

pressure, $n = 1.426$, while for the pure chloride, $n = 1.429$ and b. p. 168–170°. The specific rotations of the recovered chloride and of the pure chloride were determined in methanol as follows: $[\alpha]^{25}_D -26.4^\circ$ (c , 5.40) for the recovered chloride; $[\alpha]^{25}_D -31.6^\circ$ (c , 5.35) for the pure chloride. Similar results were obtained in another run; the recovered chloride had slightly less activity than the starting material.

Summary

1. *s*-Octyllithium has been prepared in 56% yield from 2-chlorooctane and lithium, and car-

bonated to give 2-methyloctanoic acid.

2. When optically active 2-chlorooctane is used, the 2-methyloctanoic acid obtained is optically inactive.

3. The 2-chlorooctane recovered from the reaction is only slightly racemized.

4. Phenyl isocyanate has been found to be unsatisfactory for characterization of *s*-octyllithium.

ROCHESTER, NEW YORK RECEIVED FEBRUARY 21, 1939

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CARNEGIE INSTITUTE OF TECHNOLOGY]

Kinetic Salt and Medium Effects in the Reaction between Ethylene Chlorohydrin and Hydroxyl Ion¹

BY LEON O. WINSTROM AND J. C. WARNER

In continuing our studies on the kinetic salt and medium effects and the temperature coefficients of reactions in solutions,² we have investigated the reaction between ethylene chlorohydrin and hydroxyl ion as an example of a reaction between an ion and an uncharged molecule. In this investigation, rate constants have been determined at 0, 15, 25 and 35° in water, in ethyl alcohol–water mixtures and in 1,4-dioxane–water mixtures of such composition that the dielectric constant of the mixed solvent at each temperature was equal to that of water at 35° ($D = 74.86$). The results of these experiments were used to calculate the energy of activation or critical increment of the reaction at constant solvent composition and at constant dielectric constant. The difference between these two critical increments was compared with that calculated from the relation advanced by Svirebely and Warner.^{2c} At 25°, experiments were made over a considerable range of initial concentrations and in the presence of added neutral salts. These results are compared with the predictions of the Brönsted–Christiansen theory of the salt effect.

The kinetics of this reaction was the subject of an early investigation by Evans.³ However, it is now generally recognized that he worked with impure ethylene chlorohydrin and that his hypothe-

sis that the back reaction was important was in error.^{4,5} Evans did recognize that complications were introduced by the presence of carbonate or bicarbonate ions. In later investigations, Smith⁶ studied the reaction of ethylene chlorohydrin with several hydroxides and found a drift toward higher values in his bimolecular constants, "dilution effect," with decreasing initial concentrations of reactants. Smith also made one experiment with added sodium chloride and found no appreciable effect on the velocity.

That the side reaction of ethylene chlorohydrin with water is unimportant is demonstrated by the investigation of Radulescu and Muresonu.⁷ When their pseudo-unimolecular constants for the reaction at temperatures of 56–99° are converted to bimolecular constants, a calculation of the temperature coefficient permits an estimation of the constant at 25°. The result is $k = 1.0 \times 10^{-9}$ min.⁻¹ and from this one may conclude that the side reaction of ethylene chlorohydrin with the solvent is negligible compared to the main reaction with hydroxyl ion.

Previous investigators^{3,8} have demonstrated that ethylene chlorohydrin reacting with hydroxyl ion yields ethylene oxide but the reaction with carbonate or bicarbonate ion leads to the formation of ethylene glycol.

(1) Abstracted from the thesis submitted by Leon O. Winstrom to the Committee on Graduate Instruction of Carnegie Institute of Technology in partial fulfillment of the requirements for the degree of Doctor of Science. Original manuscript received August 1, 1938.

(2) (a) Warner and Stitt, *THIS JOURNAL*, **55**, 4807 (1933); (b) Warner and Warrick, *ibid.*, **57**, 1491 (1935); (c) Svirebely and Warner, *ibid.*, **57**, 1883 (1935); (d) Eagle and Warner, *ibid.*, **58**, 2335 (1936).

(3) Evans, *Z. physik. Chem.*, **7**, 335 (1891).

(4) Brönsted, Kilpatrick and Kilpatrick, *THIS JOURNAL*, **51**, 428 (1929).

