The optical density was then preset at selected values and the times increments for the attainment of these successive optical densities were measured using two stopwatches.

Activation parameters were calculated from plots of log (k/T) *vs.* ($1/T$) by the method of least squares. Kinetic runs were carried out at four temperatures over an interval of 30°. The standard deviations[42] of $\Delta H\ddagger$ and $T\Delta S\ddagger$ were, in three typical cases, ± 0.3 kcal./mole.

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[42] W. J. Youden, "Statistical Methods for Chemists," John Wiley and Sons, Inc., New York, N. Y., 1951, p. 42.

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE SPRAGUE ELECTRIC CO., NORTH ADAMS, MASS.]

Rates, Products and Salt Effects in the Reactions of Benzyldimethylanilinium Ion with Ethoxide Ion in Ethanol

BY SIDNEY D. ROSS, MANUEL FINKELSTEIN AND RAYMOND C. PETERSEN

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The rates of reaction of benzyldimethylanilinium bromide with sodium ethoxide and lithium ethoxide in ethanol at 50.8 ± 0.1° have been measured. The effects due to added neutral salts and variations in the anion associated with the quaternary ammonium ion have been studied. Measurements were also made of the rates of solvolysis of the quaternary ammonium salts and of benzyl bromide in the same solvent and at the same temperature.

The S_N2 displacement on a quaternary ammonium ion by a negatively charged nucleophile, *e.g.*, hydroxide ion or ethoxide ion, cited as an example of this charge type,[1] has received only scant quantitative study. Two such reactions, the rates of which have been measured, are those of benzyl- and *p*-alkyl substituted benzylpyridinium ions with ethoxide ion in ethanol[2] and of *p*-nitrophenyltrimethylammonium ion with thiocyanate ion in methanol.[3] Neither of the above studies presented detailed evidence to show that the reactions were, in fact, second-order nor investigated salt effects, in spite of the fact that salt effects in reactions of this type are sufficiently large to make the determination of reaction order difficult and to make the significance of a rate constant determined at a single set of initial concentrations questionable.[4]

This paper presents data on the rate of reaction of benzyldimethylanilinium ion with ethoxide ion in ethanol at 50.8 ± 0.1°. In most of the measurements the quaternary ammonium ion was added as the bromide, but some experiments were also carried out with the nitrate and the picrate. The nucleophile was introduced as either sodium ethoxide or lithium ethoxide, and lithium nitrate and lithium chloride were used as neutral salts in some experiments. In connection with the above determinations it also became necessary to study the solvolysis of benzyl bromide and the solvolyses of benzyldimethylanilinium bromide, nitrate and picrate, all in ethanol at 50.8 ± 0.1°. Our purpose in presenting these results is to direct attention to the formidable problems that stand in the way of a quantitative understanding of this reaction.

Results

Table I presents data on the rate of the reaction of benzyldimethylanilinium bromide with sodium ethoxide, and Table II records similar results using lithium ethoxide as the nucleophile. The measurements were generally carried to 60% reaction or beyond. The rate constants, given in column 4 of these tables, were calculated from the slopes of the best straight lines through the experimental points of second-order plots, which were in all cases satisfactory, with none of the experimental points deviating appreciably from the line. The fifth column of these tables gives the square root of the average ionic strength over that portion of the run which was actually followed experimentally.

TABLE I

RATES OF REACTION OF BENZYLDIMETHYLANILINIUM BROMIDE AND SODIUM ETHOXIDE IN ABSOLUTE ETHANOL AT 50.8 ± 0.1°

$R_4N^+Br^-$, mole l.$^{-1}$	NaOEt, mole l.$^{-1}$	Added $LiNO_3$, mole l.$^{-1}$	$k_2 \times 10^4$, l. mole^{-1} sec.$^{-1}$	$\bar{\mu}^{1/2}$
0.01962	0.01054	0	38.9	0.162
.02119	.01608	0	27.3	.180
.02142	.01563	0	29.4	.180
.04912	.01065	0	27.2	.236
.04863	.01565	0	21.6	.242
.05024	.01598	0	19.8	.245
.01953	.04947	0	19.9	.248
.04884	.03072	0	16.5	.262
.05024	.08798	0	10.9	.347
.04889	.09831	0	11.3	.360
.05011	.2193	0	7.16	.500
.02037	.01653	0.02104	14.1	.233
.02095	.01653	.04052	8.80	.270
.02041	.01662	.05815	6.61	.300
.02055	.01672	.07825	5.01	.333

The data of Table III are presented to show how the rate of reaction of benzyldimethylanilinium ion with ethoxide ion is affected by varying the nature of the anion associated with the quaternary ammonium ion.

