

can be prepared and determined in this way,⁴ but deguelin either does not form solvates or they are decomposed by water. The acids tried were dichloroacetic, α -bromopropionic, α -chloropropionic, α -bromobutyric, and lactic. Crystallization induced with petroleum ether instead of water also gave no solvate.

Summary

Seven stable solvates of inactive deguelin are

reported. Deguelin crystallizes from carbon tetrachloride, chloroform, bromoform, and ethylene bromide with 1 mole of solvent to 1 mole of deguelin, and from bromobenzene, chlorobenzene, and benzaldehyde with 1 mole of solvent to 2 moles of deguelin.

WASHINGTON, D. C.

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

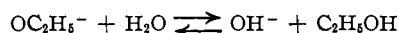
Kinetics of the Reactions of Ethyl Iodide with Bases in Ethyl Alcohol-Water Mixtures¹

BY SAM EAGLE AND J. C. WARNER

In beginning an investigation of the reactions of alkyl halides which occur in solution, we have made an extensive study of the reactions of ethyl iodide with sodium hydroxide, triethylamine, sodium acetate and with the solvent in ethyl alcohol and aqueous alcohol mixtures at 50 and 25°. Sufficient experiments have been carried out with lithium nitrate to establish the importance of the role of nitrate ion as a primary reactant exclusive of the "inert salt catalysis." The over-all rate has been corrected successfully for side reaction of the halide with the solvent and the rate of reaction with various bases has been correlated with their base strength. The effect of changing medium has been partially assigned to the influence of dielectric constant on the base strength. Approximate values of the energies of activation at constant composition and constant dielectric constant have been obtained for the various reactions. Considerable progress has been made toward an explanation of the "dilution effect" without the assumption of reaction of ethyl iodide with molecules of strong electrolytes.

Many kinetic studies on the reactions of ethyl iodide and other alkyl halides have been reported in the literature. The results of these previous investigations may be summarized briefly as follows. In the reactions of sodium ethylate and ethyl iodide in ethyl alcohol, the bimolecular constants show a pronounced "dilution effect," the value of the constant decreases with increased base concentration,² but is independent of the halide concentration. The reported temperature coefficient is 20,650 cal. The velocity constant

decreases in aqueous alcohol solutions with addition of water, and the existence of an equilibrium



is well established.^{3a} The rate increases with pressure.^{3b} The calculated constants for many of the reactions of this type show a downward drift with time which is traceable to loss of halide, side reactions, or to the magnifying of errors when using the analytical method for obtaining velocity constants.

Menschutkin⁴ measured the velocity of formation of tetraethylammonium iodide in a number of solvents and found a pronounced dependence of the rate on the medium in which the chemical change was produced. Many attempts to correlate the measured velocity constants with various properties of the solvent have been made,⁵⁻⁷ but the specific influence of the medium has been poorly understood. The energies of activation for the amine-halide reactions vary markedly with the solvent and generally fall below the normal range of around 20,000 cal., commonly found for bimolecular reactions in solution.⁸ That a part of the conversion of ethyl iodide to inorganic iodide arises from reaction with the solvent has frequently been suggested, but a thorough investigation of this side reaction has not been reported. The recent work of Taylor⁹ and Hughes and Shapiro¹⁰ on the alcoholysis of ethyl and hy-

(3) (a) De Bruyn and Steger, *Rec. trav. chim.*, **18**, 311 (1899); (b) Gibson, Fawcett and Perrin, *Proc. Roy. Soc. (London)*, **A150**, 233 (1935).

(4) Menschutkin, *Z. physik. Chem.*, **6**, 41 (1890).

(5) Grimm, Ruf and Wolff, *Z. physik. Chem.*, **B13**, 301 (1931).

(6) Soper and Williams, *J. Chem. Soc.*, 2297 (1931).

(7) Walden, *Chem. Z.*, **31**, 904 (1907).

(8) Moelwyn-Hughes, *Chem. Rev.*, **10**, 241 (1932).

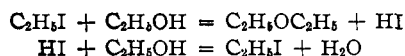
(9) Taylor, *J. Chem. Soc.*, 992 (1937).

(10) Hughes and Shapiro, *ibid.*, 1177 (1937).

(1) Abstracted from a thesis submitted by Sam Eagle to the Committee on Graduate Instruction in partial fulfillment of the requirements for the degree of Doctor of Science.

(2) Hecht, Conrad and Brückner, *Z. physik. Chem.*, **4**, 273 (1889); **5**, 589 (1890).

drogen bromides seems to establish the nature of the reaction of alkyl halides with absolute and aqueous alcohols in the absence of added bases or salts. Their experiments indicate the reactions that may be expected in an alcoholic solution of ethyl iodide



The primary reaction of ethyl iodide with the alcohol is particularly important in the silver nitrate reaction studies by Burke and Donnan¹¹ but the complete mechanism has not been established definitely.¹² The addition of other nitrates gave an increase in rate which led Burke and Donnan to the hypothesis that silver nitrate molecules were the primary reactants.

