

Plots of $\log [\text{ABAH}_2^{++}2\text{Cl}^-]$ versus time gave straight lines to 75% reaction. Rate constants were determined at 40.0°, 50.05°, 60.2°, 70.1° and are the average of at least two runs (Table I).

The rate of change of optical density of the intermediate ($\lambda_{\text{max}}^{292.5}$, 292.5 μ) was followed spectrophotometrically at 60.2° as described for azo loss with the exception that no acid was added and initial $\text{ABAH}_2^{++}2\text{Cl}^-$ concentrations were in the range 0.005–0.010 *M*. In addition to using deoxygenated demineralized water, the test-tubes were flushed with nitrogen before capping. Plots of optical density versus time gave curves with initial slopes dependent upon $[\text{ABAH}_2^{++}2\text{Cl}^-]_0$ and maxima at approximately 300 minutes (Fig. 1).

The constant temperature bath used in all runs regulated at $\pm 0.05^\circ$. The spreads of rate constants are approximately $\pm 5\%$ from the means.

Decomposition of $\text{ABAH}_2^{++}2\text{Cl}^-$ to form 2,2,3-trimethyl-3-guanylbutyramide hydrochloride (III) was carried out by dissolving $\text{ABAH}_2^{++}2\text{Cl}^-$ (5.28 g., 1.95×10^{-2} mole) in 100 ml. of distilled water and heating 1 hour on a steam-bath. The solution was cooled, the water partially removed *in vacuo*, and stored overnight at 3°. The white crystalline precipitate amounted to 0.74 g. An additional 1.08 g. was obtained by further concentration *in vacuo* and cooling for a total yield of 45%. This yield is a minimum value since evaporation of the remaining water gave a mixture of ammonium chloride and III. The compound was recrystallized from ethanol-ether or water, m.p. $>300^\circ$. Ionic chloride was indicated with silver nitrate solution. The infrared spectrum showed NH at 2.89 μ and bands at 5.90-(m) and 6.10(s) μ .

Hydrolysis of this salt in refluxing water (2 days) gave tetramethylsuccinimide (by ether extraction) in 40% yield (m.p. 188–189°, sublimed,²⁷ characteristic carbonyl bands at 5.60 and 5.85–5.90 μ). On this basis, the compound is assigned the structure 2,2,3-trimethyl-3-guanylbutyramide hydrochloride (III).

Anal. Calcd. for $\text{C}_8\text{H}_{12}\text{N}_3\text{ClO}$: C, 46.4; H, 8.8; N, 20.3; O, 7.7; Cl, 17.1. Found: C, 46.3; H, 8.6; N, 20.3; O, 7.8; Cl, 16.9. The picrate has m.p. 262–265°.

Decomposition of $\text{ABAH}_2^{++}2\text{Cl}^-$ to form tetramethylsuccinimide was accomplished by dissolving $\text{ABAH}_2^{++}2\text{Cl}^-$ (10.0 g., 3.69×10^{-2} mole) in 100 ml. of distilled water and refluxing 3.5 days. The solution was cooled, partially concentrated *in vacuo* and stored several hours at 3° to yield 2.17 g. of tetramethylsuccinimide. An additional 1.25 g. was obtained by extracting with ether to give a total yield of 60%.

Decomposition of $\text{ABAH}_2^{++}2\text{Cl}^-$ to 50% reaction was effected by dissolving $\text{ABAH}_2^{++}2\text{Cl}^-$ (10.0 g., 3.69×10^{-2} mole) in distilled water and maintaining at 60° for 300 minutes (approximate half-life for azo loss). The solution was cooled and extracted continuously with ether for 5 days to yield 0.1 g. of tetramethylsuccinimide. The aqueous solution was evaporated to dryness (*in vacuo*, low temperature) and the resulting solids (7.0 g.) continuously extracted

(27) K. Auwers and J. A. Gardne, *Ber.*, **23**, 3622 (1890), give m.p. 187°.

with chloroform for 4 days. An infrared spectrum of the non-dissolved solid (5.6 g., 80%) indicated $\text{ABAH}_2^{++}2\text{Cl}^-$ and III. Ammonium chloride is also found in the chloroform-insoluble fraction. A slightly soluble oil (1.27 g., 17%) which separates from the chloroform solution slowly deposited crystals of III upon standing. The ultraviolet spectrum of this oil in water showed the presence also of the intermediate absorbing at 292.5 μ . Evaporation of the chloroform solution yielded 0.015 g. of a white solid whose infrared spectrum and m.p. are identical to tetramethyl-5-imino-2-pyrrolidone (IV) which was obtained in greater amounts from the photochemical degradation of $\text{ABAH}_2^{++}2\text{Cl}^-$ (see below).