To assure that the results tabulated in Tables I-III really represent rates of reaction with ethoxide ion, unaffected by an accompanying first-order solvolysis of the quaternary ammonium ion, the solvolyses of benzyl bromide and of benzyldimethylanilinium bromide, nitrate and picrate in absolute ethanol at 50.8 ± 0.1° were determined. The reaction of benzyl bromide, the

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[1] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 346.

[2] C. W. L. Bevan, E. D. Hughes and C. K. Ingold, *Nature*, **171**, 301 (1953).

[3] B. A. Bolto and J. Miller, *J. Org. Chem.*, **20**, 558 (1955).

[4] The sulfonium salts, in contrast, have received more detailed attention. For some recent studies see, (a) C. G. Swain and L. E. Kaiser, THIS JOURNAL, **80**, 4089 (1958); (b) C. G. Swain, L. E. Kaiser and T. E. C. Knee, *ibid.*, **80**, 4092 (1958); (c) E. D. Hughes, C. K. Ingold and Y. Pocker, *Chemistry & Industry*, 1282 (1959).

TABLE II

RATES OF REACTION OF BENZYLDIMETHYLANILINIUM BROMIDE AND LITHIUM ETHOXIDE IN ABSOLUTE ETHANOL AT 50.8 ± 0.1°

$R_4N^+Br^-$, mole l.$^{-1}$	LiOEt, mole l.$^{-1}$	Added LiCl, mole l.$^{-1}$	$k_2 \times 10^4$, l. mole^{-1} sec.$^{-1}$	$\mu^{1/2}$
0.02083	0.01580	0	22.1	0.179
.01993	.01841	0	20.4	.182
.04861	.01585	0	16.3	.244
.01487	.04972	0	15.4	.244
.07331	.02747	0	11.5	.303
.07362	.04996	0	8.76	.332
.1067	.05057	0	7.55	.376
.02005	.01565	0.02450	9.38	.233
.02002	.01571	.04849	6.31	.282
.01998	.01569	.1064	3.75	.370
.02000	.01570	.1483	2.87	.424
.02006	.01534	.2020	1.92	.483
.02002	.01567	.4389	1.24	.686

TABLE III

EFFECT OF VARIATIONS IN THE NATURE OF THE ANION ASSOCIATED WITH THE QUATERNARY AMMONIUM ION ON THE REACTION RATE

$R_4N^+X^-$, mole l.$^{-1}$	X^-	NaOEt, mole l.$^{-1}$	$k_2 \times 10^3$ l. mole^{-1} sec.$^{-1}$
0.01965	Bromide	0.009564	3.86
.01975	Nitrate	.009642	4.18
.01945	Picrate	.009467	5.54
.009759	Picrate	.008019	7.50

rates of which are given in Table IV, is a true first-order reaction. The quaternary ammonium salts all give reasonably satisfactory first-order plots, but with the bromide at least, it is clear that the reaction is not first-order, and that here, as in the case of the sulfonium salts,[4] the anion is involved. This is indicated by the vast difference in rate between the bromide and the nitrate.[5] The results with the quaternary ammonium salts are given in Table V. These results are to be considered tentative and are only presented at this time to show that the solvolytic reaction is slow with respect to the reactions with ethoxide ion.

