen and repeating the process at least four times, which left an atmosphere of practically pure hydrogen. No hydrogen was taken up until agitation was begun.

Reagents and Materials

The catalyst was palladinized charcoal, prepared according to the directions of Ott and Schroter.[8] Three grams of pure animal charcoal from Merck and Co. was shaken with an aqueous solution of 0.45–0.50 g. of palladium chloride in an atmosphere of hydrogen until saturated. The charcoal was then filtered off, washed, dried and kept in *vacuo* over sulfuric acid until used. Each catalyst could be used for three or four experiments.

The hydrogen was a pure, commercial, electrolytic product. Before reaching the reduction flask it was passed through an alkaline solution of pyrogallol, a solution of sodium hydrosulfite and then through a long tube containing calcium chloride and soda lime. The hydrogen so purified was entirely satisfactory and good results were obtained with it.

The benzonitrile was used as obtained from Eastman Kodak Company.

The benzaldoxime was prepared from benzaldehyde and hydroxylamine and boiled at 101–103° at 6–7 mm.[9]

The mandelonitrile was prepared according to the directions of Ultée.[10] To a mixture of 26.5 g. (0.25 mole) of freshly distilled benzaldehyde and 8.2 g. (0.3 mole) of hydrogen cyanide[11] was added a few drops of concentrated potassium hydroxide solution as catalyst. The temperature rose spontaneously to 50°; after it began to cool, the mixture was placed in a freezing bath and within about an hour, with occasional shaking, crystals began to appear on scratching the walls of the container, and very soon almost the whole mixture was solid. The crystals were removed by suction on a previously cooled Buchner funnel and by again freezing the filtrate more crystals were obtained. The crystalline product was pressed, in the ice-box, between two porous plates to remove non-crystallizable matter; this left a beautiful white product that melted at 20°, which agrees with the figure given by Ultée. "International Critical Tables," Vol. I, gives the melting point for mandelonitrile as −15°. No medium was found for recrystallizing the mandelonitrile, not even when the solutions were chilled in a mixture of ether and carbon dioxide snow.

Mandelonitrile benzoate was prepared as described by Francis and Davis.[12]

Mandelonitrile acetate was prepared according to the directions of Michael and Jeanprêtre.[13]

Experimental Results

Reduction of Benzaldoxime.—Three grams of benzaldoxime (0.025 mole) was dissolved in 40 cc. of absolute alcohol containing 3 equivalents of hydrogen chloride, and

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[8] Ott and Schroter, *Ber.*, 60, 633 (1927).

[9] Bourgeois and Dambmann, *Ber.*, 26, 2857 (1893).

[10] Ultée, *Rec. trav. chim.*, 28, 254 (1909).

[11] Ziegler, "Organic Syntheses," John Wiley and Sons, Inc., New York, 7, 50 (1927).

[12] Francis and Davis, *J. Chem. Soc.*, 95, 1404 (1909).

[13] Michael and Jeanprêtre, *Ber.*, 25, 1681 (1892).

in ninety minutes reduction was complete. The catalyst was removed by filtration, the first aqueous washing evaporated to dryness, the residue taken up in hot absolute alcohol and added to the filtrate. The alcoholic filtrate was partially evaporated and diluted with excess ether. The crystals thus obtained melted at 258°; the yield of hydrochloride was practically quantitative. When but one equivalent of hydrogen chloride was used the product melted at 220–230°; it formed two benzenesulfonyl derivatives, the alkaline insoluble one melting at 67°,[14] and the alkaline soluble derivative melting at 86–87°.[15] The primary amine predominated, however. When no hydrogen chloride at all was used, a mixture of primary and secondary bases resulted.

Benzonitrile reduced under the same conditions as described for benzaldoxime resulted in pure benzylamine hydrochloride. Here, however, one equivalent of hydrogen chloride, or more, prevented the formation of secondary amine, whereas without hydrogen chloride a mixture of benzylamine, dibenzylamine and ammonia was obtained.

Reduction of Mandelonitrile.—A solution of 5.8 g. of mandelonitrile (0.0436 mole) in 90 cc. of absolute alcohol containing 0.049 mole of hydrogen chloride absorbed 2080 cc. of hydrogen in ninety minutes; the amount calculated for reduction to phenylethanolamine was 1970 cc.; for complete reduction to phenylethylamine, 2950 cc. The catalyst was removed by filtration and the filtrate was reduced to a volume of about 15 cc. and diluted with excess ether, which caused a crystalline solid to settle out; the solid, after recrystallization from absolute alcohol, melted at 215°.[16] The free base distilled at 200°[17] and when exposed to the air quickly formed a solid which effervesced with dilute acid and after washing with ether melted at 103°.[18] The product formed an alkali-soluble benzenesulfonyl derivative which melted at 68–69°.[19] It formed a benzoyl derivative which melted at 120°.[20] Comparison of the product here obtained and its derivatives with known phenylethanolarnine hydrochloride and its corresponding derivatives, showed them to be distinctly different compounds. Thus mandelonitrile was reduced to phenylethylamine. The salt is, however, obtained in small yield (52%) for rectification of the alcohol-ether mother liquors showed that a non-basic by-product was formed which was not identified.

Reduction of Mandelonitrile Benzoate.—A solution of 5.9 g. (0.025 mole) of mandelonitrile benzoate in 60 cc. of absolute alcohol containing 0.057 mole of hydrogen chloride absorbed, in sixty minutes, 1640 cc. of hydrogen; calculated for reduction to the benzoate of phenylethanolamine, 1125 cc.; for reduction to phenylethanolamine, 1680 cc. The product, isolated in the usual manner, gave the characteristic tests for phenylethylamine hydrochloride and was obtained in 84.5% yield. Attempts to use only one equivalent of hydrogen chloride, added during the course of reduction, also resulted in phenylethylamine but in poorer yields and with contaminating by-products.

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[14] Melting point of benzenesulfonamide derivative of dibenzylamine 68° [Beckmann and Fellrath, *Ann.*. **273**, 22 (1893)].

[15] Melting point of N-benzylbenzenesulfonamide, 88° [Hinsberg, *Ann.*, 265, 182 (1891)].

[16] Melting point of phenylethylamine hydrochloride 217° (Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, **1916**, Vol. **11**, p. 146.)

[17] Boiling point of phenylethylamine, 197–198" at 725 mm. (Mulliken, ref. 16).

[18] Phenylethylamine carbonate melts at 101–104° [Fileti and Piccini, *Ber.*, **12**, 1700 (1879)].

[19] Johnson and Guest, *Am. Chem.* J., **42**, 248 (1909), give the melting point of N-phenylethylbenzenesulfonamide as 68–69°.

[20] Melting point of N-phenylethylbenzamide, 113–114° [Bischler and Napieralski, *Ber.*, **26**, 1905 (1893)].

The reduction of mandelonitrile acetate was carried out after the manner of the benzoate. From 4.4 g. (0.025 mole) of the nitrile acetate there was obtained in seventy-five minutes 3.9 g. of phenylethylamine hydrochloride, a yield of 74.5%.

Conclusions

1. Benzonitrile was reduced catalytically in absolute alcoholic solution to pure benzylamine by means of palladinized charcoal when one equivalent, or more, of hydrogen chloride was present; without hydrogen chloride a mixture of benzylamine, dibenzylamine and ammonia was formed.
2. Benzaldoxime was similarly reduced to pure benzylamine when three equivalents, or more, of hydrogen chloride were present. With one equivalent, or more, of the acid a mixture of the primary and secondary bases resulted.
3. Mandelonitrile was reduced in absolute alcoholic solution containing hydrogen chloride to phenylethylamine, but the yields of primary amine were poorer because a non-basic by-product was formed.
4. The benzoate and acetate of mandelonitrile were also reduced; though the esters of phenylethanolamine were not formed, good yields of phenylethylamine were obtained.

BALTIMORE, MARYLAND

[COMMUNICATION FROM THE DEPARTMENT OF INDUSTRIAL AND CELLULOSE CHEMISTRY, McGILL UNIVERSITY]

STUDIES ON REACTIONS RELATING TO CARBOHYDRATES AND POLYSACCHARIDES. XVIII. PARA-NITROBENZYLIDENE GLYCOLS AND GLYCEROLS

BY HAROLD HIBBERT AND MURRAY G. STURROCK[1]

RECEIVED SEPTEMBER 28, 1928 PUBLISHED DECEMBER 10, 1928

In order to facilitate the isolation of the various isomeric forms obtained in condensing an aldehyde with glycerol,[2] it seemed advisable to try to find some aldehyde capable of yielding crystalline cyclic acetals.

Experiments carried out with *p*-nitrobenzaldehyde show that this material condenses readily with both ethylene and 1,3-trimethylene glycol, yielding crystalline five- and six-membered cyclic acetals, respectively. Preliminary experiments using glycerol in place of the glycols gave a mixture of a crystalline and liquid *p*-nitrobenzylidene glycerol, a detailed investigation of which is recorded in the following communication (Part XIX).

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[1] Presented to the Faculty of the Graduate School, McGill University, in June, 1927, in candidature for the degree of Master of Science. The authors' thanks are due to the National Research Council, Ottawa, for their kind support accorded one of them (M. G. S.) in the form of a Bursary.

[2] Hibbert and coworkers, THIS JOURNAL, 50, 2235, 2242, 3120 (1928).

Experimental Part

Preparation of *p*-**Nitrobenzylidene Ethylene** Glycol.—Twenty g. of *p*-nitrobenzaldehyde was mixed with 31 g. of ethylene glycol (2.5 times the theoretical) and 0.2 cc. of 40% sulfuric acid and the mixture heated, with agitation, on the steam-bath for six hours. On cooling, the product set to a solid mass of crystals. The latter were washed well with water, then a number of times with a saturated solution of sodium bisulfite and again with water. Recrystallization from alcohol gave 15 g. (60%) of pure *p*-nitrobenzylideneethylene glycol; m. p. 90.5°.

Anal. Subs., 0.1689; CO_2, 0.3430; H_2O, 0.0700. Calcd. for $C_9H_9O_4N$: C, 55.38; H, 4.60. Found: C, 55.08; H, 4.57.

The product is soluble in cold acetone, chloroform and pyridine, in *hot* carbon tetrachloride, alcohol and carbon bisulfide, but is insoluble in ligroin.

Preparation of *p*-**Nitrobenzylidene** Trimethylene Glycol.—Using a procedure similar to the above, 25 g. of 1,3-trimethylene glycol yielded 10 g. (71%) of pure *p*-nitrobenzylidene trimethylene glycol, m. p. 111.5°, having approximately the same solubilities as its lower homolog.

Anal. Subs., 0.2306; CO_2, 0.4873; H_2O, 0.1100. Calcd. for $C_{10}H_{11}O_4N$: C, 57.4; H, 5.31. Found: C, 57 6; H, 5.31.