(5) Smith, *Z. physik. Chem.*, **130**, 162 (1927).

(6) Smith, *ibid.*, **81**, 339 (1912); **A152**, 153 (1931).

(7) Radulescu and Muresonu, *Bull. soc. sci. Cluj, Roumanie*, **7**, 128 (1932).

(8) Brooks, *Chem. Met. Eng.*, **22**, 629 (1920); Schrader, *Z. angew. Chem.*, **42**, 541 (1929).

Preliminary experiments in this Laboratory established the fact that with carefully purified materials and with precautions to exclude carbon dioxide from the reaction system, bimolecular constants which showed no drift could be obtained up to at least 90% conversion. It was therefore unnecessary to apply any correction for either a back reaction or a side reaction with the solvent.

Materials and Experimental Procedure

Eastman "Best Grade" ethylene chlorohydrin was purified by the procedure of Mathews.⁹ This method has been found to yield exceedingly pure material by other investigators.¹⁰ Our purified ethylene chlorohydrin boiled at 126.5–126.7° at 729 mm.¹¹ and possessed a refractive index $n_{25}^{20} 1.4412$.⁷ When a weighed sample of our material was permitted to react to completion with an excess of barium hydroxide, 99.9% of the theoretical amount of chloride ion was obtained. Standard solutions of barium hydroxide, ammonium thiocyanate, silver nitrate and nitric acid were made from analytical grade chemicals. The distilled water used in preparing reagents and in all experiments was boiled under reduced pressure to remove dissolved gases and was cooled under an atmosphere of nitrogen. All solutions were carefully protected from contamination by carbon dioxide. The ethyl alcohol and 1,4-dioxane used in studies on the kinetic medium effect were purified by methods previously described.^{2b} Dielectric constant data for ethyl alcohol–water and 1,4-dioxane–water mixtures were taken from the work of Åkerlöf.¹² Except where otherwise stated, the nitrogen used in the storage of solutions and in the reaction flask was passed through an absorption train containing 40% solution of potassium hydroxide to remove carbon dioxide and then through a tube containing absorbent cotton to remove any spray.

A large number of thin-walled glass bulbs, with capacities ranging from 2–7 cc., were filled with purified ethylene chlorohydrin and sealed. The weight of material in each bulb was recorded. The first step in making a series of experiments during any one day was the preparation of a stock solution by breaking a bulb containing the desired amount of ethylene chlorohydrin in a weighed amount of distilled water under an atmosphere of nitrogen. The reaction flask was made by joining two long-necked 300-cc. round-bottomed Pyrex flasks by a cross arm 4 cm. in diameter and so located that each flask could contain about 200 cc. of solution without spilling over into the other. A side-arm on the neck permitted passing a stream of nitrogen whenever the stoppers were removed. Predetermined amounts of ethylene chlorohydrin stock solution and barium hydroxide solution were introduced into the separate compartments of the nitrogen-filled reaction flask. After the flask and contents were at thermostat temperature, the reaction was started quickly by pouring

the reactants back and forth through the connecting cross arm. Samples were removed at regular intervals during an experiment by loosening the stopper and starting a stream of nitrogen through the side-arm; with nitrogen flowing, the stopper was removed and the sample withdrawn with a calibrated pipet. The sample was then drained into a measured amount of nitric acid solution to stop the reaction. The "stopping" solution also contained a measured amount of standard silver nitrate solution. The silver chloride formed was removed by filtering through a highly retentive paper and the excess silver nitrate determined in an aliquot portion of the filtrate by titrating with standard ammonium thiocyanate solution, using ferric nitrate as an indicator. When samples were taken in experiments conducted at temperatures appreciably above or below room temperature, the necessary corrections were applied in the calculations of concentrations. In the studies at 15, 25 and 35°, the maximum temperature variation during an experiment was less than $\pm 0.01^\circ$. At 0° the thermostat was replaced by a five-gallon Dewar flask filled with finely cracked ice and distilled water. Absolute temperatures were established within 0.01° by use of a B. S. platinum resistance thermometer.

Experimental Results and Discussion

Bimolecular constants were calculated by use of the usual velocity equations but the values reported in the tables were obtained by the graphical method.¹³ Deviations in k , (Δk), calculated by the usual velocity equations from the reported rate constant obtained by the graphical method, are plotted against time for typical experiments in Fig. 1.