TABLE IV

SOLVOLYSIS OF BENZYL BROMIDE IN ABSOLUTE ETHANOL AT 50.8 ± 0.1°

RBr, mole l.$^{-1}$	$k_1 \times 10^6$, sec.$^{-1}$	Half-life hr.
0.03045	8.75	22.0
.05785	8.24	23.4
.1245	8.71	22.1

TABLE V

SOLVOLYSIS OF BENZYLDIMETHYLANILINIUM SALTS IN ABSOLUTE ETHANOL AT 50.8 ± 0.1°

$R_4N^+X^-$, mole l.$^{-1}$	X	$k \times 10^7$, sec.$^{-1}$	Half-life, hr.
0.02039	Bromide	8.20	235
.02074	Bromide	8.89	217
.05073	Bromide	8.44	228
.09975	Bromide	7.44	259
.1033	Bromide	7.42	259
.01968	Nitrate	~0.21	~ 9000
.01969	Picrate	~0.12	~16000

Experimental[6]

Benzyldimethylanilinium Bromide.—Although our preparation of this salt has been reported briefly before,[7] the detailed procedure is described here, since two previous reports of this salt[8] gave melting points differing markedly from each other and from the value that we found. A solution of benzyl bromide (100 g., 0.59 mole) and N,N-dimethylaniline (83.7 g., 0.69 mole) in acetone (300 ml.) was refluxed 2 hr. and then cooled to room temperature. Dry ether was added, and the precipitated salt was filtered and washed with ether; yield 149 g. (87%), m.p. 143–145° dec. The salt was purified either by recrystallization from isopropyl alcohol followed by vacuum drying for 3 hr. at 65° or by solution in ethanol, filtration, precipitation with ether and vacuum drying at 65°. Neither procedure altered the melting point.

Anal. Calcd. for $C_{15}H_{18}NBr$: C, 61.65; H, 6.21; N, 4.79; Br, 27.35. Found: C, 61.90; H, 6.16; N, 4.60; Br, 27.50.

Benzyldimethylanilinium Nitrate.—Benzyldimethylanilinium bromide (58.4 g., 0.2 mole) in water (300 ml.) was converted to the hydroxide with silver oxide (28 g., 0.12 mole) as previously described.[7] The solution was filtered by gravity, neutralized to a phenolphthalein end-point with dilute nitric acid (1:4) and then made just faintly alkaline. The pink solution was filtered through Celite and concentrated *in vacuo*. Benzene was added to aid in the removal of the last traces of water. The solid residue was dissolved in hot isopropyl alcohol to give a pink solution that was filtered. Dilute nitric acid (1:4) was added dropwise until the pink color was discharged, and the salt was precipitated with anhydrous ether; yield, 48.4 g. (88%), m.p. 156–157° dec. The salt was recrystallized three additional times from isopropyl alcohol, washed with ether and air-dried; m.p. 157–158° dec.

Anal. Calcd. for $C_{15}H_{18}N_2O_3$: C, 65.68; H, 6.61; N, 10.21. Found: C, 65.09; H, 6.83; N, 10.56.

Benzyldimethylanilinium Picrate.—Solutions of ammonium picrate (12.3 g., 0.05 mole) and benzyldimethylanilinium bromide (14.6 g., 0.05 mole), both in the minimum quantity of hot water, were mixed and warmed 10 min. On cooling, a quantitative yield of the crude quaternary ammonium picrate crystallized. Recrystallization from ethanol gave 17.4 g. (79%) of the product, m.p. 130–132° dec. A sample crystallized three additional times from ethanol for analysis had m.p. 131–132° dec.

Anal. Calcd. for $C_{21}H_{20}N_4O_7$: C, 57.27; H, 4.58; N, 12.72. Found: C, 57.50; 57.35; H, 4.41, 4.28; N, 12.43, 12.49.