Materials and Experimental Method

Eastman c. p. ethyl iodide was purified by the method of Gibson, Fawcett and Perrin.^{3b} The product boiled at 72.2–72.3° at 760 mm. When a weighed sample was permitted to react to completion with an excess of sodium hydroxide in alcoholic solution, the theoretical amount of iodide ion was obtained. Baker analytical sodium hydroxide (NaOH assay 98.7%, Na₂CO₃ 0.8%) was used without further purification and the concentration of hydroxide in any experiment was determined by titrating with standard acid. Eastman c. p. triethylamine was dried carefully and fractionated as required, precautions being taken to exclude carbon dioxide. The portions used in various experimental studies distilled at 88.7–89° at 760 mm. The molecular weight of the quaternary ammonium salt prepared by permitting a slight excess of triethylamine to react with ethyl iodide was calculated from the iodide determinations by the Volhard method with several weighed samples of the product. The molecular weight calculated was 257.4 ± 0.9. The theoretical value for quaternary ethylammonium iodide is 257.1. Mallinckrodt lithium nitrate and sodium acetate analytical reagents were freed of water of crystallization by heating and were used without further purification. Water solutions of the sodium acetate were shown to be at the phenolphthalein end-point and water solutions of the lithium nitrate were neutral. Absolute alcohol was prepared by refluxing 95% ethyl alcohol over calcium oxide and distilling, followed by a subsequent treatment with calcium oxide and silver oxide. The distilled water used in preparing reagents and reaction mixtures was boiled under reduced pressure to remove dissolved gases, cooled, and stored under an atmosphere of nitrogen. The standard solutions of silver nitrate, ammonium thiocyanate, hydrochloric acid, and sodium hydroxide used in the Volhard and acid-base titrations were made up from analytical grade chemicals.

Reaction mixtures were prepared by dissolving weighed amounts of ethyl iodide in a measured volume of ethyl

alcohol and diluting with the required volume of water to produce the desired dielectric constant as calculated from the data of Åkerlöf.¹³ The usual procedure was to prepare a stock solution of ethyl iodide under an atmosphere of nitrogen. A measured volume of this solution was added to a calibrated flask of special design containing the basic reactant: sodium hydroxide, triethylamine, sodium acetate, or lithium nitrate. Part of the reaction mixture so prepared was poured into constricted tubes which were sealed off immediately and placed in the 25° thermostat. The remainder of this solution was transferred by nitrogen pressure to a specially designed reaction flask in the thermostat at 50°. A special buret provided with a water jacket in which water at room temperature circulated was attached to the reaction flask through ground glass connections, whenever a sample of the reaction mixture was desired for analysis.

Parallel measurements were made at 25 and 50° in several cases for reaction mixtures containing sodium hydroxide, triethylamine, or sodium acetate prepared from the same stock solution of ethyl iodide. Since the solutions were made up with a weighed amount of ethyl iodide diluted to a definite volume at room temperature, the starting concentration was calculated taking into account the change in the volume of the solution when the reaction was carried out at 50°. Concentrations of sodium acetate and lithium nitrate were calculated in the same manner. The starting concentration of sodium hydroxide or triethylamine was obtained by analyzing parallel samples of reaction mixture for basicity and iodide content. The sum of the base concentration found by titration with standard acid and of the iodide ion concentration as determined by the Volhard method was taken as the starting concentration of base. Initial concentrations calculated in this manner at several different times during the course of the reaction showed maximum variations on the order of 0.5%. The concentration of ethyl iodide and of base at any time during the course of the reaction were taken as the differences of their respective starting concentrations and of the iodide ion concentration found at that time.

In a few experiments where the water content was high, ethyl iodide apparently was lost during the preparation and transfer of solutions. The iodide ion concentration determined after the reaction had gone to completion was then taken as a measure of the starting concentration of ethyl iodide. Velocity constants determined in this manner were in agreement with those found using an improved technique which eliminated possibility of loss. Before this loss had been established, our calculated constants in the high water range showed the same sort of behavior noted by Moelwyn-Hughes¹⁴ that led him to the conclusion that a side reaction resulted in the formation of a complex organic iodide which resisted the usual analytical methods. Greenspan, Liotta and La Mer¹⁵ showed that ethyl iodide, in contradiction to the ideas of Moelwyn-Hughes, was hydrolyzed to yield one mole of inorganic iodide per mole of ethyl iodide used. Our later experiments using a sealed tube technique to guard care-

(13) Åkerlöf, *THIS JOURNAL*, **54**, 4125 (1932).

(14) Moelwyn-Hughes, *J. Chem. Soc.*, 1576 (1933).

(15) Greenspan, Liotta and La Mer, *Trans. Faraday Soc.*, **31**, 824 (1935).