The reaction was first extensively investigated at 25° to establish the true bimolecular character of the reaction and to study kinetic salt effects. The first series of five experiments was made without adequate protection against carbon dioxide. These experiments, summarized in Table I, showed a drift in the constant to higher values as the initial concentrations of reactants were decreased. Later experiments established a value

TABLE I

Expts. in water at 25°, without adequate protection against carbon dioxide.

Expt.	1	2	3	4	5
$a = b$ (moles/l.)	0.1032	0.0942	0.0796	0.0310	0.0106
k (min. ⁻¹)	.561	.584	.602	.628	.632

$k = 0.600 \text{ min.}^{-1}$ at 25° and we believe the constant attained higher values at the lower concentrations in this series due to the side reaction of ethylene chlorohydrin with carbonate ion to form ethylene glycol. At the higher concentrations of barium hydroxide, we believe the constants are somewhat lower than the true value due to pre-

(9) Mathews, THIS JOURNAL, **48**, 570 (1926).

(10) De Laszlo, *ibid.*, **49**, 2106 (1927); Smith, Boord, Adams and Pease, *ibid.*, **49**, 3137 (1927).

(11) Kireev and Nikiforova, *J. Gen. Chem. U. S. S. R.*, **6**, 75 (1936).

(12) Åkerlöf, THIS JOURNAL, **54**, 4125 (1932); Åkerlöf and Short, *ibid.*, **58**, 1243 (1936).

(13) Roseveare, *ibid.*, **53**, 1651 (1931).

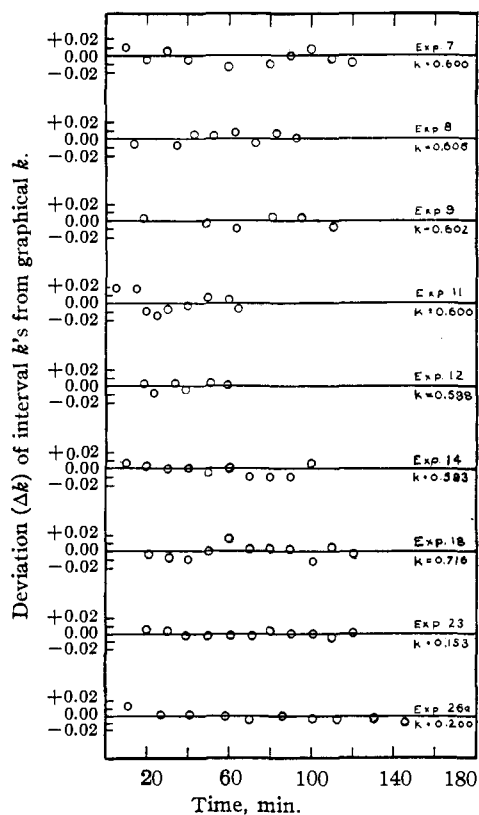


Fig. 1.

precipitation of some barium carbonate. In expts. 1 and 2, the solution was distinctly cloudy at the end of the run.

Next a series of eight experiments was made in which carbon dioxide was excluded carefully. In these experiments the initial concentrations of ethylene chlorohydrin and hydroxyl ion were equal. The results of this series are summarized in Table II.

TABLE II

Expts. in water at 25°, with adequate protection against carbon dioxide.

Expt.	$a = b$ moles/l.	k min. ⁻¹	Expt.	$a = b$ moles/l.	k min. ⁻¹
6	0.0934	0.600	7c	0.0687	0.598
7	.0700	.600	8	.0403	.606
7a	.0700	.597	9	.0206	.602
7b	.0700	.600	10	.0085	.604

Three experiments in which unequal starting concentrations of ethylene chlorohydrin and hydroxyl ion were used are summarized in Table III.

The results of expts. 6–12a show quite conclusively that the rate constants are independent of the starting concentrations of the reactants. When carbon dioxide is properly eliminated, there is no indication of the "dilution effect" observed

TABLE III

Expts. in water at 25° with unequal starting concentrations.