Preparation and Separation of the Isomeric *p*-**Nitrobenzylidene Glycerols.**—Twenty g. of p-nitrobenzaldehyde, 24 g. of glycerol and 0.2 cc. of 40% sulfuric acid were heated, with stirring, for about six to ten hours. The temperature used in different experiments varied from 100 to 160". After cooling, water was added and the mixture extracted twice with ether. The latter solution was washed with a concentrated solution of sodium bisulfite and a small amount of water. The ether was evaporated under reduced pressure and the residue taken up with warm benzene. On cooling (and further evaporation, if necessary) crystals separated which were filtered off. Evaporation of the mother liquor yielded a second crop and the process was repeated until no further crystallization took place on long standing in the cold.

The combined yield of crystals was treated with animal charcoal and recrystallized from hot benzene, giving pure *p*-nitrobenzylidene glycerol, m. p. 85°, initially, increasing on standing to 99°.

Anal. Subs., 0.1224; CO_2, 0.2411; H_2O, 0.0535. Calcd. for $C_{10}H_{11}O_5N$: C, 53.5; H, 4.93. Found: C, 53.7; H, 4.84.

The oil from the mother liquor was dissolved in benzene, the solution heated with animal charcoal, filtered and the oily layer which separated on cooling further purified by precipitating several times from small volumes of benzene at −15°. The oil thus obtained proved to be the isomer of the above crystalline compound.

Anal. Subs., 0.2004; CO_2, 0.3028; H_2O, 0.0888. Calcd. for $C_{10}H_{11}O_5N$: C, 53.3; H, 4.93. Found: C, 53.5; H, 4.84.

Preparation of the Benzoates of the Isomeric *p*-**Nitrobenzylidene** Glycerols.—The benzoates of the two isomeric glycerol acetals were prepared in each case by dissolving 3 g. of the acetal in dry pyridine, adding an equal volume of benzoyl chloride and then warming slightly. After allowing ten minutes for completion of the reaction, the product was poured into 250 cc. of water, when the benzoates separated as a white or yellow paste.

The benzoate of the crystalline isomer was recrystallized from benzene; m, p. 198°.

Anal. Subs., 0.1388; CO_2, 0.2924; H_2O, 0.0524. Calcd. for $C_{17}H_{15}O_6N$: C, 62.07; H, 4.59. Found: C, 61.92; H, 4.52.

The benzoate of the liquid isomer was recrystallized from alcohol; m. p. 178°.

Anal. Subs., 0.1284; CO_2, 0.2909; H_2O, 0.0513. Calcd. for $C_{17}H_{15}O_6N$: C, 62.07; H, 4.59. Found: C, 61.78; H, 4.43.

Summary

1. p-Nitrobenzaldehyde condenses readily with ethylene glycol and 1,3-trimethylene glycol to give the corresponding cyclic acetals.
2. Preliminary experiments indicate that p-nitrobenzaldehyde readily condenses with glycerol to give an isomeric mixture of cyclic acetals.

CANADIAN PULP AND PAPER RESEARCH INSTITUTE
MONTREAL, CANADA

[COMMUNICATION FROM THE DEPARTMENT OF INDUSTRIAL AND CELLULOSE CHEMISTRY, McGILL UNIVERSITY]

STUDIES ON REACTIONS RELATING TO CARBOHYDRATES AND POLYSACCHARIDES. XIX. STRUCTURAL, GEOMETRICAL AND OPTICAL ISOMERISM OF THE PARA-NITROBENZYLIDENE GLYCEROLS AND THEIR DERIVATIVES

BY HAROLD HIBBERT AND NEAL M. CARTER[1]

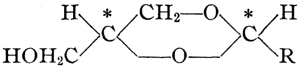
RECEIVED SEPTEMBER 28, 1928 PUBLISHED DECEMBER 10, 1928

Introduction

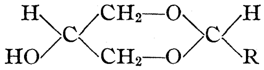
In previous communications[2] it has been pointed out that when an aldehyde (RCHO) condenses with glycerol, there results a "partition" of the aldehyde between the 1,2- and the 1,1′-hydroxyl groups, so that in the subsequent condensation structural isomers are formed, namely, five- and six-membered cyclic acetals.

An examination of these general types A and B

(A)



(B)



shows that the five-membered ring (A) should exist in two geometrically isomeric, optically resolvable racemic forms, due to the presence of the two asymmetric carbon atoms (*). On the other hand, the six-membered acetal, (B), representing as it does a case of pseudo-asymmetry, should exist only in two geometrically isomeric, non-resolvable modifications.

Only a few references to geometrical isomerism in heterogeneous ring systems are to be found in the literature. Among the better-known examples is its application to explain the difference between paraldehyde

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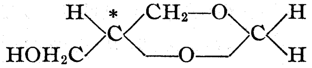
[1] Research Fellow, McGill University. This work was carried out under the auspices of the cooperative research organization embracing the Canadian Pulp and Paper Association, the Pulp and Paper Division of the Forest Products Laboratory of Canada and the Department of Industrial and Cellulose Chemistry, McGill University. The authors wish to express their thanks for the support accorded them.

[2] Hibbert and coworkers, THIS JOURNAL, 50, (a) 2235, (b) 2242, (c) 3120 (1928).

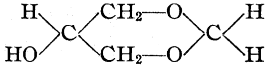
and metaldehyde.[3] Peacock,[4] in drawing attention to the existence of two optically active centers in cyclic acetals of type (A), mentions the possibility of geometrical isomerism, but his product was .of such a character that the isomerism might well have been due to a double bond in the aldehydic residue. A recent paper by Boeseken and Felix[6] is also of interest in this connection. The five-membered cyclic acetals of glycerol (with the exception of that from formaldehyde) should therefore show the interesting property of possessing simultaneously all three types of isomerism: structural, geometrical and optical. The six-membered acetals cannot give rise to optical isomerism due to absence of an asymmetrical carbon atom.[6]

The substitution of HCHO for RCKO in the formation of acetals, for example, the condensation of formaldehyde with glycerol, results in the synthesis of the two structurally isomeric acetals (C) and (D) (methylidene glycerols) in which geometrical isomerism is no longer possible.

(C)



(D)



and the authors have shown[2c] that only two structural isomers are actually formed, one of which, however, the five-membered acetal, should be capable of further resolution into two optically active enantiomorphs, due to the asymmetric carbon atom (*).

Following this, attempts were made to find a suitable product capable of yielding crystalline glycerol acetals of both types (A) and (B) and, while this has proved unsuccessful, it has nevertheless been possible (as is shown

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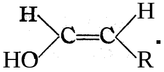
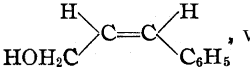
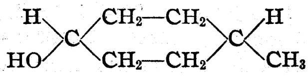
[3] Compare Baumann and Fromm, *Ber.*, 24,1426–1429, 1457 (1891).

[4] Peacock, J. *Chem. Soc.*, **107**, 816 (1915).

[5] Böeseken and Felix, *Ber.*, **61B**, 787–790 (1928).

[6] If the ring of formula (B), symmetrical about a line joining its terminal carbon atoms, be reduced to its simplest form, namely a double bond, a compound of the following type would be created:  $\begin{matrix}H\\HO\end{matrix}\!>C=C<\!\begin{matrix}H\\R\end{matrix}$. This, although unstable in itself, closely corresponds to the structure of cinnamyl alcohol:  $\begin{matrix}H\\HOH_2C\end{matrix}\!>C=C<\!\begin{matrix}H\\C_6H_5\end{matrix}$, which is admittedly an inactive compound. Compare Perkin, Pope and Wallach, J. *Chem. Soc.*, *95*, 1790–1791 (1909), and the structure of hexahydroterephthalic acid.

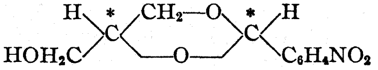
Confirmation of this view is found in the work of Gough, Hunter and Kenyon, *J. Chem. Soc.*, 2055 (1926), on the optical activity of secondary alcohols. In working with 2-, 3- and 4-methylcyclohexanols these authors found that the 2- and 3-isomers were resolvable while the 4-isomer, in accordance with the classical theory of symmetry, resisted all efforts at resolution. It will be observed that the structure of this compound



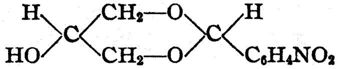
cis and *trans* forms, is quite analogous to the structure of a six-membered cyclic acetal of type (B).

in the experimental part) to isolate, in the case of the *p*-nitrobenzylidene glycerols, not only the two structurally different five- and six-membered ring isomers, but also to obtain, in the case of certain of their derivatives, the total number of isomers theoretically possible, namely, the two geometrically isomeric, racemic forms[7] of the five-membered ring type, (E), and the two geometrical isomers corresponding to the six-membered acetal, (F).

(E)



(F)



Preliminary experiments in this Laboratory[8] showed that the condensation of p-nitrobenzaldehyde with glycerol yielded two easily separable *p*-nitrobenzylidene glycerols, one crystalline and the other a slightly viscous oil. The former, even after repeated crystallizations, still exhibited a rise in melting point from 88°, when freshly crystallized, to 95–98° after standing for some days in a stoppered bottle. This change corresponds closely with that recorded by Irvine and coworkers[9] when investigating the benzylidene glycerols, and was attributed by them to partial decomposition.

The solid 1,1′-*p*-nitrobenzylidene glycerol (I) thus appeared to consist of a mixture of two geometrical isomers. Attempts to obtain the higher melting form in a pure state by recrystallization were unsuccessful due to the above-mentioned fact that the more stable derivative under these conditions again yields crystals with the lower melting point.[10] This change was at first attributed to a partial conversion of one ring structure into the other, but this did not explain why the melting-point of the crystals should *rise* if they tended to revert to the viscous, oily isomer. Work was therefore undertaken with the object of obtaining crystalline derivatives by replacement of the hydrogen in the remaining hydroxyl group of the free acetals, so as no longer to permit of such a *structural* change, thereby facilitating the isolation of the theoretically possible geometrical isomers. This has now been successfully accomplished and the synthesis and relationship of these derivatives is indicated below.