(11) Burke and Donnan, (a) *J. Chem. Soc.* **85**, 555 (1904); (b) *Z. physik. Chem.*, **69**, 148 (1909).

(12) Tian and Gand, *Compt. rend.*, **204**, 1811 (1937).

fully against the loss of ethyl iodide support the evidence of the latter investigators¹⁵ and indicate that the discrepancies reported by Moelwyn-Hughes arose from loss of ethyl iodide in preparing his reaction samples.

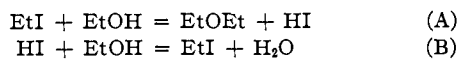
Temperature as determined by Beckmann thermometers checked against a B. S. resistance thermometer to 0.01°, was maintained during the experiments to within 0.03°.

Experimental Results and Discussion

All of our constants have been obtained by graphical methods to eliminate the errors arising from the use of a single concentration determination at a particular time in evaluating the integration constant of a differential equation. The notation used in this section of the paper follows:

- a = starting concentration ethyl iodide in moles per liter
 b = starting concentration of base in moles per liter
 k_n = bimolecular constant for EtI-EtOH
 x = concentration of iodide ion at time t (in minutes)
 k_w = bimolecular constant for EtI-H₂O reaction
 k_c = effective bimolecular constant for EtI-solvent reaction
 k_s = pseudo-first order constant for EtI-solvent reaction
 k = ordinary experimental bimolecular velocity constant for EtI-base reaction
 k_b = bimolecular velocity constant peculiar to base corrected for solvent reaction
 k_u = pseudo-first order constant for base at high concentration
 s = slope of $\log [(b-x)/(a-x)]$ plotted against t
 s' = slope of $\log [(b'-x)/(a-x)]$ plotted against t
 $b' = b + (k_s/k_b)$
 $F = (b-x)/(a-x)$

The Solvolysis Reactions of Ethyl Iodide in Alcohol-Water Mixtures.—The reaction of ethyl iodide with absolute alcohol produces ethyl ether and hydriodic acid, and the acid so produced reacts with the alcohol to reproduce ethyl iodide.



At the start of the reaction, the influence of the hydriodic acid is slight so that the velocity constant for reaction (A) may be determined from the limiting slope at zero time of the function $\log(a-x)$ plotted against t . This follows from equation (2)

$$dx/dt = k_s[\text{EtOH}][\text{EtI}] = k_s[\text{EtI}] = k_s(a-x) \quad (1)$$

$$k_s t = 2.303 \log \frac{a}{a-x} \quad (2)$$

When aqueous alcohol is used as solvent the subsidiary reaction (B) is reversed and the plot of $\log(a-x)$ against time is linear to high percentage conversions. The value of k_s in an alcohol-water mixture represents the sum of the alcoholysis and hydrolysis effects in that particular solution.

$$k_s = k_a[\text{EtOH}] + k_w[\text{H}_2\text{O}] \quad (3)$$

These alcoholysis constants k_a and k_w are constants only in a given alcohol-water mixture and may be regarded as functions of the dielectric constant. Since it would be very difficult to split the contribution of the water from that of the alcohol in a given solvent, an effective bimolecular constant k_c has been defined by equation (4). This constant k_c is the effective bimolecular constant for all types of hydroxylic molecules in the alcohol-water mixture and is

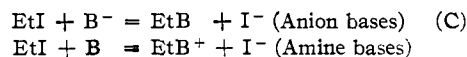
$$k_s = k_c([\text{EtOH}] + [\text{H}_2\text{O}]) = k_c[\text{ROH}] \quad (4)$$

comparable to the values of k_b given for the various bases investigated. Values of k_s obtained from experiments in alcohol and alcohol-water mixtures are given in Table I with the corresponding values of k_c .

TABLE I

Expt.	% EtOH	D	a	k_s	k_c
At 50°					
9a	100	20.85	0.0100	1.3×10^{-8}	7.8×10^{-7}
14	100	20.85	.0131	1.3×10^{-8}	7.8×10^{-7}
1	92.6	23	.0123	2.2×10^{-8}	12×10^{-7}
12	75.8	30	.0173	5.1×10^{-8}	21×10^{-7}
13	55.5	40	.0152	8.3×10^{-8}	25×10^{-7}
6	36.9	50	.0102	14.0×10^{-8}	35×10^{-7}
16d	18.4	60	.0153	23.0×10^{-8}	49×10^{-7}
At 25°					
9e	100	24.3	.0102	4.9×10^{-7}	2.9×10^{-8}
16e	18.4	67.9	.0153	77×10^{-7}	17.2×10^{-8}

Rate Equations for Reaction of Ethyl Iodide with Bases.—When a base is added to a solution of ethyl iodide in absolute or aqueous alcohol, the subsidiary reproduction of ethyl iodide as in equation (B) is prevented and the reaction becomes second order with respect to the ethyl iodide and added base