Isolation of Products.—Sodium (4.6 g., 0.2 mole) was allowed to react with ethanol (250 ml.). Benzyldimethylanilinium bromide (29.2 g., 0.1 mole) was added, and the solution was refluxed 4.5 hr. The reaction mixture was poured into water, and the solution was extracted two times with benzene. The benzene solution was extracted two times with 25% sulfuric acid. The benzene layer was washed with saturated sodium bicarbonate solution and dried over anhydrous magnesium sulfate. Distillation of the benzene solution gave 9 g. (66.2%) of benzyl ethyl ether,

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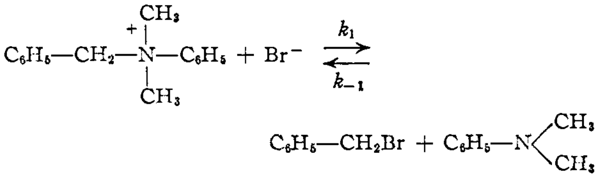
(5) A possible mechanism for the solvolysis of the bromide is,



$$C_6H_5{-}CH_2{-}\overset{+}{N}(CH_3)_2{-}C_6H_5 + Br^- \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} C_6H_5{-}CH_2Br + C_6H_5{-}N(CH_3)_2$$

$$C_6H_5{-}CH_2Br + C_2H_5OH \xrightarrow{k_2} C_6H_5{-}CH_2OC_2H_5 + HBr$$

with none of the above k's being rate determining and with the possibility of other as yet unidentified reactions interfering. The present data are not sufficiently precise to warrant testing this mechanism, but we plan to continue this study in the near future.

(6) Analyses are by Clark Microanalytical Laboratory.

(7) M. Finkelstein, R. C. Petersen and S. D. Ross, THIS JOURNAL, **81**, 2361 (1959).

(8) K. Nador and L. Gyermek, *Acta Chim. Acad. Sci. Hung.*, **2**, 95 (1952); M. S. Kharasch, G. H. Williams and W. Nudenberg, *J. Org. Chem.*, **20**, 937 (1955).

b.p. 61.5–63° at 9–10 mm., n^{24}D 1.4915. The acid extracts were made strongly basic and extracted with ether. The ether extracts were dried over anhydrous magnesium sulfate. The ether was removed, and slightly more than 0.1 mole of 85% picric acid, dissolved in ethanol, was added. This gave 30.5 g. (87.1%) of dimethylanilinium picrate, m.p. 150–151° dec. Recrystallization from ethanol–benzene raised the m.p. to 156–158° dec.

In a separate experiment, sodium (4.6 g., 0.2 mole) was allowed to react with ethanol (250 ml.), benzyldimethylanilinium bromide (29.2 g., 0.1 mole) was added and the solution was refluxed 7 hr. A small portion (12 g.), boiling to 76°, was distilled from the total reaction mixture. The remaining solution was poured into water. The solution was extracted two times with ether. The ether solution was extracted two times with two 100-ml. portions of 25% sulfuric acid, washed with saturated sodium bicarbonate solution and water and dried over anhydrous magnesium sulfate. Removal of the ether gave the crude benzyl ethyl ether fraction. The acid extracts were made basic and extracted two times with ether. The ether solution was dried over anhydrous magnesium sulfate. Removal of the ether gave the crude dimethylaniline fraction. All three of the above fractions were analyzed by vapor phase chromatography using a model 154B Perkin–Elmer Vapor Fractometer. These analyses indicated the presence of the following products: methyl ethyl ether, less than 4.8%; benzyl ethyl ether, 80.8%; dimethylaniline, 86%.

Rate Measurements.—Absolute ethanol from the U.S. Industrial Chemicals Co. was distilled from calcium hydride before use. Reagent grade lithium nitrate and lithium chloride were dried *in vacuo* before use. Eastman Kodak Co. white label benzyl bromide was distilled at 6 mm., and a middle cut, b.p. 69–70°, was taken. This was redistilled at 6 mm., and a fraction boiling at 69° was used. Stock solutions of lithium ethoxide and sodium ethoxide were prepared by treating the appropriate metal with absolute ethanol. Required concentrations were obtained by diluting appropriate aliquots of the stock solutions.

Separate determinate solutions of the benzyldimethylanilinium salts and the ethoxides were prepared at 25°. Neutral salts were added as required to the ethoxide solutions. The concentrations at 50.8°, which are used throughout in this paper, were calculated from the concentrations at 25° and the known change in the volume of ethanol with temperature. The solutions were mixed at room temperature. Aliquots were taken and sealed in separate tubes. The tubes were placed in an oil-bath at 50.8 ± 0.1°, withdrawn after desired time intervals and chilled. The contents were added to an excess of standard acid, and the excess acid was determined by titration to a phenolphthalein end-point with standard alkali. In the case of the picrate and one run each with the bromide and nitrate, the titration was performed with a *p*H meter.