Isomeric Derivatives from 1,1′-*p*-Nitrobenzylidene Glycerol (I).—Methylation of the crystalline mixture of isomeric 1,1′-*p*-nitrobenzylidene glycerols (I) yielded two isomeric 1,1′-*p*-nitrobenzylidene glycerol 2-methyl ethers (III and IV), the constitution of each being definitely

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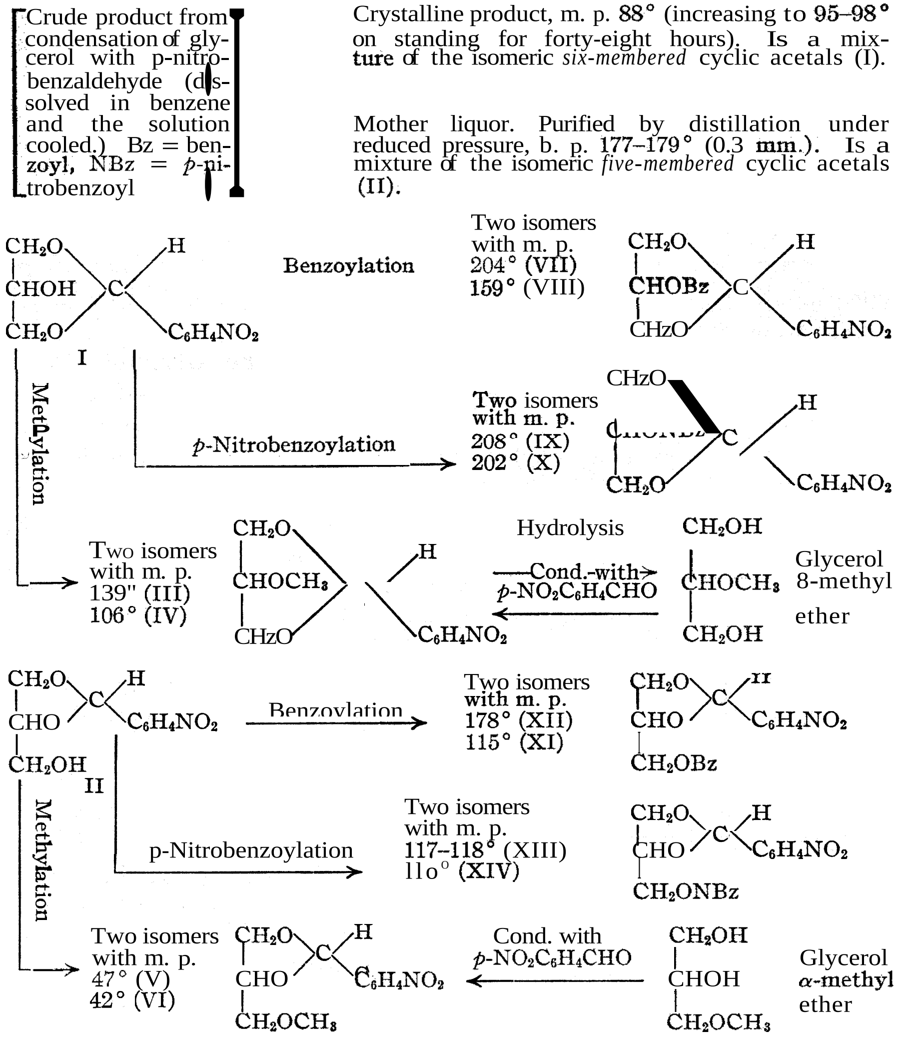
[7] The resolution of certain of these racemic forms will afford additional evidence of the ring structures, and is shortly to be undertaken.

[8] Hibbert and Sturrock, THIS JOURNAL, 50, 3374 (1928).

[9] Irvine, Macdonald and Soutar, J. Chem. *Soc.*, 107, 344 (1915).

[10] A similar case of conversion of geometrical isomers on solution occurs with iodoacrylic acid. The isomer melting at 65° is converted into that melting at 139–140° on recrystallization from ligroin [Stolz, *Ber.*, 19, 542 (1886)].



Crude product from condensation of glycerol with p-nitrobenzaldehyde (dissolved in benzene and the solution cooled.) Bz = benzoyl, NBz = *p*-nitrobenzoyl

Crystalline product, m. p. 88° (increasing to 95–98° on standing for forty-eight hours). Is a mixture of the isomeric *six-membered* cyclic acetals (I).

Mother liquor. Purified by distillation under reduced pressure, b. p. 177–179° (0.3 mm.). Is a mixture of the isomeric *five-membered* cyclic acetals (II).

proved by their separate hydrolysis, and identification in each case of the resulting product by means of its physical properties (boiling point and refractive index), as glycerol β-methyl ether.

This result was further confirmed by condensing *p*-nitrobenzaldehyde with glycerol β-methyl ether (obtained by hydrolysis of 1,1′-benzylidene glycerol 2-methyl ether), and again identifying the resulting product as a mixture of III and IV. This latter experiment also served to definitely identify acetal I and its derivatives as belonging to the six-membered ring type.

In separating III from IV by fractional crystallization there was observed the same peculiar tendency for crystals of one form to commence growing on facets of the other that was experienced in separating other pairs of stereoisomeric derivatives of this acetal. In some cases when working initially with small quantities, the presence of two isomers of different melting points was only established by isolating the two forms by hand, using for the purpose a needle point under a lens. Ordinary careful recrystallization yielded a product of indefinite melting point unless the process was at least partially mechanical.

Following the isolation of the two isomeric methyl ethers, that of the corresponding benzoates VII and VIII and of the p-nitrobenzoates IX and X was accomplished.

Isomeric Derivatives from **1,2-*p*-Nitrobenzylidene** Glycerol (II).—The 1,2-*p*-nitrobenzylidene glycerol (II) was purified by distillation under very low pressure (0.5 mm.). The distillate obtained was an apparently homogeneous, slightly viscous, amber-colored oil which resisted all attempts at crystallization. On methylation it was converted into a yellowish oil which crystallized only after inoculation with crystals of the two forms of the anticipated 1,2-*p*-nitrobenzylidene glycerol 1′-methyl ethers (V and VI), which were obtained by direct synthesis from glycerol α-methyl ether and *p*-nitrobenzaldehyde. Although two isomeric methyl ethers should be formed in the methylation of the 1,2-*p*-nitrobenzylidene glycerol II, it was only possible to isolate one of these (V) in appreciable amount, due probably to the further depression of their already low melting points (42 and 47°, respectively), by impurities in the mother liquor. It is also possible that in the distillation process, or during methylation, conditions exist which favor the formation of the one ether (V) at the expense of the other (VI). Nevertheless, it was found possible to obtain definite evidence of the presence of the second isomer (VI), and the simultaneous production of traces of 1,1′-*p*-nitrobenzylidene 2-methyl ether (III) showed that the method of purification of the 1,2-*p*-nitrobenzylidene glycerol (II) by distillation was not sufficient to free it from the last traces of its structural isomer, the 1,1′-*p*-nitrobenzylidene glycerol (I).

Both isomeric forms (XIII and XIV) of the p-nitrobenzoate of the five-membered acetal (II) were prepared from the latter, and one form (XI) of the benzoate. The second isomeric benzoate (XII) had been previously isolated[7] in this Laboratory in connection with work done on another phase of this general problem.

Failure to isolate the two stereoisomeric forms of each of the two free acetals (I and II) is possibly to be attributed to the influence of the higher polarity associated with the hydrogen of the free hydroxyl group in facilitating the conversion of the labile into the stable form.[11] The pro-

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[11] By conversion of the liquid acetal (II) into a mixture of its corresponding isomeric

duction, however, of both cis and *trans* isomers from apparently homogenous products upon treatment with certain reagents has been recorded.[3,12]

The close similarity of the melting points of certain of the stereoisomers obtained in this investigation is in accord with other known cases.

	Cis isomer, m. p.	*Trans* isomer, m. p.
1,2-Cyclobutane	137–138°	131°
Limonene nitrosochloride	103–104"	105–106°
Menthylamine	207–208°	209–210°

No efforts have as yet been made to determine the exact configuration of the geometrical isomers. The repeated occurrence of one well-developed crystalline, yellow or greenish form, and one more or less amorphous, white form in the case of certain of the stereoisomeric pairs suggests that the former may be the *trans* form.[13]

Experimental Part

Preparation and Separation of the 1,1′- and 1,2-*p*-Nitrobenzylidene Glycerols I and 11.—After several standard methods of acetal preparation had been attempted, a new procedure for this condensation was developed which is apparently applicable to any case where the aldehyde and polyalcohol have sufficiently high boiling (or melting) points.

One hundred and sixty-six g. of *p*-nitrobenzaldehyde (m. p. 106°, recrystallized from hot water) was heated for twenty niinutes at 120° with 110 g. (3% excess over the theoretical amount) of glycerol and six drops of 40% sulfuric acid as catalyst. During this period suction was gradually applied to the reaction flask until toward the end a pressure of 15 mm. was reached. This removed the water formed in the reaction as fast as it was generated; loss of weight calculated as water, 20.1 g. (105% of theoretical). The resulting homogeneous, light reddish oil was dissolved in sufficient benzene to keep in solution at 30° the crystals that tend to separate. The solution was washed at this temperature with dilute aqueous sodium bicarbonate to remove the excess glycerol and the sulfuric acid, then with water, and finally dried over sodium sulfate. On cooling the benzene solution to 0° overnight, large yellowish needle-like prisms of 1,1′-p-nitrobenzylidene glycerol (I) formed, both in the benzene solution and in the reddish oil which settled out during the cooling. These were filtered off and on recrystallization from benzene melted initially at 88°. On standing for a week the melting point had risen to 95° and the clear crystals had lost their transparency. After some time a maximum melting point of 98° was apparently reached, although recrystallization from benzene, at any stage, yielded crystals with the original m. p. of 88°.

The product is readily soluble in alcohol, ether, acetone, ethylene bromide and warm benzene but insoluble in ligroin and water. It is odorless and exhibits no tendency toward hydrolysis even after exposure to the air for prolonged periods of time.

Anal. Subs., 0.1224: CO_2, 0.2411; H_2O, 0.0535. Calcd. for $C_{10}H_{11}O_5N$: C,

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benzoates XI and XII, and subjecting each of these separately to an alkaline hydrolysis involving only the benzoyl group, it is hoped to isolate the two forms of the acetal in a crystalline state.

[12] Wallach, Ann., 252, 113 (1899); Baeyer, *ibid.*, 245, 103 (1888).

[13] Paal and Schulze, *Ber.*, 35, 168 (1902).

53.35; H, 4.93. Found: C, 53.70; H, 4.84. Mol. *wt.* Subs., 0.3001; ethylene bromide, 39.50; *ΔT*, 0.404°. Mol. wt. found: 222. Theoretical: 225.

The mixture of reddish oil and benzene obtained as a filtrate in the separation of the above crystals became homogeneous on warming, and evaporation to one-fourth of its original bulk, followed by cooling yielded a second small crop of the crystalline isomer (I). This was removed by filtration and the oil thus obtained, when distilled under a pressure of approximately 0.5 to 1.0 mm., yielded at first a trace of unchanged *p*-nitrobenzaldehyde, later, a clear, amber colored, slightly viscous oil boiling between 195–215°. Redistillation of the latter under slightly lower pressure (approximately 0.3 mm.) yielded 95 g. of a similar oil boiling between 177 and 179°. Later experiments showed that this product still contained a small amount of the crystalline isomer (I). This distillate, which is the purest sample of 1,2-*p*-nitrobenzylidene glycerol (II) yet obtained, resisted all efforts at crystallization. When cooled to −70° a hard glass resulted, and a methyl alcohol solution, cooled to the same temperature, yielded an amorphous sludge which melted during the filtration at −20°. Other solvents proved equally ineffective as crystallizing media.