The usual bimolecular form, when the base concentration is the greater, yields

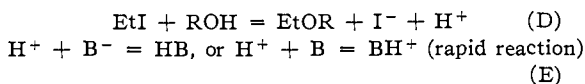
$$dx/dt = k[\text{B}][\text{EtI}] = k(b-x)(a-x) \quad (5)$$

$$kt = \frac{2.303}{(b-a)} \log \frac{a(b-x)}{b(a-x)} \quad (6)$$

A plot of $\log(b-x)/(a-x)$ against t thus gives a straight line of slope S and the bimolecular constant may be obtained from

$$k(b-a) = 2.303S \quad (7)$$

If we are interested in getting a measure of the reactivity peculiar to a given base, we should take into account that part of the chemical change which is produced by reaction of ethyl iodide with the solvent. Since we are dealing only with hydroxylic solvents, we have



We have developed the following equation to take into account the solvent effect.

$$\begin{aligned} dx/dt &= k_b[\text{B}][\text{EtI}] + k_o[\text{ROH}][\text{EtI}] = k[\text{B}][\text{EtI}] & (8) \\ dx/dt &= k_b(b-x)(a-x) + k_o(a-x) = k(b-x)(a-x) & (9) \end{aligned}$$

$$dx/dt = k_b(b + k_s/k_b - x)(a-x) = k_b(b' - x)(a-x) \quad (10)$$

$$k_b t = \frac{2.303}{b' - a} \log \frac{a(b' - x)}{b'(a - x)} \quad (11)$$

The velocity constant k_b peculiar to a given base B can be obtained from the slope S' from the plot of $\log(b' - x)/(a - x)$ vs. t as indicated by the equations

$$k_b(b' - a) = k_b \left(b + \frac{k_s}{k_b} - a \right) = 2.303S' \quad (12)$$

$$k_b = \frac{2.303S'}{b - a} - \frac{k_s}{b - a} \quad (13)$$

When b is somewhat larger than k_s/k_b and a , S' becomes equal to S within the limits of experimental error and the correction for the side reaction with the solvent takes the form

$$k_b = k - \frac{k_s}{b - a} \quad (14)$$

k_s is evaluated from the independent study of the solvent reaction, k is determined from (7); and finally k_b from (14). This latter equation leads to considerable error when b approaches a in value. In such cases, the correction is better made from (9), which yields

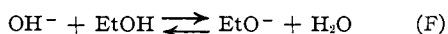
$$k_b = k - \frac{k_s}{b - x} \quad (15)$$

Equation (15) reduces to (16) when b is much greater than x .

$$k_b = k - \frac{k_s}{b} \quad (16)$$

Most of our experiments have been made with base concentrations around 0.05 M and ethyl iodide 0.01 M . Under these conditions, the correction for the solvent reaction by (14) is justified.

Reaction with Sodium Hydroxide.—When sodium hydroxide is dissolved in absolute or aqueous ethyl alcohol, a significant concentration of ethylate ions is produced in establishing the equilibrium represented in (F)

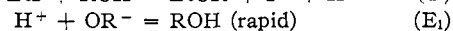
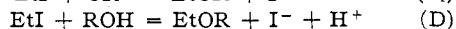
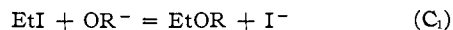


Since no precise data are available on this equilibrium, we have merely calculated the constants k and k_b which represent composites of the individ-

ual velocity constants for hydroxyl and ethylate ions. We then have

$$b = [\text{OR}^-] = [\text{OH}^-] + [\text{EtO}^-] \quad (17)$$

and the over-all reactions are



The ordinary bimolecular constants k and the constants peculiar to the sodium hydroxide k_b are given in Table II.

TABLE II

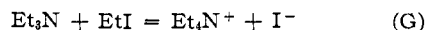
REACTION OF EtI WITH NaOH IN EtOH-H₂O MIXTURES

Expt.	% EtOH	D	b	a	k	k_b
At 50°						
11a	100	20.85	0.0568	0.01100	0.0826	0.082
13a	75.8	30.0	.0522	.01118	.085	.084
7a	75.4	30.2	.00697	.00996	.114	.097
7b	75.4	30.2	.0288	.00996	.0835	.081
7c	75.4	30.2	.0407	.00996	.082	.080
14a	55.5	40.0	.0606	.01000	.0505	.049
15a	36.9	50.0	.0383	.00837	.048	.043
16a	18.4	60.0	.0314	.01533	.0393	.025
8a	18.1	60.2	.0095	.0174	.065	.036
6a	18.1	60.2	.01038	.00597	.075	.023
4a	18.1	60.2	.0278	.00626	.0351	.024
6b	18.1	60.2	.0461	.00672	.0294	.0236
8b	18.1	60.2	.0557	.0179	.0322	.0261
5a	18.1	60.2	.1875	.00608	.0232	.0219
At 25°						
11b	100	24.3	.0582	.01024	.0062	.0062
13b	75.8	35.0	.0536	.01148	.0056	.0056
14c	66.3	40.0	.0582	.01019	.0046	.0046
15b	36.9	56.9	.0395	.00854	.00336	.0032

Reaction with Triethylamine.—When triethylamine is dissolved in hydroxylic solvents, some ionization occurs which produces the strongly basic solvent anions.