In the solvolysis reactions, determinate solutions of the appropriate salts were made up at 25° and sealed in tubes. These were removed from the 50.8° bath at appropriate time intervals and analyzed for acid content. In the case of the picrate a *p*H titration was necessary because of the yellow color. A dilution procedure was used to analyze for the acid formed during the solvolysis of the bromide. This was necessitated by a purple color which developed during the reaction and obscured the phenolphthalein end-point.

In the solvolysis of benzyl bromide, aliquots were withdrawn at appropriate intervals, chilled and poured into benzene. The solution was extracted three times with water, and the aqueous extract was analyzed for acid.

Discussion

The reaction between benzyldimethylanilinium ion and ethoxide ion in refluxing ethanol proceeds cleanly to give dimethylaniline and benzyl ethyl ether as the major products. In synthetic experiments it has been possible to show that these two products are formed in yields of greater than 80%. There is in addition some attack on a methyl group attached to the nitrogen of the quaternary ammonium ion. This is evidenced by the presence of small amounts of methyl ethyl ether in the product. However, less than 4.8% of this ether is formed. In these synthetic experiments the ethoxide ion was in twofold excess, whereas the rate measurements were, for the most part, with the quaternary ammonium ion in excess and at the lower temperature of 50.8 ± 0.1°. It is, therefore, unlikely that methyl ethyl ether formation seriously complicates the rate measurements. At the worst, the reported rates for attack of ethoxide ion on the benzyl carbon atom are very slightly high because of this concurrent attack on the methyl group.

The problem of determining the order of this reaction is seriously complicated by effects due to the influence of the ionic strength. The usual criterion for a particular order of varying the initial concentrations and finding the rate constant unchanged is not applicable here because of the large negative salt effect characteristic of a reaction of this charge type.[9] If attention is focused only on the measurements in Tables I and II in which no neutral salt was added, it is found that the time required to attain 50% reaction varies from a minimum of 80 minutes to a maximum of 500 minutes. This is to be contrasted with the results for the reaction in the absence of ethoxide ion (Table V), where the half-life is more than 200 hours for the quaternary ammonium bromide and more than 9000 hours for the nitrate. The reaction in the presence of ethoxide ion is, thus, 23 or more times as fast as in its absence. The order in ethoxide is, therefore, not zero.

There are two experiments which indicate that the order must be the same in both the ethoxide ion and the quaternary ammonium ion. For 0.04861 *M* benzyldimethylanilinium bromide and 0.01585 *M* lithium ethoxide the observed bimolecular rate was 16.3×10^{-4} l. mole^{-1} sec.$^{-1}$. An experiment at the same $\bar{\mu}^{1/2}$ but with the quaternary ammonium ion initially at 0.01487 *M* and ethoxide ion initially at 0.04972 *M* gave a rate constant of 15.4×10^{-4} l. mole^{-1} sec.$^{-1}$. Similarly, 0.05024 *M* benzyldimethylanilinium bromide and 0.01598 *M* sodium ethoxide gave a rate constant of 19.8×10^{-4} l. mole^{-1} sec.$^{-1}$ for the rate constant, whereas 0.01953 *M* quaternary ammonium bromide and 0.04947 *M* sodium ethoxide gave 19.9×10^{-4} l. mole^{-1} sec.$^{-1}$ for the rate constant. Such results can be obtained only if the reaction is of the same order in both reactants. We have already shown that the order in ethoxide ion is greater than zero. Mechanisms in which both ionic species are involved in fractional orders have been rejected as improbable. If the order in ethoxide ion is greater than one, the reaction would have to be of fourth-order or higher. We conclude, therefore, that the over-all reaction is second-order, first-order in ethoxide ion and first-order in the quaternary ammonium ions.

Because the salt effect is large in this reaction, it would be desirable to eliminate it from consideration by referring the measurements to some standard state of reference with respect to the ionic strength. One approach is to make measurements at various ionic strengths and estimate by extrapolation the limit approached as the ionic

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(9) K. J. Laidler, "Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1950, pp. 124–132.