Expt.	Init. concn., moles/l.		k , min. ⁻¹
	Ethylene chlorohydrin	Hydroxyl ion	
11	0.1235	0.0620	0.600
12	.0607	.1214	.598
12a	.0598	.1196	.600

by Smith,⁶ and since in these experiments the reaction has been followed to from 80–95% completion, it may be concluded that the reaction is truly bimolecular in character and is not complicated by side reactions or the back reaction. Furthermore, the fact that rate constants are essentially independent of the barium hydroxide concentration indicates that there is no appreciable kinetic salt effect on the reaction. To test this conclusion, experiments were conducted with added sodium nitrate and potassium nitrate. The influence of ionic strength on the rate of the reaction in water at 25° is summarized in Table IV, and $\log k$ is plotted against ionic strength in Fig. 2.

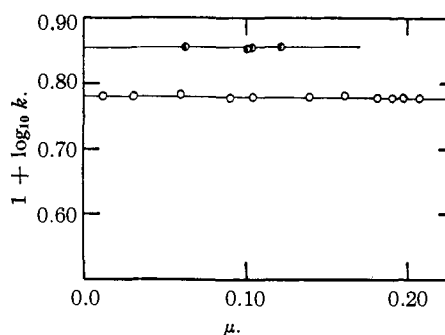


Fig. 2.—○, H₂O at 25°; ●, alcohol-water mixture at 25°.

The slight indication of a negative linear salt effect is probably within the experimental error and these rather comprehensive data support the single observation of Smith.⁶ The kinetic salt effect is in agreement with the predictions of the Brönsted–Christiansen theory.

Inasmuch as one object of this investigation was a comparison of the critical increments in water (solvent of fixed composition) and solvent media of constant dielectric constant, our next experiments at 25° were conducted in ethyl alcohol–water and in 1,4-dioxane–water mixtures of such compositions that the mixed solvents at 25° had the same dielectric constant ($D = 74.86$) as water at 35°, the highest temperature used in our experiments. To obtain information on the kinetic salt effect in a mixed solvent, neutral salts

TABLE IV
 Kinetic salt effect in water at 25°.

Expt.	Added salt	Initial concn., moles/l.		Ionic strength	<i>k</i> , min. ⁻¹
		Ethylene chlorohydrin	Hydroxyl ion		
10	None		0.0085	0.0128	0.604
9	None		.0206	.0310	.602
8	None		.0403	.0605	.606
11	None	0.1235		.0929	.600
7	None		.0700	.1049	.600
6	None		.0934	.1401	.600
15	0.0915 <i>M</i> NaNO ₃		.0398	.1512	.600
16	.102 <i>M</i> KNO ₃		.0403	.1621	.599
12	None	0.0607		.1821	.598
13	0.0882 <i>M</i> NaNO ₃		.0687	.1912	.596
13a	.0945 <i>M</i> NaNO ₃		.0687	.1975	.598
14	.1052 <i>M</i> KNO ₃		.0687	.2082	.593
13b	.1059 <i>M</i> NaNO ₃		.0700	.2108	.594

were added in two experiments in alcohol-water mixtures. All these data are summarized in Table V. $\log k$ is plotted against ionic strength in the alcohol-water mixtures in Fig. 2. In these mixed solvents, the rate constants are higher than in water, but again they are essentially independent of starting concentrations and of the ionic strength. As might be expected,^{2d} other properties than the gross dielectric constant have an influence upon the rate in these mixed solvents and rates are not exactly equal in the isodielectric

solvents, being somewhat lower in the dioxane-water than in the alcohol-water mixtures.

The results of experiments in water at 35, 15 and 0°; in ethyl alcohol-water and in dioxane-water mixtures of $D = 74.86$ at 35, 15 and 0° are summarized in Table VI.

The Kinetic Medium Effect.—The average velocity constants at the various temperatures and in the media used are summarized in Table VII.

These data in different media at constant temperature cannot be used to test Scatchard's¹⁴ theory of the kinetic medium effect in reactions between ions and uncharged molecules because no information is available on the molal lowering of the dielectric constant caused by adding small amounts of ethylene chlorohydrin to the solvents used in our experiments. However, our results may be compared to the predictions of the theoretical equation of Harned and Samaras¹⁵ for reactions of this type.

$$\frac{\ln k - \ln k_0}{D_0 - D} = \frac{2e^2}{2a_i D_0^2 k T} = -\frac{2W_0}{kT} \quad (1)$$

In Table VIII, values of $(\ln k - \ln k_0)/(D_0 - D)$ obtained in our experiments are compared with values calculated from Eq. (1) assuming $a_i = 2.0 \times 10^{-8}$ cm.