Reaction of ethyl iodide with these anions is negligible because of their low concentrations. The ionization constant¹⁶ is 5.65×10^{-8} in ethyl alcohol and 5.69×10^{-4} in pure water at 25°. Experiments with the nitrate salt of triethylamine showed that Et_3NH^+ is not active. The essential reaction is



Since the constant for reaction with the amine was generally lower than for the sodium hydroxide, the correction for the solvent reaction was of greater importance. The limitations of Eq. (14) under the conditions of Expt. 12a necessitated the calculation of k_b by Eq. (16) but all other constants in Table III were calculated in the usual manner.

(16) Li and Stewart, THIS JOURNAL, 59, 2596 (1937).

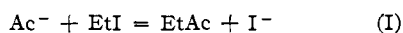
TABLE III
REACTION OF EtI WITH Et₃N IN EtOH-H₂O MIXTURES

Expt.	% EtOH	D	b	a	10 ³ k	10 ³ k _b
At 50°						
12a	100	20.85	0.0153	0.01000	3.34	2.5
12b	100	20.85	.0394	.01000	2.74	2.3
16b	100	20.85	.0682	.00984	2.28	2.06
13c	75.8	30.0	.0548	.01100	7.62	6.5
14d	55.5	40.0	.0589	.01000	14.4	12.7
15c	36.9	50.0	.0458	.00850	32.7	29
4b	18.1	60.2	.0194	.00671	55.0	37
At 25°						
16c	100	24.3	0.0692	0.01007	0.168	0.160
14f	66.3	40.0	.0600	.01019	0.425	0.377
14e	55.5	45.7	.0600	.01019	1.31	1.25
15d	36.9	36.9	.0468	.00867	3.08	2.95

Reaction with Sodium Acetate.—Interaction of acetate ions with the solvent produces solvent anions, but these are negligible as far as reaction with ethyl iodide is concerned. The equilibrium constant¹⁷ for reaction (H) is of the order 10⁻¹⁰ over the complete range of alcohol-water composition.



The essential reaction with the ethyl iodide is (I), although the solvent reaction is even more



important in this case than it is for triethylamine. The constants given in Table IV were calculated as previously described.

TABLE IV
REACTION OF NaAc WITH EtI IN EtOH-H₂O MIXTURES

Expt.	% EtOH	D	b	a	10 ³ k	10 ³ k _b
At 50°						
12c	100	20.85	0.0586	0.01000	1.50	1.23
13d	75.8	30	.0585	.01118	2.56	1.48
14g	55.5	40	.1178	.01000	1.89	1.12
15c	36.9	50	.1163	.00823	2.51	1.22
At 25°						
12d	100	24.3	0.0600	0.01024	0.070	0.060
14i	66.3	40	.1200	.01019	.087	.065
14h	55.5	45.7	.1200	.01019	.090	.063

Reaction with Lithium Nitrate.—The reaction of lithium nitrate was so slow at the temperature investigated that we limited our kinetic studies to high concentrations of salt and to low percentage conversions. Pseudo-first order constants k_{11} were obtained readily by plotting $\log(u - x)$ against time. The experiments were originally carried out to determine the "neutral salt effect" on the solvent reaction, but our ob-

(17) Kilpi and Wansila, *Z. physik. Chem.*, **A177**, 427 (1937).

servations soon led us to the conclusion that the most important effect was due to the nitrate ion as a primary reactant. We found that samples of ethyl iodide in anhydrous ethyl alcohol reached an equilibrium at 96–97° when about 30% of the halide had been converted to iodide ion. This was checked by both the Volhard and acidity determinations. An exact evaluation of the equilibrium concentrations was impossible because of the slow oxidation of iodide to free iodine. Quite different results were obtained in the presence of 0.5 M lithium nitrate in which case 94–96% of the original ethyl iodide was accounted for by the Volhard method, and only one to two per cent. could be accounted for by acidity determinations after equilibrium was attained. The sweet odor associated with ethyl nitrate was noted, which is in agreement with the products observed by Burke and Donnan¹¹ in the reaction with silver nitrate. The formation of ethyl nitrate accounts for the difference between the hydrogen and iodide ion concentrations. Further evidence for reaction with the salt is the linear relation found between the constants k_u and the nitrate ion concentrations. From Equation 16 it is evident that

$$k_u = k_b b + k_s \quad (18)$$

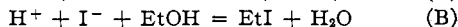
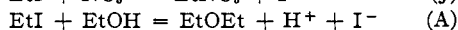
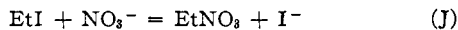
Table V summarizes the experiments with lithium nitrate.