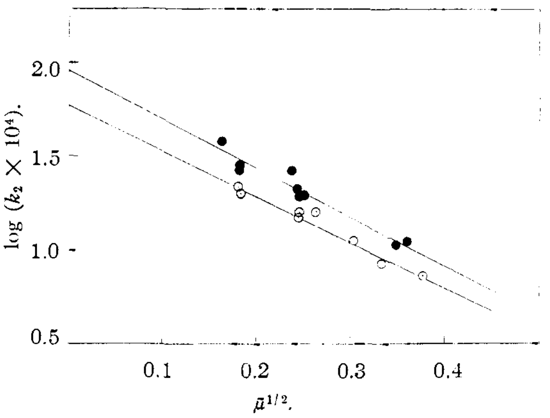

Fig. 1.—log ($k_2 \times 10^4$) *vs.* $\bar{\mu}^{1/2}$ for the reactions of benzyldimethylanilinium bromide with sodium ethoxide and lithium ethoxide in absolute ethanol at 50.8 ± 0.1°. The upper line (solid circles) is for the reaction with sodium ethoxide; the lower line is for the reaction with lithium ethoxide.

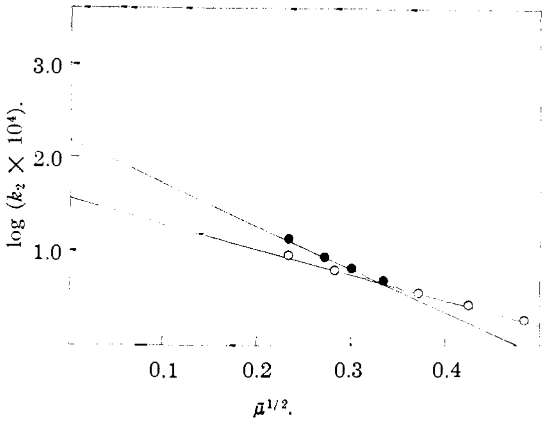

Fig. 2.—log ($k_2 \times 10^4$) *vs.* $\bar{\mu}^{1/2}$ for the reactions of benzyldimethylanilinium bromide with sodium ethoxide and lithium ethoxide, both with a neutral salt added, in absolute ethanol at 50.8 ± 0.1°. The solid circles are for the reaction with sodium ethoxide in the presence of added lithium nitrate. The open circles are for measurements with lithium ethoxide and added lithium chloride.

strength approaches zero. An alternate procedure is to make all measurements at some large concentration of neutral salt such that the ionic strength is kept nearly constant at about 0.75 *M*, where the change in activity coefficients with changing ionic strength approaches zero.[10] Because of the sparing solubility of suitable neutral salts in ethanol we have chosen the former method.

For a given measurement of the rate, there is some question of what value of the ionic strength to use in the extrapolation to zero ionic strength. For example, in a typical experiment with 0.04884 *M* benzyldimethylanilinium bromide and 0.03072 *M* sodium ethoxide (Table I), μ is 0.07956 *M* initially and 0.06113 *M* at 60% reaction. Nevertheless, the instantaneous rate constants are constant, within experimental error, over the course of this run, and all of the experimental points fall on a straight-line, second-order plot. For this reason we have arbitrarily treated the observed rate constants as a function of the average ionic strength over that portion of the reaction which was followed experimentally.

In Fig. 1, log k_2 is plotted against the square root of the average ionic strength, $\bar{\mu}^{1/2}$, for the reactions of benzyldimethylanilinium bromide with both sodium ethoxide and lithium ethoxide. The upper line (solid circles) is for the reaction with sodium ethoxide; the lower line is for the reaction with lithium ethoxide. The method of least squares was used to define the two straight lines. Figure 2 shows similar plots for the experiments in which neutral salts were added. The solid circles are for the reaction of the quaternary ammonium bromide with sodium ethoxide in the presence of added lithium nitrate. The open circles are for the experiments using lithium ethoxide as the nucleophile and lithium chloride as the neutral salt. Again the method of least squares was used to draw the straight lines through the experimental points. For the slowest run shown on Fig. 2 the time required to reach 50% reaction is less than 70 hours, whereas the half-life for the solvolysis of the quaternary ammonium bromide is more than 2000 hours. Since chloride ion and nitrate ion are both less nucleophilic than bromide ion,[11] and since the solvolytic reaction probably also involves an attack by the anion on the quaternary ammonium ion and is, therefore, subject to a negative salt effect, it is improbable that the neutral salts are involved in any reactions which seriously interfere with the reaction being measured.