The liquid isomer is practically odorless and has the same solubilities as the crystalline isomer (I). Analysis, which would not be affected by contamination with (I), gave the following results.

Anal. Subs., 0.1833: CO_2, 0.3556; H_2O, 0.0810. Calcd. for $C_{10}H_{11}O_5N$: C, 53.35; H, 4.93. Found: C, 52.90; H, 4.94.

Total yield of mixed I and II (crude): 248 g. (99%); yield of I (crude): 121 g. (48%); yield of II (crude): 127 g. (51%).

It will be noted that this does not give the same ratio of I to II that was found in the interconversion experiment described later.

Synthesis of the Isomeric 1,1′-*p*-Nitrobenzylidene Glycerol 2-Methyl Ethers (III and IV)

(A) Methylation of the Isomeric 1,1′-*p*-Nitrobenzylidene Glycerols (I).—One hundred grams of 1,1′-*p*-nitrobenzylidene glycerol (I) was methylated with 160 g. of dry silver oxide and 100 g. of methyl iodide at 30° over a period of three hours, sufficient dry ether being added at intervals to keep the mass well mixed by the mechanical stirrer. The bulky reaction mixture was extracted five times with boiling benzene and once with boiling ethyl alcohol. Removal of both solvents under reduced pressure left 70 g. (68%) of the crude crystalline ethers. These were dissolved in warm ethyl alcohol (60°) and the flask was then allowed to cool until spontaneous crystallization set in at around room temperature, when the remaining solvent was poured off. If the cooling is too sudden, or the liquid is agitated, an apparently homogeneous, crystalline mass of needles with indefinite melting point (90°) results, which under a lens appears as small granules (m. p. 106°) growing from the facets of well-developed needles, melting at 139°. To obtain a satisfactory separation of the two isomers which appeared to be present, the following procedure was adopted.

The total yield of mixed ethers was dissolved in one liter of absolute alcohol at 70° and all traces of crystals removed by washing down the neck of the Erlenmeyer flask with hot alcohol. The flask was then surrounded by a large volume of water at 65–70° and the whole allowed to cool slowly until approximately one-fourth of the weight of the solid had crystallized out, which necessitated lowering the temperature to nearly 0°. The crystals were filtered off and the mother liquor was then evaporated down under reduced pressure to two-thirds its original bulk, and the same procedure of cooling followed. By repetition of this process until cooling of the final mother liquor to −10°

yielded only a negligible amount of crystals, four or five successive crystalline crops were obtained. The first two had a melting point of 137–139°, the middle crop an indefinite melting point around 90°, and the final crops a melting point of 102–105°.

By suitable recrystallization and combination of these fractions from the same solvent, the two pure 1,1'-*p*-nitrobenzylidene glycerol 2-methyl ethers were isolated to the extent of 30 g. of III, 35 g. of IV and 5 g. of the unseparated isomers.

III was obtained as grayish needles (m. p. 139°), odorless, readily soluble in warm alcohol and ligroin, soluble in cold benzene, ether and acetone and insoluble in water.

Anal. Subs., 0.1937: CO_2, 0.3923; H_2O, 0.0938. Calcd. for $C_{11}H_{13}O_5N$: C, 55.21; H, 5.48. Found: C, 65.21; H, 5.42. *Mol. wt.* Subs., 0.2144; ethylene bromide, 43.40; AT, 0.240°. Mol. wt. found: 243. Theoretical: 239.

IV preponderated as silky white needles (m. p. 106°), odorless, and slightly more soluble in organic solvents than its isomer, III.

Anal. Subs., 0.2030: CO_2, 0.4169; H_2O, 0.1007. Calcd. for $C_{11}H_{13}O_5N$: C, 55.21; H, 5.48. Found: C, 55.38; H, 5.52. *Mol. wt.* Subs., 0.2089; ethylene bromide, 42.62; AT, 0.234". Mol. wt. found: 251. Theoretical: 239.

That III and IV are two geometrical isomers is further substantiated by the following experiment.

(B) Condensation of Glycerol &Methyl Ether with *p*-**Nitrobenzaldehyde.** Synthesis of **1,1'-*p*-Nitrobenzylidene** Glycerol 2–Methyl Ethers.—One g. of glycerol *β*-methyl ether (prepared by hydrolysis of 1,1'-*benzylidene* glycerol 2-methyl ether)'" was condensed with 1.5 g. (slight excess) of recrystallized p-nitrobenzaldehyde, using a small drop of 40% sulfuric acid as catalyst. The reaction flask was placed under reduced pressure and heated to 120° for fifteen minutes. Spontaneous crystallization of the resulting material readily took place on cooling and from the crystalline product two isomers melting at 139 and 106" were obtained by careful crystallization from methyl alcohol, following the procedure outlined above. These proved to be identical with the previously prepared isomers (III and IV). Glycerol 8-methyl ether obtained by hydrolysis of 1,1'-*methylidene* glycerol 2-methyl ether[So] also yielded these same isomers (III and IV).

Hydrolysis of the Isomeric **β-Methyl** Ethers of 1,1'-*p*-Nitrobenzylidene Glycerol **(III and IV).—The** hydrolysis of the higher melting isomer III was effected by refluxing it for five hours with 60% ethyl alcohol in the presence of 2 cc. of concentrated hydrochloric acid, and subsequent removal of the acid with lead carbonate. The lower melting isomer IV was hydrolyzed by refluxing it for eight hours with 10% methyl alcohol and 2 cc. of concentrated hydrochloric acid, and removal of the acid by careful neutralization with potassium hydroxide solution. In both cases the neutral solution was then evaporated to less than one-fourth of its bulk. This removal of the alcohol, followed by cooling to a few degrees below 0°, brought about the separation of the greater part of the *p*-nitrobenzaldehyde formed in the reaction. This was filtered off, the filtrate evaporated under diminished pressure and the glycerol 6-methyl ether distilled from the remaining solids under a pressure of 13 mm. with as low a bath temperature as possible. In both cases glycerol 8-methyl ether, b. p. 122–3° (13 mm.), refractive index (n^{20}_D = 1.4480), was the sole liquid reaction product. The yield from isomer III was 8.3 g.; from isomer IV, 8.8 g., that is, approximately 90% in both cases.

Synthesis of the Isomeric 1,2-*p*-Nitrobenzylidene Glycerol 1'-Methyl Ethers (V and VI)

A preliminary methylation of a small quantity of 1,2-*p*-nitrobenzylidene glycerol (II) yielded only a non-crystallizable oil. It was therefore thought advisable to effect the synthesis of the expected methyl ethers by a more direct process in which, due to the use of fewer reagents, a purer product capable of crystallization might be obtained. The following procedure proved satisfactory.

(C) Condensation of Glycerol or-Methyl Ether with **_p_-Nitrobenzaldehyde.**—Twenty g. of glycerol α-methyl ether, prepared by hydrolysis of 1,2-*iso*propylidene glycerol 1′-methyl ether was condensed with the calculated amount (30 g.) of recryss tallized *p*-nitrobenzaldehyde under the influence of 2 drops of 40% sulfuric acid, by heating for twenty minutes at 110° under 20 mm. pressure. The resulting clear, amber-colored liquid was dissolved in ether, washed with dilute potassium carbonate solution and dried over solid potassium carbonate. On evaporation of the ether, a clear, light-colored oil remained which did not crystallize even on long standing at 0°. Fortunately, however, a single crystal had been obtained in a preliminary trial experiment where the product had been accidentally subjected to a temperature of −20° for some days. Inoculation with this crystal at 0° caused the immediate solidification of the above oil. Methyl alcohol was chosen as most suitable for recrystallization since on just dissolving the product in this solvent at 18°, crystallization rapidly begins below 0°. The process of deposition was carefully watched during the cooling from 0 to −20° and as soon as the characteristic formation of a lattice work of large yellow, prismatic crystals ceased (−10°), the mother liquor was then allowed to warm a few degrees and the crystals separated. Upon further cooling to −20° a deposit of white, feather-like crystals appeared on the sides and bottom of the container.

The yellow prisms proved to be 1,2-*p*-nitrobenzylidene gycerol 1′-methyl ether (V), m. p. 47°, soluble at 20° in all ordinary organic solvents except ligroin, but insoluble in water.

Anal. Subs., 0.1903: CO_2, 0.3856; H_2O, 0.0896. Calcd. for $C_{11}H_{13}O_5N$: C, 55.21; H, 5.48. Found: C, 55.21; H, 5.26. *Mol. wt.* Subs., 0.2016; ethylene bromide, 42.42; AT, 0.217'. Mol. wt., found: 258. Theoretical: 239.

The white, feathery crystals retained their characteristics, even after recrystallization from the same solvent, thus sharply distinguishing them from the above yellow prisms. Analysis proved the compound to be 1,2-*p*-nitrobenzylidene glycerol 1′-methyl ether (VI), m. p. 42°, isomeric with the above ether (V). It is slightly more soluble in most solvents than its isomer.

Anal. Subs., 0.1926: CO_2, 0.3933; H_2O, 0.0927. Calcd. for $C_{11}H_{13}O_5N$: C, 55.21; H, 5.48. Found: C, 55.65; H, 5.38. *Mol. wt.* Subs., 0.2759; ethylene bromide, 44.51; AT, 0.284". Mol. wt., found: 257. Theoretical: 239.

These results, keeping in mind the difficulty experienced by Gilchrist and Purvis[14] in analyzing glycerol methyl ethers, and the confirmative results obtained in the following synthesis by direct methylation, leave no doubt that V and VI are the two geometrical isomers sought.

(D) Methylation of the Isomeric **1,2-_p_-Nitrobenzylidene** Glycerols (II).—Twenty g. of the redistilled 1,2-*p* nitrobenzylidene glycerol (II) was methylated by the addition of 35 g. of dry silver oxide and 55 g. of methyl iodide over a period of three hours at 30°. The reaction mixture was extracted with boiling methyl alcohol and the extract dried over solid potassium carbonate. The alcoholic solution was evaporated to a volume of 30 cc. and then cooled to −20°, when a lower oily layer separated out. This could not be induced to crystallize until inoculated with a trace of the mixture of the two isomers obtained in synthesis (C), just described. The resulting sludge which formed at −20° was separated by filtration at this low temperature as a crystalline product which melted at room temperature (yield, 15 g., 75% of the theoretical). Careful

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[14] Gilchrist and Purvis, J. Chem. *Soc.*, 127,2744 (1925).

fractional crystallization from methyl alcohol at −20° yielded three distinct products. The first fraction, melting at 138°, proved to be identical with one of the 1,1′-*p*-nitrobenzylidene glycerol 2-methyl ethers (III) obtained by methylation of the six-membered acetal (I), although the very small amount obtained (0.5 g.) indicated that its presence was due to the impossibility of completely separating the two structurally isomeric #-nitrobenzylidene glycerols (I and II) by distillation. The middle fraction consisted of 7 g. of yellow crystals melting at 47°, and was recognized by means of its melting point, crystalline form and solubilities as one of the two isomeric 1,2-*p*-nitrobenzylidene glycerol 1'-methyl ethers (V) synthesized in the previous experiment *(C)*. The remaining fraction yielded 2 g. of white, fluffy crystals melting at 41–42', identical in every respect with the second of the above two ethers (VI). The isolation of this product was rendered very difficult by its ill-defined crystalline form and the extraordinary tendency of remaining impurities in the last fraction to depress the melting point of the mixture to approximately room temperature.