TABLE V
REACTION OF LiNO₃ WITH EtI IN ALCOHOL-WATER MIXTURES

At 50°, 100% EtOH, D = 20.85, a = 0.01059, k _b = 7.8 × 10 ⁻⁶					
b	0	0.0611	0.122	0.224	0.489
10 ⁶ k _u	1.3	1.8	2.3	4.0	5.0
92.6% EtOH, D = 23, a = 0.0105, k _b = 8.8 × 10 ⁻⁶					
b	0	0.058	0.144	0.38	
10 ⁶ k _u	2.22	2.79	3.45	4.14	
36.9% EtOH, D = 50, a = 0.01021, k _b = 8.6 × 10 ⁻⁶					
b	0	0.099	0.248	0.398	0.497
10 ⁶ k _u	14.0	14.6	16.2	17.2	19.1
At 25°, 100% EtOH, D = 24.3, a = 0.01024, k _b = 2.0 × 10 ⁻⁶					
b	0	0.061	0.244	0.488	
10 ⁷ k _u	4.9	5.9	10.5	14.9	

The graphical method was used in obtaining k_b from Eq. (18) because of the high experimental error inherent in measurements to small conversions. The runs at 25° were studied over a period of two months, at the end of which time

from 3-10% of the ethyl iodide was converted to inorganic iodide. Our experiments indicate the following mechanism for the reaction with lithium nitrate



In the presence of added salt, the alcoholysis of ethyl iodide does not produce an equivalent amount of hydrogen and iodide ions because the nitrate ion produces ethyl nitrate (J). In 0.5 molar solution, over three times as many molecules of ethyl iodide are reacting with nitrate ions as are reacting with the alcohol molecules. ($k_{\text{NO}_3^-} = 7.8 \times 10^{-5}$, $k_s = 1.3 \times 10^{-5}$.) Ethyl iodide which has reacted in (A) and has been regenerated in (B) again has an opportunity to choose between nitrate ions and alcohol molecules so that finally a steady state is reached wherein practically all the ethyl iodide has been converted to ethyl nitrate and inorganic iodide. The isolation of nitrate ion as a primary reactant throws some light on the results of Burke and Donnan¹¹ for the ethyl iodide reaction with silver nitrate. The increased rate which they observed in the presence of ammonium and calcium nitrates undoubtedly was due to increasing the concentration of nitrate ions and does not support their argument for reaction with silver nitrate molecules. The silver ion plays an important role in their reaction by removing the iodide ion as silver iodide, thus minimizing the importance of reaction (B).

Correlation of Results with Modern Acid-Base Theory.—The magnitude of the velocity constants k_b for sodium hydroxide, triethylamine, sodium acetate, lithium nitrate, and the solvent molecules seems to be related very closely to the basic strengths of these reactants. Figure 1 shows that triethylamine and solvent molecules exhibit pronounced increases in reactivity with increasing dielectric constant of solvent whereas constants for the anion bases (hydroxide, acetate, and nitrate) either decrease slightly or show little change with changing medium. The decrease in the sodium hydroxide constants may be dependent on the shifting equilibrium between hydroxyl and ethylate ions, but the general behavior

of the various bases is in accord with the theory of acidity developed by Brönsted, Hammett and others.¹⁸ This theory predicts a decrease in acidity for cation acids such as Et_3NH^+ and ROH_2^+ with increases in the dielectric constant and ionic strength. Et_3N and ROH molecules should then be more active as bases at high dielectric constants and high ionic strengths. We find a pronounced increase in k_b for these molecular bases as the dielectric constant is increased. The theory likewise predicts that the acidity of unchanged acids such as ROH , HAc , and HNO_3 in basic solvents will be only slightly influenced by changes in dielectric constant and ionic strength. Only a slight dependence of the base strength for the conjugate anions OR^- , Ac^- , and NO_3^- would be expected, and our constants for anion bases seem

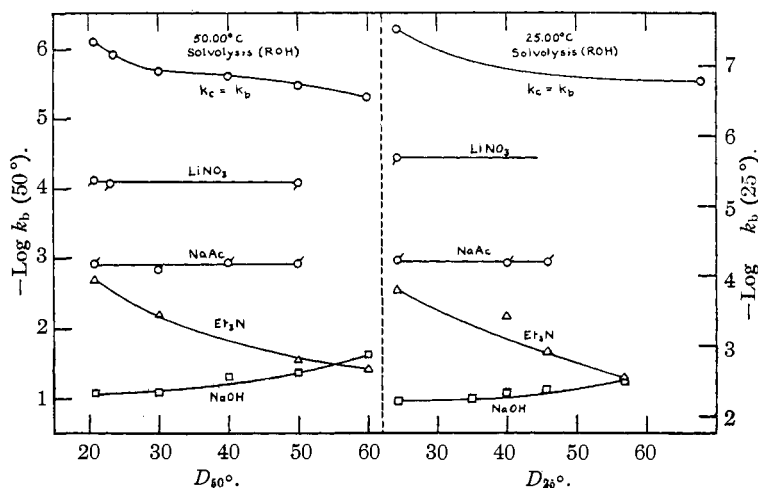


Fig. 1.