Photochemical decomposition of $\text{ABAH}_2^{++}2\text{Cl}^-$ was carried out by storing in the sunlight of the laboratory a solution of $\text{ABAH}_2^{++}2\text{Cl}^-$ (270 g., 0.995 mole) in 2 l. of deoxygenated, demineralized water contained in a polyethylene bottle. After nearly 6 months there had precipitated approximately 20 g. (13% yield) of a white crystalline material, m.p. 285–288° dec., with NH band in the infrared at 3.08 μ and bands at 5.90(s) and 6.1(m) μ .

Hydrolysis of this compound under neutral (refluxing water, 24 hr.) or basic conditions (overnight, room temperature) produced tetramethylsuccinimide.

This compound is assigned the structure tetramethyl-5-imino-2-pyrrolidone (IV).

Anal. Calcd. for $\text{C}_8\text{H}_{14}\text{N}_2\text{O}$: C, 62.3; H, 9.1; N, 18.2. Found: C, 62.3; H, 9.2; N, 18.1.

Tetramethylsuccinimide nitrate was obtained by a procedure similar to that of Hammond and Neuman^{7a}: $\text{ABAH}_2^{++}2\text{NO}_3^-$ (0.3 g., 9.26×10^{-4} mole, obtained by addition of aqueous AgNO_3 to a solution of $\text{ABAH}_2^{++}2\text{Cl}^-$) was mixed with 2 ml. of anhydrous dimethyl sulfoxide and heated to 95°. Dissolution of material and loss of nitrogen occurred. After approximately 20 minutes, the solution was cooled and mixed with approximately 6 ml. of benzene. Just sufficient ethanol was added to give a homogeneous solution. After standing overnight, the white precipitate was filtered off, washed with ether and dried to yield 0.006 g. of tetramethylsuccinimide nitrate (3% yield) whose infrared spectrum was identical to that of the sample supplied by Hammond and Neuman.^{7b} In dimethyl sulfoxide the sample showed λ_{max} 302.5 μ , ϵ 258.

To a sample of tetramethylsuccinimide nitrate^{7b} (0.0040 g., 1.85×10^{-5} mole) in 5 cc. of ethanol was added 3 drops of 70% nitric acid. After 30 minutes the solvent was evaporated and the solids dried overnight to yield 0.0037 g. (92.5%) of material with an infrared spectrum essentially identical to starting imidine (N–H band at ~ 3.0 (s) μ , other bands at ~ 5.95 (w) and ~ 6.1 (m) μ) with the exception of an additional weak band at ~ 9.2 μ .

A similar sample left overnight in the acid solution yielded a material in which the 5.95 and 6.1 μ peaks had reversed in intensity.

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Changes in Reaction Order Due to Ion Association in the Reaction of Benzyl dimethylanilinium Ion and Thiocyanate Ion

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The rates of reaction of benzyl dimethylanilinium ion and thiocyanate ion to form benzyl thiocyanate and dimethylaniline have been studied in four solvents, *N*-methylpropionamide, benzyl alcohol, *s*-tetrachloroethane and chloroform. There are significant changes in reaction order in this series of solvents. These variations can be explained by considering the appropriate ion association equilibria and the specific rates for the reactions of ions and ion pairs.

In a previous report from this Laboratory,¹ it was shown that the rate of reaction of benzyl di-

(1) S. D. Ross, M. Finkelstein and R. C. Petersen, *J. Am. Chem. Soc.*, **82**, 5335 (1960).

methylanilinium ion with ethoxide ion in ethanol varies with both changing initial concentrations and added neutral salts in a manner which is not satisfactorily accommodated by the Brønsted

theory of salt effects combined with the Debye-Hückel limiting law for the activity coefficients of ions. It was suggested that these results are interpretable in terms of ion association equilibria and specific rates for the associated and non-associated reactants.

This approach in treating the effects of ionic interactions on the rates of reaction of ionic species has been advocated by Acree,² strongly supported by Olson and Simonson³ and more recently advanced by Brändström,⁴ Lichtin,⁵ and Winstein.⁶ It is our present purpose to present further experimental evidence in support of this point of view.