Conversion of the Isomeric **1,1′-*p*-Nitrobenzylidene** Glycerols (I) into the Two **1,1′-*p*-Nitrobenzylidene** 2-Benzoyl Glycerols (VII and **VIII**).—Five g. of 1,1′-*p*-nitrobenzylidene glycerol (I) which had stood until its melting point had risen from 88 to 96" was benzoylated in the usual manner by mixing with 5 g. of anhydrous pyridine, then adding 3.1 g. of benzoyl chloride and allowing to stand for twenty-four hours at room temperature. The mixture was then treated for five minutes with 100 cc. of a 1% solution of sulfuric acid at 20° to remove excess pyridine. After washing with warm water, the apparently amorphous granular mass was dried at 70° and dissolved in ethyl acetate at 60°. On cooling slowly, the deposition of two crystalline forms was observed. To isolate these, the containing vessel was heated until the crystals had redissolved and was then immersed in a large volume of water at 60°, and the whole allowed to cool slowly to room temperature. A straw-colored mass of lustrous plates formed on the sides of the vessel, which increased in bulk until the temperature was lowered to 0°. Further lowering caused the separation of a white, fluffy precipitate in the body of the liquid, which redissolved on allowing it to warm to 0°. Separation and analysis of the first crystalline product showed it to be 1,1′-*p*-nitrobenzylidene 2-benzoyl glycerol (VII), m. p. 204°, soluble in ether, acetone, warm ethyl acetate, benzene and boiling ligroin, but insoluble in water; yield, 2 g.

Anal. Subs., 0.1388: CO_2, 0.2924; H_2O, 0.0524. Calcd. for $C_{17}H_{15}O_6N$: C, 62.07; H, 4.56. Found: C, 61.92; H, 4.52.

By evaporation of the mother liquor from the above crystals to half its bulk and again cooling to 0°, a dense, white mass coagulated in the body of the liquid. Filtration yielded an almost amorphous, fluffy, lustrous white mass (m. p. 159°), which also proved to be 1,1′-*p*-nitrobenzylidene 2-benzoyl glycerol (VIII), isomeric with VII. It is slightly more soluble in organic reagents than its isomer; yield, 1.5 g.

Anal. Subs., 0.1385: CO_2, 0.3127; H_2O, 0.0564. Calcd. for $C_{17}H_{15}O_6N$: C, 62.07; H, 4.56. Found: C, 61.60; H, 4.55.

From a sample of the freshly recrystallized 1,1′-*p*-nitrobenzylidene glycerol (I) only the benzoate melting at 204° (VII) was obtained.

Conversion of **1,1′-*p*-Nitrobenzylidene** Glycerol (I) into the Two Isomeric **1,1′-*p*-Nitrobenzylidene 2-*p*-Nitrobenzoyl** Glycerols (**IX** and **X**).—Twenty-five g. of *p*-nitrobenzylidene glycerol (I), which had stood until the melting point had risen from 88 to 96°, was dissolved in hot chloroform and 5 g. of pyridine added. This was run slowly into a mixture containing 21 g. of *p*-nitrobenzoyl chloride, 10 g. of pyridine and sufficient chloroform to keep the product liquid at 70". An exothermic reaction took place, the product after standing overnight at room temperature changing into a solid mass. This was dissolved in more chloroform, washed with dilute sodium bicarbonate solution, dried over calcium chloride and the chloroform and pyridine removed as far as possible by heating under reduced pressure; yield, 32 g. The resulting amorphous product was shaken thoroughly with 0.1 N sulfuric acid to remove the remaining traces of pyridine, then washed with water and dried at 70°. Recrystallization from hot toluene yielded two distinct crystalline forms of the *p*-nitrobenzoate, which persisted in growing jointly from separate nuclei. It was not found possible, using this or other solvents, to obtain well-formed crystals. The separation of the two isomeric *p*-nitrobenzoates (IX) and (X) was effected by separating the crystals from appropriate nuclei by hand, using a hand lens. The higher melting isomer (IX) was obtained in the form of straw-colored, well-developed, brittle spicules (m. p. 208°). It dissolves to an appreciable extent in hot benzene, alcohol, carbon tetrachloride and chloroform, although solution only takes place slowly. It is readily soluble in ethyl acetate, ether, acetone and hot toluene, but is insoluble in water.

Anal. Subs., 0.2035: CO_2, 0.4072; H_2O, 0.0686. Calcd. for $C_{17}H_{14}O_8N_2$: C, 54.53; H, 3.77. Found: C, 54.68; H, 3.77.

The second isomer (X) was isolated by hand, in the same manner, in the form of rosets of microscopic, white needles, m. p. 202°, possessing similar solubility relations to those of the corresponding isomer (IX).

Anal. Subs., 0.1219: CO_2, 0.2446; H_2O, 0.0412. Calcd. for $C_{17}H_{14}O_8N_2$: C, 54.53; H, 3.77. Found: C, 54.72; H, 3.74.

Conversion of 1,2-*p*-Nitrobenzylidene Glycerol (II) into 1,2-*p*-Nitrobenzylidene 1'-Benzoyl Glycerol (XI).—Five. g of the redistilled 1,2-*p*-nitrobenzylidene glycerol (II) was benzoylated in exactly the same manner as its isomer I. The benzoylated product, after recrystallization from ethyl acetate, yielded only one benzoate in the form of greenish-yellow, granular crystals, m. p. 115°. Its behavior toward solvents was similar to that of the benzoate (VII) obtained from the six-membered acetal (I).

Anal. Subs., 0.1320: CO_2, 0.3001; H_2O, 0.0529. Calcd. for $C_{17}H_{15}O_6N$: C, 62.07; H, 4.56. Found: C, 62.02; H, 4.48.

It was not possible to isolate tie second, theoretically possible isomer, although investigation by another worker,[8] using the crude, undistilled acetal (11), yielded a product with m. p. 178°. This was soluble in warm benzene, and appears to be the second isomer (XII).

Anal. Subs., 0.1284: CO_2, 0.2909; H_2O, 0.0513. Calcd. for $C_{17}H_{15}O_6N$: C, 62.07; H, 4.56. Found: C, 61.78; H, 4.43.

Conversion of 1,2-*p*-Nitrobenzylidene Glycerol (II) into the Two 1,2-*p*-Nitrobenzylidene 1'-p-Nitrobenzoyl Glycerols (XIII and XIV).—Twenty-five g. of undistilled 1,2-*p*-nitrobenzylidene glycerol (II) was *p*-nitrobenzoylated, using the same procedure as that adopted for the p-nitrobenzoylation of acetal I. The reaction mixture took much longer to crystallize prior to removal of the pyridine, and finally yielded 21 g. of a yellow, amorphous powder. The solubility of this mixed product in toluene is much greater than that of the structurally isomeric mixture of IX and X, hence benzene was used for recrystallizations. The same peculiar, simultaneous growth of two crystal forms from different nuclei was noted, as encountered when separating IX from X.

By manual separation under a lens, straw-yellow, brittle needles (smaller than those of the corresponding structural isomer IX) of m. p. 117–118° were obtained. These were soluble in toluene, ether, acetone, chloroform, hot alcohol or benzene, but insoluble in water. Analysis proved the product to be 1,2-*p*-nitrobenzylidene 1'-*p*-nitrobenzoyl glycerol (XIII).

Anal. Subs., 0.2033: CO_2, 0.4059; H_2O, 0.0676. Calcd. for $C_{17}H_{14}O_8N_2$: C, 54.53; H, 3.77. Found: C, 54.40; H, 3.72.

The isomeric 1,2-*p*-nitrobenzylidene 1'-*p*-nitrobenzoyl glycerol **(XIV)** was also isolated by manual separation as small, white nodules of microcrystalline structure with m. p. 110°, closely resembling the isomer **(XIII)** in solubilities and crystalline form. Only a very small amount was obtained, due to the laborious manipulation necessary to separate it from the corresponding isomer (XIII), since although considerable amounts of each were present, they were frequently too overgrown to permit of satisfactory separation.

The following summary of the properties of the *p*-nitrobenzoates of the two *p*-nitrobenzylidene glycerols shows the definite relationships existing between the pairs of corresponding isomers.

p-Nitrobenzoates of	Crystalline form	M. p.	Soluble in toluene
1,1'-*p*-Nitrobenzylidene glycerol **(I)**	Brittle, yellowish spicules **(IX)**	208°	Only when hot
	White, microcrystalline nodules **(X)**	202°	„
1,2-*p*-Nitrobenzylidene glycerol **(II)**	Brittle, yellowish spicules **(XIII)**	117–118°	In the cold
	White, microcrystalline nodules **(XIV)**	110"	„

Mutual Interconversion of the Five- and Six-Membered Acetals.—Addition of 0.01% by weight of dry hydrogen chloride to either 1,1'-*p*-nitrobenzylidene glycerol **(I)** or 1,2-*p*-nitrobenzylidene glycerol **(11)**, followed by heating to 130° for a period of one and one-half hours, brought about the establishment of an equilibrium between I and II. Several experiments were carried out, varying the quantities of materials, but using the same amount of catalyst. The same proportions of I and II, in approximately the ratio of 1 to 5, were always obtained.

The separation of the equilibrium mixture into its components was carried out as previously described (p. 3381) by the use of warm benzene. Moreover, as an additional test of the permanence of this phenomenon, the two isomeric acetals (I and II), isolated from one equilibrium experiment, were each allowed once more to attain equilibrium separately. A similar ratio to that above was again obtained.