to be influenced but slightly with changing media. Figure 2 is the typical Brönsted plot showing the relation of the velocity constants for OR^- , Et_3N , Ac^- , and ROH to the dissociation constants of the conjugate acids ROH , Et_3NH^+ , HAc , and ROH_2^+ . The dissociation constant of acetic acid and the ion product of the solvent have been determined at 20° by Kilpi and Wansila¹⁷ over the complete range of composition for alcohol-water solutions. The constants for triethylamine have been reported at 25° by Li and Stewart¹⁶ and Ablard.¹⁹ The various dissociation constants for the conjugate acids plotted in Fig. 2 were calculated by combining the data of these investigations at 20 and 25°. The values

(18) Brönsted, *J. Phys. Chem.*, **30**, 777 (1926); *Chem. Rev.*, **5**, 45 (1928); Hammett, *THIS JOURNAL*, **60**, 2666 (1928).

(19) Ablard, Thesis, Carnegie Institute of Technology, June, 1937.

for all points in the figure should be accurate within better than a logarithmic unit. Figure 2 suggests that the reactivity of the various bases with ethyl iodide is closely related to the ability of the base to act as a proton acceptor. This suggests that the rate determining step in the reaction may involve the production of an intermediate basic ion by the removal of a proton from the ethyl iodide molecule. The basicity of the solvent

noted by Conrad¹ and his workers may be eliminated. Since salt effects are usually more important at low dielectric constants and since Brönsted's theory predicts greater basicity for the solvent in the presence of electrolytes, it seems likely that k_s values determined at zero ionic strength are not true measures of the solvent reaction at low dielectric constants in the presence of added electrolytes.

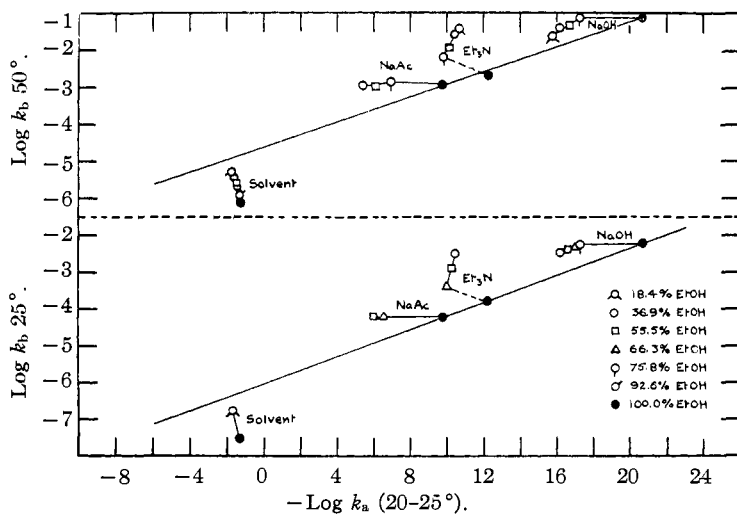


Fig. 2.

would then have a great influence on the concentration of the active intermediary ion and the wide differences in rate in different solvents which Menschutkin⁴ found for the ethyl iodide-triethylamine reaction are readily explained.

The "Dilution Effect."—We note that Brönsted's theory predicts an increased basicity for ROH molecules at high ionic strengths. This would argue for a higher value of the solvent constant k_s in the presence of added electrolytes than was obtained in the absence of added salts. We would then expect that the solvent correction which we have made using the k_s values determined at zero ionic strength would not be sufficient with higher concentrations of added base. A comparison of the values of k and k_b for the sodium hydroxide reaction in 18.1% alcohol (Table II) shows that the correction for the solvent reaction eliminates the "dilution effect" for base concentrations from 0.01 to 0.2 molar. We have not yet studied the reaction in absolute alcohol sufficiently to report on the nature of the correction there. The magnitude of k_s for this solvent allows such a small correction that it is doubtful whether the large "dilution effect"

Influence of Temperature.—Approximate values of the energies of activation for k_b are given in Table VI. Constants have been determined at only the two temperatures and the investigation has been extensive rather than intensive in scope, so the values given should not be used for any quantitative calculations. It is evident that the energy of activation at constant dielectric constant is much greater than at constant composition for the triethylamine and solvent reactions, while little difference is found for the anion bases.