Consider a salt, S, made up of two ions, I⁺ and I⁻, which reacts to give neutral products, C and D. Consider further that this salt may exist in solution in various states of association, as ion pairs, P, as triple ions, T⁺ and T⁻, and as quadrupoles, Q. For these associated states, we may write the equilibrium constants

$$K_1 = (I^+)(I^-)/(P) \quad (1)$$

$$K_2 = \frac{[P][I^+]}{[T^+]} = \frac{[I^+]^2[I^-]}{K_1[T^+]} \quad (2)$$

$$K_3 = \frac{[P][I^-]}{[T^-]} = \frac{[I^-]^2[I^+]}{K_1[T^-]} \quad (3)$$

$$K_4 = [P]^2/[Q] \quad (4)$$

For purposes of simplification, it is further assumed that there is no special preference for the formation of either T⁺ or T⁻; *i.e.*, that $K_2 = K_3$ and $(T^+) = (T^-)$. The formation of the products, C and D, may, in principle, involve any of these associated species, but the probability is that the more highly associated species will react at rates which are negligibly small compared to the free ions, and our purposes are adequately served by considering only reactions involving free ions and ion pairs. Ion pairs are included since it is clear that the transition state for formation of C and D must have the characteristics of an ion pair, although every possible ion pair configuration is not necessarily a transition state. The rate equation is, therefore

$$-d[S]/dt = d[C]/dt = d[D]/dt = k_1[I^+][I^-] + k_2[P] \quad (5)$$

Given the foregoing, it may be readily shown that if we can find limiting situations in which one species strongly predominates over all the others, then the order of the reaction in the salt, S, will depend on which species predominates. For example, if the salt is completely ionized, then

$$[S] = [I^+] = [I^-] \quad (6)$$

$$[P] = [S]^2/K_1 \quad (7)$$

$$-d[S]/dt = k_1[S]^2 + (k_2/K_1)[S]^2 = k'[S]^2 \quad (8)$$

and the reaction is second-order in the salt, S. Similarly, if the salt is present in solution largely or entirely as ion pairs

$$[S] = [P] \quad (9)$$

$$[I^+] = [I^-] = \sqrt{K_1[S]} \quad (10)$$

$$-d[S]/dt = k_1K_1[S] + k_2[S] = k'[S] \quad (11)$$

(2) S. F. Acree, *Am. Chem. J.*, **48**, 353 (1912).

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

(4) A. Brändström, *Arkiv. Kem.*, **11**, 567 (1957).

(5) N. N. Lichtin and K. N. Rao, Abstracts, Division of Physical Chem. of the Am. Chem. Soc., Chicago, Illinois, Sept. 7-12 (1958), p. 125 and personal communications.

(6) S. Winstein, L. G. Savedoff and S. Smith, *Tetrahedron Letters*, **9**, 24 (1960).

TABLE I

Predominant species	Reaction order in S
Free ions	Second
Ion pairs	First
Triple ions	Two-thirds
Quadrupoles	One-half

and the reaction is first-order in the salt, S. The results of similar treatments of the other two associated species are included in Table I. It is clear from Table I that if, by varying the solvent, we can vary the association of the salt so that particular species strongly predominate, we should be able to observe differences in reaction order for the reaction of S to form C and D.

The salt chosen for study was benzyldimethylanilinium thiocyanate, which reacts to give benzyl thiocyanate and dimethylaniline. The reaction involved is a nucleophilic displacement on carbon by thiocyanate ion and is similar in type to the previously studied reaction with ethoxide ion.¹ This particular salt was chosen because it is soluble in both polar and non-polar solvents and because its rate of disappearance in solution can be followed readily by analyzing for thiocyanate ion as a function of time. In this paper, we report the results of rate studies in the highly polar solvent, N-methylpropionamide, in the relatively non-polar solvent, chloroform, and in two solvents of intermediate polarity, *s*-tetrachloroethane and benzyl alcohol.

Results

Data on the rate of reaction of benzyldimethylanilinium thiocyanate to form benzyl thiocyanate and N,N-dimethylaniline in N-methylpropionamide as solvent at $50.8 \pm 0.1^\circ$ are shown in Table II. All experiments were followed to beyond 60% reaction and, in some cases, the reaction was carried to almost 80% of completion. Good second-order plots, with all points on the line, were obtained in every case. The rate constants do vary with both the initial reactant concentrations and the ionic strengths, and, as will be shown later, both the direction and magnitude of these changes are in accord with the operation of a Brønsted salt effect in this system.