One might have expected that all of the experimental points in Figs. 1 and 2 would fall on one straight line or, at least, that the four lines would extrapolate to a single value for the reaction rate at zero ionic strength. Such is not the case. The experiments with lithium ethoxide extrapolate to a value of 58.2×10^{-4} l. mole^{-1} sec.$^{-1}$ for the rate constant. With added lithium chloride the value at $\mu = 0$ is 37.6×10^{-4} l. mole^{-1} sec.$^{-1}$. The experiments with quaternary ammonium salt and sodium ethoxide give 90×10^{-4} l. mole^{-1} sec.$^{-1}$ as the extrapolated rate constant. When lithium nitrate is added as a neutral salt the rate at $\mu = 0$ is 165×10^{-4} l. mole^{-1} sec.$^{-1}$. This is a most unsatisfactory situation. We are left with no suitable reference standard of ionic strength for these measurements. It is, thus, not possible to cite any single value for the rate of reaction of benzyldimethylanilinium ion and ethoxide ion in absolute ethanol at 50.8 ± 0.1°. This is in spite of the fact that all four sets of rate data appear to be linear functions of the ionic strength.

The failure of the Brönsted theory of salt effects, combined with the Debye–Hückel limiting law for the activity coefficients of ions, to explain satisfactorily the effects of the addition of neutral salts on ionic reaction rates has been observed and discussed before.[12] Olson and Simonson[13] have shown

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[10] L. P. Hammett, "Physical Organic Chemistry," McGraw Hill Book Co., Inc., New York, N. Y., 1940, p. 94.

[11] C. G. Swain and C. B. Scott, THIS JOURNAL, **75**, 141 (1953); W. L. Petty and P. L. Nichols, Jr., *ibid.*, **76**, 4385 (1954).

[12] One of our sets of data does fit the simple theory. For the reaction of the quaternary ammonium ion and sodium ethoxide with added lithium nitrate, a plot of log k_2 − log k_2^0, where k_2^0 is the reaction rate in the absence of added neutral salt, *vs.* $\bar{\mu}^{1/2} - \bar{\mu}_0^{1/2}$ is linear,

that the effect of the addition of neutral salts on ionic reaction rates is not dependent upon the ionic strength of the solutions. Their position is summarized as follows. "In reactions between ions of opposite charge sign, both salt ions may affect the rate, but the effect of one type may be dominant. The effects are quantitatively interpretable in terms of an ion association constant and specific rate constants for the associated and non-associated reactants."

This approach, taken by Olson and Simonson to treat the effects of ionic interactions on the rates of reaction of ionic species, is even more pertinent for reactions in alcohol than in water, for in ethanol, with its lower dielectric constant, ion association is far more important. In ethanol aggregates higher than ion-pairs probably should be considered, but for the sake of simplicity, we will limit this discussion to 1:1 associations. Our simplest experiments involve initially two salts (AB and CD) and four different ions in solution. This case will, therefore, involve the four equilibria

$$\begin{aligned} AB &\rightleftarrows A^+ + B^- \\ CD &\rightleftarrows C^+ + D^- \\ AD &\rightleftarrows A^+ + D^- \\ CB &\rightleftarrows C^+ + B^- \end{aligned}$$

and as many as nine or more possible specific rate constants for the associated and non-associated species reacting to form products. In the most complicated case which we studied the solution contained three salts and six different ions. In this system there are nine equilibria, and the number of possible specific rate constants is multiplied proportionately.