It is interesting to note that the energy of activation for the triethylamine-ethyl iodide reaction in solvents of constant composition is lower than is normally found for reactions in solution. That this in general is true for the amine-halide reactions has been emphasized by Moelwyn-

TABLE VI
APPROXIMATE ENERGIES OF ACTIVATION IN THE ETHYL IODIDE REACTIONS

The solvolysis constants used in correcting for the solvent reaction at 25°, for compositions other than 100 and 18.4% alcohol, were obtained by dividing the value of the constant at 25° by 28. This correction follows from the magnitude of the energy of activation for the solvolysis reaction in 100 and 18.4% alcohol.

Base	Solvent	Approx. energy of activation, cal.
NaOH	100% EtOH	19800
	75.8%	20700
	55.5%	18800
	36.9%	19800
	$D = 40$	18100
Et ₃ N	100%	19600
	55.5%	17800
	36.9%	17500
	$D = 40$	26900
NaAc	100%	23200
	55.5%	22000
	$D = 40$	21800
LiNO ₃	100%	28000
ROH	100%	25100
	18.4%	26000

Hughes.²⁰ The energy of activation for this reaction in solvents of constant dielectric constant appears to be "normal." However, the values reported in this paper are not sufficiently precise for use in testing modern theories.

Summary

Experimental velocity measurements have been made for the reactions of ethyl iodide with the solvent, sodium hydroxide, triethylamine, sodium acetate, and lithium nitrate in aqueous alcohol mixtures at 25 and 50°.

Velocity constants have been calculated by

(20) Moelwyn-Hughes, "Kinetics of Reactions in Solution," Oxford University Press, London, 1935, p. 1122.

graphical methods which correct for the solvent reaction and have been correlated with modern acid-base theories.

An explanation of the "dilution effect" has been suggested and evidence has been presented which indicates that the nitrate ion is a direct reactant with ethyl iodide so that the influence of lithium nitrate is not primarily "inert salt catalysis."

Approximate values of the energies of activation for the reaction of ethyl iodide with the various bases have been calculated.

SCHENLEY PARK
PITTSBURGH, PENNA.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Thermodynamics of Aqueous Sodium Chloride Solutions from 0 to 40° from Electromotive Force Measurements

BY HERBERT S. HARNED AND MELVIN A. COOK

This communication contains a brief summary of the thermodynamic properties of aqueous sodium chloride solutions from 0 to 40° derived principally from the measurements of cells without liquid junction containing a dilute sodium amalgam. Our recent studies of solutions of sodium¹ and potassium hydroxides² and potassium chloride³ have shown that reasonable agreement between the results derived from electromotive forces with those derived from calorimetric or vapor pressure data is obtained if certain precautions regarding extrapolation and the numerical treatment of the data be observed. In the present communication, we have subjected the earlier data of Harned and Nims⁴ to a more recently developed technique of calculation with the result that better agreement with results of other measurements is obtained.

Activity Coefficients.—The electromotive force data of Harned and Nims were extrapolated by the use of the equation

$$\log \gamma = -\frac{u/\sqrt{c}}{1 + A\sqrt{2c}} + Bc - \log(1 + 0.036m) \quad (1)$$

Only the results in the region of concentration of 0.1 to 1 *M* were employed. As shown by us,³ this method leads to an accurate extrapolation

whereas if the equation is applied over a wider concentration range, for example 0.1 to 3 *M*, low values of *A* and γ are obtained. Using the precise evaluation of γ in dilute solution by Brown and MacInnes⁵ from cells with liquid junction and the accurate determination of the relative partial molal heat content, \bar{L}_2 , from 10 to 25° by Gulbransen and Robinson,⁶ we are able to obtain an entirely independent check of our extrapolation. The values of \bar{L}_2 at 0.1 *M* determined by the latter are given as a function of temperature by

$$\bar{L}_{2(0.1)} = -1277 + 4.62T \quad (2)$$

Upon substitution in the equation for the variation of the activity coefficient with temperature, integration, and evaluation of the integration constant by employing Brown and MacInnes' value of 0.7784 for γ at 0.1 *M* and 25°

$$-\log \gamma_{0.1} = \frac{139.56}{T} + 1.1625 \log T - 3.2358 \quad (3)$$

is obtained from which $\gamma_{0.1}$ may be computed as a function of temperature. A comparison of the two methods of extrapolation is illustrated in Table I.

The value of the apparent ionic diameter, *a*, was found equal to 4.0 ± 0.1 Å. at all temperatures. In the computations by equation (1),

(1) Harned and Hecker, *THIS JOURNAL*, **55**, 4838 (1933).

(2) Harned and Cook, *ibid.*, **59**, 496 (1937).

(3) Harned and Cook, *ibid.*, **59**, 1290 (1937).

(4) Harned and Nims, *ibid.*, **54**, 423 (1932).

(5) Brown and MacInnes, *ibid.*, **57**, 1356 (1935).

(6) Gulbransen and Robinson, *ibid.*, **56**, 2637 (1934).