Summary

1. *p*-Nitrobenzaldehyde condenses with glycerol to give two different structural types of cyclic acetals: a five- and a six-membered *p*-nitrobenzylidene glycerol, respectively.
2. From the five-membered 1,2-*p*-nitrobenzylidene glycerol two isomeric 1,2-*p*-nitrobenzylidene glycerol 1'-methyl ethers, presumably corresponding to the two theoretically possible, geometrically isomeric, racemic forms, have been prepared.
3. From the structurally isomeric six-membered 1,1'-*p*-nitrobenzylidene glycerol two isomeric 1,1'-*p*-nitrobenzylidene glycerol 2-methyl ethers, corresponding to the two theoretically possible, non-resolvable, geometrically isomeric forms, have been isolated.
4. The corresponding benzoates and *p*-nitrobenzoates of the free five- and six-membered cyclic acetals have been prepared and identified.
5. The ready interconversion under the influence of a trace of dry hydrochloric acid of each of the two structurally isomeric acetals, namely,

1,2-*p*-nitrobenzylidene glycerol and 1,1′-*p*-nitrobenzylidene glycerol, into an equilibrium mixture has been shown.

CANADIAN PULP AND PAPER RESEARCH INSTITUTE
MONTREAL, CANADA

NOTE

A Temperature Regulator for Carius Furnaces.—The constant attention necessary to regulate the temperature of an ordinary gas-fired Carius furnace may be avoided by equipping it with a thermostat used to control the temperature of ovens on gas cooking stoves. Such a thermostat[1] is very easily installed, inexpensive and is accurate to about 5". The approximate range of the device is 100–325°.

The only precaution to be observed is not to turn the burner on full if, for example, a temperature of 100° is required, for the heat from the walls of the furnace will raise the temperature above 100° even after the thermostat has reduced the flame. The burner should be turned on approximately as it would be if no regulator were being used.

Thermostats of this type should be satisfactory for controlling the temperature of other gas-fired furnaces used in chemical work.

CONTRIBUTION FROM THE
SCHOOL OF CHEMISTRY
UNIVERSITY OF MINNESOTA
MINNEAPOLIS, MINNESOTA

G. B. HEISIG

RECEIVED SEPTEMBER 10, 1928
PUBLISHED DECEMBER 10, 1928

ADDITIONS AND CORRECTIONS

1922, VOLUME 44

The System Fe_2O_3–SO_3–H_2O, by E. Posnjak and H. E. Merwin.

P. 1984. In line 19 from the bottom read 1.681 instead of 1.618.

1927, VOLUME 49

Substituted O-Alkyl Hydroxylamines Chemically Related to Medicinally Valuable Amines, by Lauder W. Jones and Randolph T. Major.

The authors write as follows: "On p. 1531, line 9, the statement, 'Although O-methylhydroxylammonium chloride has been known for some time, the properties of the free base have not been described.' This statement is incorrect since the free base has been prepared by Traube and others, as described in *Ber.*, 53, 1485 (1920). This reference was accidentally overlooked. On p. 1486 of the article by Traube, the preparation of methoxy-urea was also described. However, no analysis of the compound was given and the melting point ascribed to it, 82–83°, was lower than that found for it by us and given on p. 1537, line 17, of our article. On p. 1533, line 27, the statement is found, 'Pure formyl *p*-nitrophenylhydrazone forms red crystals;' this should be, 'Pure formaldehyde-p-nitrophenylhydrazone forms yellow crystals.' The heading 'α-Alkyl-β-methoxythiourea' near the top of p. 1539 should bc 'α-Allyl-β-methoxythiourea.' In the next line the work 'alkyl' should be 'allyl.' "

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[1] Supplied by the Kraus Mfg. Co.

A Method for Determining the Tensile Strength of Gelatin Jellies, by A. Rosinger and A. A. Vetter.

P. 2996. Under Fig. 1 the explanatory line reading "*a* = **3.6.** ***h***, cm." should read "a = 3.16. h, cm."

1928, VOLUME 50

Studies on the Analysis and Chemistry of Neoarsphenamine, by Alfred E. Jurist and Walter G. Christiansen.

P. 191. The heading of the column numbered 10 should read "% Non-sulfoxylate sulfur [3 − (7 + 9 + 5)]," instead of "% Non-sulfoxylate sulfur [3 − (7 + 9)]."

The Equilibrium Pressure over Coexisting Salt Hydrates at Temperatures below 0^{C}, by J. B. Austin.

P. 336. In line 15 for "less" read "greater."

A New Method for the Study of Cataphoretic Protein Mobility, by Harold A. Abramson.

The author writes, "Where concentrations of protein are expressed as '1×10^{-n} g per liter,' these should be read as '1×10^{-n} g. per *cc.*' For example, '1×10^{-7} *g.* per liter is 1×10^{-7} g. per cc.' "

P. 391. In line 4, "1×10^3 g. per liter" should read "1×10^{-3} g. per cc."

P. 392. On the right-hand margin of Fig. 1, "μ-potential" should be "ζ-potential."

II. The Low Pressure Decomposition of Nitric and Nitrous Oxides, by James H. Hibben.

P. **942.** The equation at the top of the page should read

$$\text{[Equation 2]}\quad N = \frac{Ze^{-\left(\frac{Q + (1/2n' - 1)RT}{RT}\right)}\left[\left(\frac{Q + (1/2n' - 1)RT}{RT}\right)^{1/2n' - 1}\right]}{\left|\underline{1/2n' - 1}\right.}$$

instead of the form printed.

Note on the J. Lawrence Smith Method for the Analysis of Samarskite, by Roger C. Wells.

P. 1021. In the third line from the bottom of the page, "1040 million years" should read "830 million years."

Note. The Preparation of ***p*-Iodo-anisole,** by F. F. Blicke and F. D. Smith.

P. 1230. In line 7, "139–139.5°" should read "239–239.5°."

Δ^2-Cyclopentenylethyl Alkyl Acetic Acids and their Bactericidal Action toward B. Leprae. **XII,** by J. A. Arvin and Roger Adams.

P. 1791. In Table II the heading "Dilutions of sodium in thousands" should read "Dilutions of sodium salts in thousands."

P. 1791. In the third line from the bottom "cyclopentenylethyl bromide" should read "cyclopentenyl ethanol."

P. 1792. In lines 6–7 "methyl 8-hydroxyl-dl-hydnocarpate" should read "methyl 9-hydroxy-dl-hydnocarpate."

P. 1794. In lines 13–14 "8-aldehydo-octanoate" should read "methyl 8-aldehydo-octanoate."

P. 1794. Line 18 should read "*Anal.* Calcd. for $C_{17}H_{30}O_3$: C, 72.3; H, 10.71. Found: C, 71.91; H, 10.01." instead of "***Anal.*** Calcd. for $C_{15}H_{30}O_3$: C, 71.91; H, 10.01. Found: C, 72.29; H, 10.70."

P. 1794. In line 23 "$C_{14}H_{28}O_3$" should read "$C_{16}H_{28}O_3$."

Note. Luminescence of Aliphatic Grignard Reagents, by R. T. Dufford.

P. 1823. In line 12, after "Research Laboratories" insert "Incandescent Lamp Department of General Electric Co., Cleveland, Ohio."

P. **1823.** In line 18 insert the word "Nela" before "Laboratories."

The Normal Potential of the Iodine-Iodide Electrode, by Grinnell Jones and B. B. Kaplan.

P. 2076. In line 18, "log $f = -\ 3\,7\,3\,4 + 0.125c$" should read "log f $= -0.373\sqrt{c} + 0.125$ c."

The Transition Temperature of Carbon Tetrachloride as a Fixed Point in Thermometry, by James C. McCullough and Harris E. Phipps.

P. 2213. Reference should also be made to an article by Goldschmidt, Z. *Krist.*, 51, 21 (1912), in which the transition temperature of carbon tetrachloride is given as —45 ± > 5°C.

Diketones. I. The Reaction between 4-Phenylsemicarbazide and Acetylacetone, by Alvin S. Wheeler and R. D. Norton.

P. 2488. The senior author writes, "I wish to state that F. P. Brooks should be included as one of the authors of the paper.—A. S. WHEELER."

Some 1,2-Dialkyl Cyclopentane Derivatives, by Francis H. Case and E. Emmet Reid.

P. 3062. In the third line of the second paragraph "2-cyano-2-methyl-cyclopentane-one-1" should read "2-cyano-2-ethyl-cyclopentane-one-1."

P. 3063. In lines 4–5 from the bottom of the page "1-propyl-2-ethylcyclo-ethylcyclopentanol-1" should read "1-propyl-2-ethylcyclopentanol-1."

P. 3064. In the first line of the third paragraph of the Experimental Part "a-Ethyl-a-carbethoxy-cyclopenienone" should read "a-Ethyl-a-carbethoxy-cyclopentanone."

NEW BOOKS

Theoretical and Experimental Physical Chemistry. By J. C. CROCKER AND FRANK MATTHEWS. The Macmillan Company, New York, 1928. viii + 581 pp. 146 figs. 16 × 25.5 cm. Price, $6.00.

This large book is presented as a combination laboratory manual and textbook as well as a syllabus of physical chemistry for qualifying examinations.

As a laboratory manual it is inferior to the separate practical physical chemistries already published. The details of laboratory technique are inadequately considered and the errors of measurement (their sources, magnitudes and modes of decrease and of correction) are not presented. An insufficient number of experiments is offered, with the omission of such exercises as thermometry, barometry, pyrometry, colorimetry, nephelometry, standardizations of weight volume and balance, specific gravity of solids and volumenometry, the effusiometer and the gas balance, velocity of reaction, transition points, glass working and the calculation and plotting of results. Furthermore, the following particular forms of apparatus are omitted: Westphal balance, isoteniscope, Abbé refractometer, immersion refractometer, dropweight surface tension apparatus, Bingham viscometer and plastometer

As a textbook, it is, in many ways, an excellent presentation. The paper is good, the type is large and the drawings are clear. Practically all the parts of Physical Chemistry are taken up and they are adequately dcveloped. It is an unusually complete syllabus. However, the instructor will feel the lack of a list of problems and queries at the end of the chapters. The parts of the book have this sequence: gases, spectrometry, constitution and physical properties, chemical energetics, heterogeneous equilibrium, solutions and disperse systems, electrochemistry, chemical kinetics and reactivity and the theory of the atom.

A few minor criticisms should be noted. Illinium is not mentioned although rhenium and brevium are placed among the elements. Cassiopeium is given as an alternate name for the accepted element lutecium. "The Phase Rule" by Findlay is not in the list of reference books on that subject. The applications of active carbon and silica gel are not mentioned. In three-component systems, the right-angled isosceles triangle is used instead of the customary equilateral triangle.

However, the unusual attractiveness and completeness of the book recommend it for every library and for use as a textbook. A particularly meritorious quality is the proportionate development of all the topics in the entire field of physical chemistry so that no part is over-emphasized or neglected but each is given about the same extent of consideration.

RESTON STEVENSON

Physikalish-chemische Übungen. **(Manual of** Physical Chemistry.) By Dr. W. KUHN, Lecturer in Physical Chemistry at the University of Ziirich. **Verlag** A.-G. Gebr. Leeman and Co., Ziirich, Switzerland, 1928. 102 pp. 25 **figs.** 15.5 × 22.5 cm.