The Influence of Temperature.—In Fig. 3 values of $\log k$ given in Table VII are plotted against $1/T$ for water as solvent (constant solvent composition), for ethyl alcohol-water mixtures of $D = 74.86$ and for dioxane-water mixtures of $D = 74.86$. Energies of activation (ΔE), calculated analytically over the temperature intervals employed, are given in Table IX.

(14) Scatchard, *Chem. Rev.*, **10**, 229 (1932).

(15) Harned and Samaras, *THIS JOURNAL*, **54**, 15 (1932).

TABLE V

Expts. at 25° in ethyl alcohol-water and dioxane-water mixtures, $D = 74.86$.

Expt.	Wt. % added solvent	Added salt	$a = b$ moles/l.	Ionic strength	k , min. ⁻¹
18	6.42	C ₂ H ₅ OH None	0.0405	0.0607	0.716
20	6.42	C ₂ H ₅ OH 0.0403 <i>M</i> NaNO ₃	.0405	.1010	.714
17	6.42	C ₂ H ₅ OH None	.0694	.1041	.713
19	6.42	C ₂ H ₅ OH 0.0695 <i>M</i> KNO ₃	.0405	.1202	.717
21	4.16	C ₄ H ₈ O ₂ None	.0677		.701
22	4.16	C ₄ H ₈ O ₂ None	.0426		.700

TABLE VI

Summary of experiments at 35, 15 and 0°. Initial concentrations of reactants equal.

Expt.	Temp., °C.	Wt. % added solvent	D	$a = b$ moles/l.	k , min. ⁻¹
30	35	None	74.86	0.0418	2.15
31	35	None	74.86	.0508	2.17
24	15	None	82.28	.0412	0.153
24a	15	None	82.28	.0726	.156
23	15	None	82.28	.0983	.153
23a	15	None	82.28	.0983	.152
25a	15	12.61 EtOH	74.86	.0671	.217
25	15	12.61 EtOH	74.86	.0758	.215
26a	15	8.20 dioxane	74.86	.0898	.200
27a	0	None	88.33	.0911	.0167
27	0	None	88.33	.0944	.0167
29a	0	21.43 EtOH	74.86	.0752	.0308
29	0	21.43 EtOH	74.86	.0787	.0304
28a	0	14.18 dioxane	74.86	.0712	.0271
28	0	14.18 dioxane	74.86	.0864	.0269

TABLE VII

T, °K.	In H ₂ O, variable D ₀			Constant D = 74.86			
	k	Log k	D ₀	In EtOH-H ₂ O k	Log k	In dioxane-H ₂ O k	Log k
308.1	2.17	0.3365	74.86
298.1	0.600	-.2218	78.54	0.715	-0.1457	0.700	-0.1549
288.1	.153	-.8153	82.28	.216	-.6656	.200	-.6990
273.1	.0167	-1.7772	88.33	.0306	-1.5143	.0270	-1.5686

In water, as a solvent, there seems to be a definite increase in the energy of activation with temperature.¹⁶ However, in the solvents of constant dielectric constants there are no drifts in the values of the energy of activation with temperature and any variations are probably within the experimental error.

TABLE VIII

T, °K.	Added solvent	(ln k - ln k ₀)/(D ₀ - D)			Equation (1)
		ln k - ln k ₀	D ₀ - D	Expt.	
298.1	EtOH	0.1753	3.68	0.0477	0.0453
298.1	Dioxane	.1541	3.68	.0420	
288.1	EtOH	.3447	7.42	.0463	.0430
288.1	Dioxane	.2678	7.42	.0360	
273.1	EtOH	.6065	13.47	.0450	.0392
273.1	Dioxane	.4814	13.47	.0357	

TABLE IX
ENERGIES OF ACTIVATION

	In H ₂ O D variable	In EtOH-H ₂ O D = 74.86	In dioxane-H ₂ O D = 74.86
ΔE _{0-15°}	22,900	20,330	20,810
ΔE _{15-25°}	23,210	20,320	21,030
ΔE _{25-35°}	23,440	20,240	20,890
ΔE _{avg.}		20,300	20,910