The reverse reaction, that of benzyl thiocyanate and N,N-dimethylaniline to form benzyldimethylanilinium thiocyanate, is slow with respect to the reaction above but, nevertheless, measurable. An estimate of its rate was obtained by determining instantaneous bimolecular rate constants, plotting *vs.* time and extrapolating to zero time. Two experiments, one with the amine initially at 0.0332 M and benzyl thiocyanate at 0.0643 M and the other with the amine at 0.1119 M and the thiocyanate at 0.0609 M, gave values of 3.86×10^{-6} l. mole⁻¹ sec.⁻¹ and 3.54×10^{-6} l. mole⁻¹ sec.⁻¹, respectively, for the rates at $t = 0$. Since the lowest rate constant reported in Table II is almost 14 times larger than these rate constants, the values given in Table II are not appreciably affected by this reverse reaction.

In the above experiments, N-methylpropionamide was chosen as the solvent because of its extreme polarity. At 50.8°, its dielectric constant,

TABLE II
RATES OF REACTION OF BENZYLDMETHYLANILINIUM THIOCYANATE, S, IN N-METHYLPROPIONAMIDE AT $50.8 \pm 0.1^\circ$

S, mole l. ⁻¹	Added salt, mole l. ⁻¹	$\mu_0^{1/2}$	$k_2 \times 10^5$, l. mole ⁻¹ sec. ⁻¹
0.0178		0.133	6.46
.0298		.173	6.21
.0299		.173	6.22
.0563		.237	5.81
.0619		.249	5.95
.0706		.266	5.83
.0900		.300	5.66
.0904		.301	5.68
Lithium nitrate			
.0292	0.0371	0.257	5.96
.0284	.0770	.325	5.67
.0296	.111	.375	5.42
Benzyl dimethylanilinium nitrate			
.0296	0.0152	0.212	5.92
.0299	.0300	.245	5.72
.0296	.0456	.274	5.67
.0298	.0614	.302	5.36

estimated from data in the literature⁷ by extrapolation, is 132, and it was, therefore, reasonable to hope that in this medium the limiting case of complete dissociation might be realized. In an effort to investigate a system in which the predominant species in solution is the ion pair, benzyl dimethylanilinium thiocyanate was studied in both *s*-tetrachloroethane, which has a dielectric constant of 8.2 at 20° ,⁸ and benzyl alcohol, whose dielectric constant is 13.1 at 20° ⁹ and 9.5 at 70° .¹⁰

The results of measurements in both of these solvents are shown in Table III. All of the individual runs gave good first-order plots, and measurements were carried to beyond 70% reaction in each solvent. In *s*-tetrachloroethane, the reaction is not truly first-order, since the rate constants vary with the initial concentrations. In contrast, the three values obtained for the unimolecular rate constant in benzyl alcohol are constant within experimental error and independent of the initial concentrations. This result, as has been pointed out, would be anticipated if the salt existed predominately as ion pairs in this solvent. In *s*-tetrachloroethane, where a higher initial concentration gives rise to a lower first-order rate constant, species more highly aggregated than ion pairs are presumably present.

This possibility was not pursued further with a detailed study of the reaction in *s*-tetrachloroethane. Instead the reaction was investigated in chloroform, which has a dielectric constant of 4.806 at 20° .¹¹ This lower dielectric constant should enhance aggregation of the salt, and, in fact, the rate in chloroform can be fitted exactly

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TABLE III
RATES OF REACTION OF BENZYLDMETHYLANILINIUM THIOCYANATE, S, IN *s*-TETRACHLOROETHANE AND IN BENZYL

Solvent	T, °C.	ALCOHOL	
		S, mole l. ⁻¹	$k \times 10^5$, sec. ⁻¹
<i>s</i> -Tetrachloroethane	24.8 ± 0.1	0.0315	1.38
<i>s</i> -Tetrachloroethane	$24.8 \pm .1$.0612	1.11
Benzyl alcohol	$50.8 \pm .1$.0157	1.34
Benzyl alcohol	$50.8 \pm .1$.0280	1.31
Benzyl alcohol	$50.8 \pm .1$.0540	1.32

TABLE IV
RATES OF REACTION OF BENZYLDMETHYLANILINIUM THIOCYANATE, S, IN CHLOROFORM AT $24.8 \pm 0.1^\circ$

S, mole l. ⁻¹	$k \times 10^5$, mole ^{1/4} l. ^{-1/4} sec. ⁻¹
0.0254	3.96
.0308	3.95
.0363	3.84
.0612	3.94

as a two-thirds-order reaction. These results are given in Table IV, which lists the two-thirds-order rate constants. It should be pointed out that these measurements can be fitted equally well with the rate expression

$$-d[S]/dt = k_1[S] + k_2[S]^{3/2} \quad (12)$$

In accordance with our analysis, both of these results indicate that the chloroform solution contains species more highly associated than ion pairs.