Most of the experiments covered in this small manual are chosen from the old and reliable group. The absence of any work on the densities of gases, and the inclusion of an experiment on the quinhydrone electrode, and of one on the simultaneous effect of two catalysts (iron and copper on the hydriodic acid–persulfate reaction), are perhaps the most novel features. Each experiment or topic is introduced by a concise statement and discussion of the principles involved, these theoretical portions occupying more than half of the book. They are generally well written, though there are a few weak points, such as the prominence given to the long-discredited capillary electrometer method for determining "absolute" potentials, and a serious error on page 11, where the relation between freezing-point lowering and activity coefficient of an electrolyte is stated in a way which is inadmissible even as an approximation.

The experiments themselves are very briefly described and no references are given, so some supplementary information to the student would usually be necessary or desirable. A feature which will recommend the manual to many is the fact that the apparatus required is all comparatively simple and inexpensive,

R. G. VAN NAME

The Properties of Silica. An Introduction to the Properties of Substances in the Solid, Non-Conducting State. BY ROBERT B. SOSMAN, Ph.D., Member of the Staff of the Geophysical Laboratory, Carnegie Institution of Washington. American Chemical Society Monograph Series. The Chemical Catalog Company, Inc., 419 Fourth Avenue, New York, 1927. 856 pp. Illustrated. 15.5 X 23.5 cm. Price, $12.50.

This volume is a comprehensive treatise on the properties of substances in the crystalline and glassy states with special reference to silica. The subject is treated in the following parts: 1, Fundamentals; 2, Phases and their Transformation; 3, Symmetry and Structure; 4, Thermal Energy; 5, Mechanical Energy; 6, Silica in the Electric and Magnetic Fields; 7, Silica in the Periodic Electromagnetic Field; 8, Applications. An introductory chapter on the properties of substances in general is followed by chapters on the constitution and polymorphic forms of silica and their specific properties. The several chapters dealing with properties contain a brief statement of the meaning of the property under consideration; a summarized statement of present knowledge of the property as applied to silica; in some cases, a discussion of the degree of constancy of the "constants" for the forms of silica; a critical review of the experimental work which has led to general statements; and the formulation of hypotheses useful in summarizing the facts already known or in pointing the way to productive research. The author's recognition of the importance of hypotheses in the development of science renders the work of particular value in classifying and interpreting the voluminous literature on silica and in directing future experimentation. His statement of one essential quality of a genuine hypothesis, page 244, is quoted in full as an illustration of the author's point of view. "It [an hypothesis] must not explain the phenomena with too much facility. It is no real virtue in a theory of polymorphism, for instance, that it is capable of explaining not only all the existing data but also any imaginable facts of polymorphism which remain undiscovered. A theory which is capable of explaining all imaginable data in its field is, conversely, incapable of predicting any one experimental fact to the exclusion of any other; or, in the pragmatic philosophy, it is not a theory at all but a form of words. It has happened more than once in the history of science that two formulas which sounded very different, but whose corollaries were experimentally indistinguishable, have led to needlessly long and bitter polemics. Hence it will be well to devote our closest scrutiny to the deductions that follow from a given hypothesis, rather than to the plausibility and general attractiveness of the formulation itself."

In the presentation of the subject matter the author has made free use of section and paragraph headings and of carefully prepared tables and illustrations. The completeness and authoritative character of the book render it indispensable to those interested not only in the specific properties of silica but in the general characteristics of substances in the solid, non-conducting state.

HARRY B. WEISER

The Modern Calorimeter. By WALTER P. WHITE, Ph.D., Physicist in the Geophysical Laboratory of the Carnegie Institution of Washington. American Chemical Society Monograph Series. The Chemical Catalog Company, Inc., 419 Fourth Avenue, New York, 1928. 194 pp. 16 figs. 15 5 X 23.5 cm. Price, $4.00.

"The whole plan of the present book illustrates one method in scientific work, namely, the guidance of experimentation by analysis of the various physical processes and sources of error concerned. . . . . Its main idea is not instruction, though it should have some value as such, but the development of the subject through criticism and discussion. . ." In these words, the author strikes the keynote of the book.

Probably no technique in physical chemistry has ever been subjected to more careful scrutiny nor more scholarly analysis than has calorimetry in this book by Dr. White. The author has rendered a real service in collecting together in one convenient place all his work of the past twenty years in this field.

The book will not be read easily by the casual reader. The new worker in calorimetry would prefer to find specific directions for making a calorimeter, gladly accepting arbitrary, authoritative statements in which the author could rightfully indulge. But such is not the purpose of the book. The author gives all the factors which must be considered and references to modern literature but he does not give exact dimensions, nor the way to wind and insulate a heating coil, nor how to set the leads into the cover. In fact very few experimental data are included and in no case is an actual thermochemical experiment with its calculation given.

The investigator in this field may be confused by the large number of suggestions. He may prefer to plough ahead and amass data, evaluating his accuracy by experimental tests with his own apparatus under his own working conditions. He may rely on checking his results with accepted values and thermodynamic relations. But this is exactly the author's point—he warns the experimenter against starting his work until he has all the variables clearly before him. This careful, deductive analysis of errors emphasized by Dr. White should more often precede careful experimental work in all fields of research.

Not every worker in calorimetry will agree with the author in the relative evaluation of various factors but all workers will unite in expressing appreciation for the scholarly treatment and helpful collection of material.

In the first chapter the author gives an excellent discussion of errors, which is equally applicable to any experimental work. He distinguishes clearly between accidental and systematic errors and between accuracy and delicacy of measurement.

The various sources of error in calorimetry are discussed fully—radiation, convection, evaporation, adsorption, conduction, heat of stirring, time lag and thermal lag. Then follows a description of various methods including the constant temperature jacket, the adiabatic method, the vacuum-walled calorimeter, the twin calorimeter and the aneroid calorimeter. Special apparatus is fully discussed, including covers, stirrers, convection shields, leads and electrical connection, but detailed descriptions are not given. The last chapter summarizes in a very satisfactory manner the precautions necessary for different degrees of precision from 1 part in 300 to 1 part in 10,000.

Accessory manipulations are not given. The discussions are limited to "the measurement of heat by means of temperature change in suitable bodies." Accordingly no mention is made of heat of combustion, heat of mixing or heat of vaporization or specific heats or the flow method of calorimetry.

The book is well organized and free from errors.

No one should undertake a research in calorimetry without first studying this book.

FARRINGTON DANIELS

Bibliography of Crystal Structure. BY JARED KIRTLAND MORSE. Bulletin of the Crystal Structure Laboratory, Department of Physics, Ryerson Physical Laboratory, University of Chicago. The University of Chicago Press, Chicago, Illinois, 1928. xix + 164 pp. 8 figs. **15 × 23** cm. Price, $3.00.

This new monograph contains the following sections: an introduction, six papers originally published in the *Proceedings of the National Academy of Sciences* and a bibliography of crystal structure. The introduction describes the facilities, program and aspirations of the Crystal Structure Laboratory at the University of Chicago, ending with a somewhat thinly veiled solicitation of funds for the establishment of research fellowships and assistantships for the Laboratory. The papers represent the contributions from the Laboratory and with the exception of one devoted to the space group of potassium, rubidium and cesium sulfates, are very largely the theoretical deductions of the author of the monograph, particularly the structure and dimensions of the benzene ring and of ethane and methane. The bibliography is arranged alphabetically by authors under each year from 1912 to 1927. It is based admittedly on the bibliography published by Dr. Wyckoff in 1924 and brought up to date. This bibliography will undoubtedly prove useful to some workers in the field of crystal structure, although arrangement by subject matter such as is found, for example, in the "International Critical Tables," presents data in a more readily available form. No bibliography can be expected to be perfect in completeness, and in the present instance there are numerous omissions, particularly of papers the titles of which may not clearly indicate x-ray studies. Although the abbreviations for periodicals recommended by Chemical *Abstracts* are used, some of the spellings of chemical terms adopted by the American Chemical Society are overlooked. For example, "caesium" is used instead of the approved "cesium" and "sulphate" instead of the approved "sulfate." The price of three dollars for this paper-bound monograph is undoubtedly toq high, particularly inasmuch as the volume seems to be designed as a missionary for the author's laboratory. It seems, therefore, that in spite of the very evident painstaking work of Dr. Morse in preparation, the circulation and utilization will be limited.

GEORGE I,. CLARK

Photometric Chemical Analysis (Colorimetry and Nephelometry). By JOHN H. YOE, Ph.D., Professor of Chemistry, University of Virginia. Volume I, Colorimetry. John Wiley and Sons, New York, 1928. xxi + 771 pp. *72* figs. **15.5 × 23.5 cm. Price 58.50.**

This welcome addition to the reference books of analytical chemistry possesses many features which will be of interest to those who frequently have occasion to use colorimetric methods. The first seven chapters are devoted to a discussion of the general principles of colorimetry, colorimeters, methods of calculation, calibration errors, colloids and colorimetric stabilizers. Parts II, III and IV deal with the estimation of inorganic, organic and biological substances. Part V comprises a very extensive bibliography (181 pages) of the literature of colorimetry. The bibliography not only lists the publications bearing upon the subject, but is made much more useful by including with each reference a summary of the important points of the investigation. Under the methods of analysis each determination is discussed in detail, so that reference to the original article is rendered practically unnecessary. The discussion of each method usually includes notes which are of value in deciding upon its applicability. While the book is unusually complete and encyclopedic in character, it would have added to its value considerably had the author adopted a more critical attitude. The evaluation of a single method where several different methods are discussed for the determination of a given substance is left to the judgment of the reader. This, however, was apparently not done without deliberation. "The author earnestly hopes that workers in this field will cooperate in improving (and 'weeding out' if necessary) some of the less accurate and imperfectly studied methods given in this treatise. It is mainly with this idea in mind that these procedures have been included." The book is well indexed and type and binding are excellent.

LAWRENCE T. FAIRHALL

Organic Chemistry for Advanced Students. BY JULIUS B. COHEN, Ph.D., D.Sc., F.R.S., Emeritus Professor of Organic Chemistry in the University of Leeds. Fifth edition. Longmans, Green and Co., 55 Fifth Avenue, New York, 1928. Three volumes. Part I, Reactions. vii + 427 pp. 5 figs. Part II, Structure. vii + 487 pp. 63 figs. 2 plates. Part III, Synthesis. vii + 440 pp. 14 × 22 cm. Price, $6.00 per volume.