Assuming the velocity constant, after being freed from any salt effects, to be a function of only the temperature and the dielectric constant, Svirbely and Warner^{2c} related the energy of activation at constant solvent composition to that at constant dielectric constant by the equations

$$\frac{d \ln k^0}{dT} = \left(\frac{\partial \ln k^0}{\partial T} \right)_D + \left(\frac{\partial \ln k^0}{\partial D} \right)_T \frac{dD}{dT} \quad (2)$$

$$(\Delta E^0)_{\text{Fixed comp.}} = (\Delta E^0)_D + 2.3 RT^2 \left(\frac{\partial \log k^0}{\partial D} \right)_T \frac{dD}{dT} \quad (3)$$

Taking $(\partial \log k^0 / \partial D)_T$ from experiment or from the Christiansen-Scatchard¹⁴ theory and $dD/dT = -bD$ from the work of Åkerlöf¹² it has been found^{2c,17} that eq. (3) yields the proper relation between the two energies of activation in the conversion of ammonium cyanate into urea.

Since in the present investigation velocity constants are essentially independent of ionic strength

(16) (a) La Mer, *J. Chem. Phys.*, **1**, 289 (1933); *J. Franklin Inst.*, **225**, 709 (1938). (b) Eyring, *J. Chem. Phys.*, **3**, 107 (1935); *Chem. Rev.*, **17**, 65 (1935). (c) La Mer and Kammer, *THIS JOURNAL*, **57**, 2662 (1935).

(17) Svirbely and Schramm, *THIS JOURNAL*, **60**, 330 (1938); Linder and Svirbely, *ibid.*, **60**, 1613 (1938).

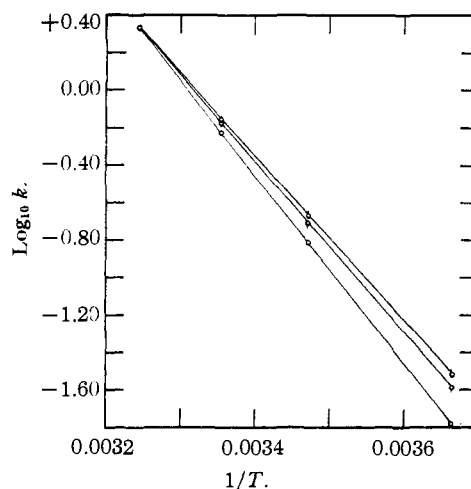


Fig. 3.—Solvent: ○, H₂O; ○, EtOH-H₂O, D = 74.86; ◻, dioxane-H₂O, D = 74.86.

(Fig. 2), eq. (3) may be applied using experimental rather than extrapolated constants. That eq. (3) satisfactorily gives the relation between the two energies of activation in the reaction between ethylene chlorohydrin and hydroxyl ion is demonstrated by the comparison between experimental and calculated values in Table X.

TABLE X

Solvent	t, °C.	ΔE _{H₂O} - ΔE*			ΔE _{H₂O} Exptl.
		Avg. Exptl.	Eq. (3)	Eq. (3)	
EtOH-H ₂ O	0	20,300	2480	22,780	ΔE _{0-15°} = 22,900
Dioxane-H ₂ O	0	20,910	2000	22,910	
EtOH-H ₂ O	15	20,300	2750	23,050	ΔE _{15-25°} = 23,210
Dioxane-H ₂ O	15	20,910	2190	23,100	
EtOH-H ₂ O	25	20,300	2830	23,130	ΔE _{25-35°} = 23,440
Dioxane-H ₂ O	25	20,910	2650	23,560	

However, we must again emphasize the approximate character of eq. (3) which assumes that rate constants, freed from salt effects, are functions of only the temperature and the dielectric constant. From this investigation and many others,^{2,16ac} it is apparent that certain specific medium effects are at least secondary factors. Rate constants usually differ somewhat in various isodielectric solvents.

Summary

The reaction between ethylene chlorohydrin

and hydroxyl ion has been studied with the following results.

1. When carbon dioxide is carefully excluded, the reaction appears to be strictly bimolecular in character with no complications due to side reactions or reverse reactions up to more than 90% completion.