In the light of the foregoing it is not surprising to find that our measured rate constants cannot be accommodated in a satisfactory manner as a function of the ionic strength. Even more important, the apparent anomalies are understandable in terms of the above hypothesis. For example, the very substantial differences in rate observed for the reactions with sodium ethoxide and lithium ethoxide and the very different effects observed with the two neutral salts which we have studied are both qualitatively in accord with the intervention in these systems of the equilibria which we have described. Finally, the results of the first three experiments shown in Table III are readily encompassed by this picture. The three measurements are all at the same ionic strength and differ only in the nature of the anion associated with the quaternary ammonium ion, yet there are appreciable increases in rate as one goes from the bromide to the nitrate to the picrate. Moreover, these rates are in the order of degree of association of the quaternary ammonium salts, for the bromide is more associated than the nitrate, which is in turn more associated than the picrate.[14]

The present results are at least qualitatively in accord with the Olson hypothesis. A quantitative treatment has not been attempted and is unwarranted at this time. In the absence of measurements of the association constants of the pertinent salts in ethanol at 50.8°, there are so many adjustable parameters that even a success in fitting the data would be of questionable significance.

passes through the origin and has the correct theoretical slope, equal to

$$\frac{2N^2\epsilon^3(2\pi)^{1/2}}{2.303(DRT)^{3/2}(1000)^{1/2}}$$

This may, however, be largely fortuitous.

(13) A. R. Olson and T. R. Simonson, *J. Chem. Phys.*, **17**, 1167 (1949).

(14) Data on the degree of dissociation of the above quaternary ammonium salts in ethanol are not available. Data on the dissociation of tetrabutylammonium salts in acetone at 25° are available (H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, N. Y., 3rd ed., 1958, p. 704). The ionization constants for tetrabutylammonium bromide, nitrate and picrate are 3.29×10^{-3}, 5.46×10^{-3} and 22.3×10^{-3} mole $l.^{-1}$, respectively.

[CONTRIBUTION FROM THE TOKYO INSTITUTE OF TECHNOLOGY, ŌOKAYAMA, MEGURO-KU, TOKYO, JAPAN]

The Reactions of Primary Nitroparaffins with Isocyanates[1]

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The reactions of isocyanates with primary nitroparaffins, such as nitroethane, 1-nitropropane and phenylnitromethane, in the presence of a catalytic amount of tertiary alkyl amine have been found to give *sym*-disubstituted ureas, furoxane and carbon dioxide in excellent yields, instead of the expected addition compounds of N-substituted α-nitro-fatty acid amides. The reaction is thought to proceed through the intermediates amine and nitrile oxide, formed by the decomposition of the addition compound of isocyanate and *aci*-nitroparaffin with spontaneous evolution of carbon dioxide. The disubstituted urea is formed by the reaction of amine with isocyanate; the furoxane is formed by the dimerization of nitrile oxide. The intermediate nitrile oxide can be demonstrated by the formation of isoxazoline or oxadiazoline when isocyanate, nitroparaffin and tertiary amine are allowed to react in the presence of unsaturated compounds. The reaction is not observed in the absence of teritary alkyl amine or when tertiary nitroparaffins such as *t*-nitrobutane are allowed to react with isocyanate.

The reaction between the sodium salt of nitromethane and phenyl isocyanate has been found[2,3] to give α-nitroacetanilide and nitromalonanilide. Boyd and Leshin[4] recently extended the reactions of nitromethane and ethyl nitroacetate with isocyanates such as 1-naphthyl, *o*-chlorophenyl and *o*-tolyl isocyanates, and obtained a series of N-substituted α-nitroacetanilides and α-carbethoxy-α-nitroacetanilides. However, it has been reported that nitroethane, 1- and 2-nitropropane and phenylnitromethane do not condense with phenyl isocyanate, either in the presence of potassium

(1) T. Hoshino and T. Mukaiyama, partly published in Japanese Patent Publication 34-9855 (1959).

(2) A. Michael, *Ber.*, **38**, 22, 39, 46 (1905).

(3) W. Steinkopf and H. M. Daege, *ibid.*, **44**, 497 (1911).

(4) R. N. Boyd and R. Leshin, THIS JOURNAL, **75**, 2762 (1953).