The fifth edition of this well-known work is composed in essentially the same manner as the earlier editions. The same subjects are now discussed more fully, with the inclusion of recent material to bring the treatment up to date. .Certain new subjects are introduced and constitute additions to the structure which supports the substance—but the structure is recognizably the same. Professor Cohen originally made an excellent choice of the significant facts and theories of organic chemistry. With each new edition he has, in general, treated the same features of the science, expanding the discussion as indicated by new research in the particular fields. He has exercised good judgment in the addition of significant new material. The work may perhaps be criticized for not making mention of certain new developments—chaulmoogric acid, high-pressure synthesis of methanol, etc., and organic compounds of germanium and lead, to specify a few of the omissions. It may be criticized for including in this fifth edition too much discussion of certain topics which were undoubtedly of prime importance at the time of the appearance of the first edition. Tautomerism is not now as mysterious as it used to be; its phenomena may be generalized and the wisdom of distinguishing various types of tautomeric change may perhaps be questioned. The relative merits of the several formulas early proposed for benzene have not been a live issue since Thiele proposed his doctrine of partial valence. Too much discussion of such matters gives the student a false idea of the present status of organic chemistry. Paradoxical as it seems, the science by dealing with an increasing diversity of facts is attaining a simplicity of point of view and an increasing power of correlation. A textbook which will make this situation clear to the student is now needed.

The faults of Cohen's work increase its value for certain purposes. The first chapter of the first volume is the best survey in English of the early history of organic chemistry. No student can read the entire three volumes without gaining an excellent idea of the history of the most important theories and lines of research. He will see how mankind has acquired the present science—and that seeing is probably the best way by which he may acquire the science for himself. He may or he may not chance to notice that the organic chemistry so acquired comprises, like the chemistry of the time of Robert Boyle, not only gold, and silver, and ivory, but apes and peacocks, too. Advanced students of organic chemistry have need of a textbook in which all of the important facts are suggested, all of the important lines of research are indicated, in which—apes and peacocks thrown overboard—all of the important correlations are set forth in a simple manner.

Volume I, entitled "Reactions," deals with the valency of carbon, the mechanism and dynamics of organic reactions and with abnormal reactions. Its most noteworthy new material is on the electron theory of valence, in particular on its application to aromatic compounds. Volume II, entitled "Structure," deals almost entirely with the relations between chemical constitution and physical properties, density, color, optical activity, etc., with the various types of isomerism, and with the structure of benzene. It contains new material on Sugden's principle of the "parachor," on the Walden inversion and the pinacoline rearrangement, and on the stereochemistry of the hydro-aromatic compounds and of organic compounds of inorganic elements. Volume III, entitled "Synthesis," deals with special types of complex molecules, the carbohydrates, enzyme action, the purines, proteins, terpenes and camphors, and the alkaloids—and appears to the reviewer to treat the special subjects in a well-balanced and adequate manner. The arrangement, however, is one which might well confuse a student. Substitution in aromatic compounds is discussed in one volume, the structure of benzene in another. If our knowledge of structure is gained from an observation of reactions, and if it is the mechanism of reactions which indicates the possibilities of synthesis, then the student will wonder how reactions, structure and synthesis can be treated separately, and will probably feel—as the reviewer does—that some other manner of subdividing the subject would result in greater fluency of understanding. The work suffers from having been revised, not that the revision hasn't been well done upon the old structure, but that some other structure—some other topical outline of the subject—would be better.

The books are well printed and are equipped with adequate subject and author indexes.

TENNEY L. DAVIS

Aids to Biochemistry. BY E. ASHLEY COOPER, D.Sc., F.I.C., A.R.C.S.. and S. D. NICHOLAS, B.A., A.I.C., Lecturers in Chemistry, University of Birmingham. William Wood and Company, 51 Fifth Avenue, New York, 1927. vii + 188 pp. 12 figs. 11 X 16.5 cm. Price, $1.50.

This book was written to present the general principles of biochemistry to medical and science students who have already studied the subject by means of larger textbooks or lecture courses. It is intended primarily for "purposes of revision." The subject is arranged both for reading and as a manual for experimental work.

The success of such a work for revision, or review, of specific courses of study depends upon the extent to which the material presented parallels that given in the study courses. This book will probably not appeal to those in this country who are prone to follow course work. On the other hand, it should prove valuable to one who desires short, concise statements of the fundamental facts and tests of biochemistry. The material is well and accurately presented; there are included chapters on naturally occurring amines and amides, biochemical mechanism of physiological action (disinfectants), alkaloids and tests for alkaloidal compounds and identification of organic compounds which are not usually met in biochemical books current in this country.

PAUL E. HOWE

A Textbook of Biochemistry for Students of Medicine and Science. BY A. T. CAMERON, M.A., D.Sc. (Edin.), F.I.C., F.R.S.C., Professor of Biochemistry, University of Manitoba. The Macmillan Company, New York, 1928. x + 462 pp. 12 figs. 2 plates. 14 X 21 cm.

The material is divided into seven sections as follows; Introduction and some Physical–Chemical Conceptions, Chapters 1–3; The Foodstuffs, their Derivatives and Related Compounds, Chapters 4–11; The Chemistry of Digestion, the Circulation and the Excreta, Chapters 12–18; Intermediate Metabolism, Chapters 19–28; The Chemistry of Reproduction, the Chemical Controlling Agencies of the Organism, Chapters 29–30; Quantitative Metabolism, Chapters 31–32; and a supplementary section with chapters entitled, An Introduction to the Chemistry of Immunology, The Utilization of Biochemical Processes in Industry and A Biochemical Introduction to Pharmacology. This is a first-class textbook with few errors and few misleading statements. After having read on p. *36* that from the crystal form of osazones "it is possible to identify the sugars that give rise to them" the student will be disappointed to read later that three of the four important hexoses give the same osazone. It is evident from the discussion on p. 162 that the author is unfamiliar with Cleveland's study of the role of protozoa in digestive processes in termites. In the discussion of the buffering system of the blood on pp. 201–205 the role of carbonic acid is given due attention but the importance of proteins is minimized. Strangely enough in a table on p. 177 showing the composition of normal human blood carbonic acid is classed simply as a waste product. The amounts of sodium and potassium in blood are correctly given in this table but an incorrect ratio of the two in blood is given on p. 347. Aside from a few such errors as these there is ample proof of a thorough knowledge of biochemical literature. The subject matter is presented logically and in good style. This textbook should be particularly useful to the student of biochemistry seeking reliable information of a general character unaccompanied with unwarranted speculation.

D. B. DILL

Biologische Kolloidchemie. (Biological Colloid Chemistry.) By DR. RAPHAEL ED. LIESEGANG. Theodor Steinkopff, Residenzstrasse 32, Dresden-Blasewitz, Germany, 1928. xii + 127 pp. 15.5 × 22.5 cm. Price, unbound, RM 8; bound, RM 9.50.

The author of this monograph covers a large field of literature inspiring those who search for problems still open for research, and with a very personal shade. The following chapters are treated: the colloidal medium of organisms, changes of dispersity, electric charge adsorption, swelling, surface tension, viscosity.

L. MICHAELIS

Physiology and Biochemistry of Bacteria. Volume I. Growth Phases, Composition and Biophysical Chemistry of Bacteria and their Environment and Energetics. By R. E. BUCHANAN, Ph.D., Professor of Bacteriology, Iowa State College and ELLIS I. FULMER, Ph.D., Professor of Biophysical Chemistry, Iowa State College. The Williams and Wilkins Company, Baltimore, Maryland, 1928. xi + 516 pp. 78 figs. 15.5 × 23.5 cm. Price, $7.50.

After a brief introductory statement, the subject matter of this book is divided into four chapters dealing, respectively, with growth phases, chemical composition, physico-chemical characteristics and energy relationships. Presumably, a consideration of bacterial enzymes, nutritive requirements, products of growth and so on are to be covered in a second volume. It is apparent on cursory inspection that at least one of the authors is a mathematician and physico-chemist who seems, in obeying his impulse in favor of mathematical treatment, to have to a great degree lost sight of the stated subject of the book. The reviewer does not wish in any way to minimize the importance of a mathematical treatment, however involved, of any biological phenomenon which thereby may be clarified. The reasons for his criticism of Buchanan and Fulmer's book will perhaps become clearer after an analysis of the contents.

The chapter on growth phases concerns itself with a subject upon which the authors have in the past done considerable experimental work and there may be justification in treating this at length, and mathematically. On the other hand, the chapter by the same authors in Jordan and Falk's recent book, together with the original papers which are available in most libraries, would appear adequately to cover the ground.

The chapter on chemical composition, some 75 pages in length, brings together a mass of material on this still relatively obscure subject. Many of the references are very old, and little critical analysis of the facts appears to have been attempted, nor is there any relationship evident between space allotment and importance of the various topics. For example, a consideration of bacterial pigments covers 20 pages, while "bios" is dismissed in two paragraphs. Thirteen pages are devoted to a discussion of carbohydrates and gums, of which an extremely inadequate account of the recent work of Heidelberger, Avery and others occupies only half a page. It must be obvious to most students who have followed this subject that both the chemical and biological work done on the polysaccharides of, for example, the pneumococci far outweighs both in accuracy and in significance any reports on the same subject preceding the year 1923.

The chapter on physico-chemical relationships covers some 230 pages, of which perhaps 25 pages deal with bacteriology in any apparent way. Surface tension, for example, is considered at some length, but with only occasional references to possible applications to bacteriology. Reference is made to the meiostagmin reaction on page 156 and again on page 172, but not by name, nor with any reference to Ascoli and Izar's work in 1910, since which the method appears to have been no further investigated. It would seem, moreover, that some review of the recent work by Larson and others on soaps in bacterial cultures should have been undertaken. The chapter contains, in all, about 150 numbered equations, and some 65 tables of physical constants, etc. If the gas laws and one or two other matters had been included, it might well serve as a textbook of physical chemistry.

The last chapter commences with a consideration of laws of motion, units of force and work, and a table of the values of the gravity constant at various positions on the earth's surface. This is followed by a long mathematical discussion of energy in its various forms, chemical thermodynamics and entropy. The book ends with an excellent compilation of existing information on the energy sources available to, and types of oxidation used by, bacteria. It might, perhaps, have been well to include some account of the work of Hopkins and his collaborators in connection with the mention of "philothion" on page 434, but in a bacteriological book this omission is not serious.

To the reviewer it seems that the field of physiology and biochemistry of bacteria is full of fascinating and important problems, many of which can here be investigated under optimal experimental conditions, and may have intensely significant bearings in broader fields. For this reason, he feels that a short book, so written as to stimulate interest rather than to discourage it, which would collect into compact form all the available information in a really critical way, would be of great value. The present volume falls far short of attaining this end. There are plenty of authoritative textbooks of physical chemistry and physics to which the earnest student of biology can readily go for the information he needs in a specific problem. The difficulty in Buchanan and Fulmer's book is to pick out from the mass of mathematics the biological facts which he may require.

J. HOWARD MUELLER

Author Index to Volume L, 1928[1]

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[1] **This index was prepared in the Editorial Offices of Chemical *Abstracts* through the courtesy of Dr. E. J. Crane and under his direction.**

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