2. The second order rate constants are independent of the initial concentrations of each reactant over the range investigated.

3. The absence of any appreciable kinetic salt effect in water and in alcohol-water mixtures has been demonstrated by the constancy of rate con-

stants over a considerable range of ionic strength in the presence and absence of added salts.

4. A decrease in the dielectric constant of the solvent increases the rate of the reaction in good agreement with the theory of Harned and Samaras.

5. The energy of activation has been determined in a solvent of fixed composition (water) and in two mixed solvents of constant gross dielectric constant. The relation between the two energies of activation is in agreement with the predictions of Svirbely and Warner.

SCHENLEY PARK
PITTSBURGH, PENNA.

RECEIVED MARCH 13, 1939

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF CORNELL UNIVERSITY]

The Sesquioxide and Hydroxides of Gallium

BY A. W. LAUBENGAYER AND H. R. ENGLE

Gallium is among those metals whose hydroxides are amphoteric and tend to precipitate in a highly hydrous and gelatinous condition, with properties varying widely depending upon the details of the methods used in their preparation. Because equilibrium is exceedingly difficult to establish in such hydrous systems, the isolation of definite compounds and the study of the stability relationships between these compounds is not easily accomplished. Weiser¹ and Milligan and Weiser² have reviewed the work which has been done on the system gallium oxide-water. Alpha and beta modifications of the oxide and a compound $\text{Ga}_2\text{O}_3 \cdot \text{H}_2\text{O}$ or $\text{GaO}(\text{OH})$ have been reported but our knowledge of the system has been very incomplete.

purpose of obtaining more exact information concerning the phases which occur, their stability ranges and relationships, and their properties. Improved methods for establishing equilibrium with the help of fused mineralizing agents and of superheated steam in a bomb have been used to supplement the common dehydration studies.

Experimental

Identification of Phases Appearing.—The substances obtained by the various experimental methods were identified by chemical analysis and by X-ray and microscopic examination.

The compositions of the samples were determined by ascertaining the amount of water lost upon ignition in platinum at 1200–1300° after the sample had first been dried to constant weight in the air at 105°.

All of the samples secured were very finely divided and only the powder X-ray diffraction method could be applied. The samples were examined with Mo $K\alpha$ radiation in a General Electric X-ray diffraction apparatus. The characteristic spectra which were found for the various substances isolated are mapped in Fig. 1.

The patterns obtained for $\beta\text{-Ga}_2\text{O}_3$ and $\text{GaO}(\text{OH})$ check with those reported by Milligan and Weiser² for $\beta\text{-Ga}_2\text{O}_3$ and $\text{Ga}_2\text{O}_3 \cdot \text{H}_2\text{O}$. That for $\alpha\text{-Ga}_2\text{O}_3$ is similar to the one reported by the same investigators for $\alpha\text{-Ga}_2\text{O}_3$ using Cu $K\alpha$ radiation, except that the lines are displaced. The pattern for $\text{Ga}(\text{OH})_3$ is new, since this compound has not been isolated before.

All of the samples were examined by means of the microscope. In most cases the particles were so small that, even when oil immersion methods were used, little information concerning the products could be obtained. Under the most favorable conditions a few of the products contained crystals large enough for optical study.

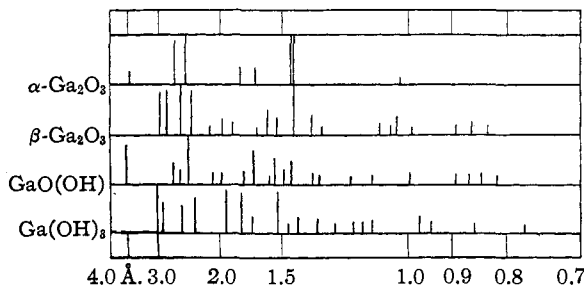


Fig. 1.—Diagrams of the X-ray diffraction patterns obtained with Mo $K\alpha$ radiation.

In the present investigation a comprehensive study of the system has been undertaken with the

(1) Weiser, "Inorganic Colloid Chemistry," Vol. II, John Wiley and Sons, Inc., New York City, 1935.

(2) Milligan and Weiser, *THIS JOURNAL*, **59**, 1670 (1937).