Experimental

Benzyl dimethylanilinium Thiocyanate.—Silver oxide (24 g.) was added slowly with magnetic stirring to a solution of benzyl dimethylanilinium bromide (58.4 g., 0.2 mole) in water (500 ml.). Stirring was continued 3 hours after the addition. The silver bromide which formed was filtered, and ammonium thiocyanate (15.2 g., 0.2 mole) was added. The mixture was permitted to stand overnight in a refrigerator. The water was removed *in vacuo*. Benzene was added, and this, too, was removed *in vacuo*. The crude product which resulted was crystallized from isopropyl alcohol-ether; m.p. $94-96^\circ$, yield 42.8 g. (79%). Recrystallization and drying *in vacuo* at room temperature raised the melting point to $97-98^\circ$.

Anal. Calcd. for $C_{15}H_{18}N_2S$: SCN, 21.48. Found: SCN, 21.41, 21.37.

Solvents.—Eastman Kodak Co. white label N-methylpropionamide was distilled at 10 mm. and a middle cut, b.p. 101° , was used. Baker and Adamson reagent grade chloroform was used without purification. This solvent contains 0.75% ethanol as stabilizer. Eastman Kodak Co. white label benzyl alcohol was distilled at 11 mm., and a middle fraction, b.p. $96-97^\circ$, was taken. Analysis by vapor phase chromatography showed that this solvent contained a maximum of 2% benzaldehyde. *s*-Tetrachloroethane was distilled at 24 mm. A large forerun was discarded, and only a middle fraction, b.p. 54° , was used. Vapor phase chromatography indicated that this solvent was free from impurities in any detectable concentration.

Rate Measurements.—Measurements in N-methylpropionamide and in benzyl alcohol were made as follows. Determinate solutions of benzyl dimethylanilinium thiocyanate were made up at room temperature. Where a neutral salt was used, it, too, was added determinately. Aliquots were taken and sealed in separate tubes. At zero time, the tubes were placed in an oil-bath at $50.8 \pm 0.1^\circ$. After appropriate time intervals, tubes were withdrawn and chilled. The contents were then partitioned between benzene (50 ml.) and water (25 ml.). The benzene layer was extracted two additional times with water, and the combined aqueous extracts were acidified with 4 *N* nitric acid (10 ml.) and analyzed for thiocyanate ion by the Volhard method. For the measurements in *s*-tetrachloroethane and in chloroform a weighed amount of the salt was added to the reaction vessel. The appropriate volume of the solvent,

equilibrated at the reaction temperature, $24.8 \pm 0.1^\circ$, was quickly added at zero time, and the salt was shaken into solution. An aliquot was rapidly removed and analyzed as above to determine the initial salt concentration. In every experiment, there was good agreement (within 3%) between the initial concentration calculated from the weighing and the initial concentration determined by analysis.

Isolation of Products. A. From N-Methylpropionamide.—Benzyl dimethylanilinium thiocyanate (10 g., 0.037 mole) in N-methylpropionamide (200 ml.) was kept in a stoppered flask at 50.8° for 592 hours. The reaction mixture was poured into cold water (1 l.), and the solution was extracted three times with ether and twice with hexane. The combined organic layers were extracted with three 100-ml. portions of 1:1 hydrochloric acid. The acid extract was washed twice with hexane, and these hexane extracts were added to the previous organic extracts. The combined organic extracts were washed with water, twice with saturated sodium bicarbonate solution and again with water. After drying the solution over magnesium sulfate, the solvents were removed by distillation. The residue was taken up in hot ethanol and a first crop of product was obtained by cooling in Dry Ice-acetone. A second crop was obtained by concentrating the mother liquors. The total yield of benzyl thiocyanate was 3.91 g. (71%), m.p. $43-44^\circ$. The acidic solution was made basic with cold concentrated sodium hydroxide solution and extracted with ether. The ether extracts were dried over magnesium sulfate, and the ether was removed by distillation through a Vigreux column. The residue was dissolved in ethanol and treated with a hot solution of picric acid (12 g.) in ethanol (100 ml.). Yellow crystals of dimethylaniline picrate were obtained; yield 9.21 g. (71%), m.p. $160-161^\circ$ dec. after two crystallizations from ethanol.

B. From s-Tetrachloroethane.—A solution of benzyl dimethylanilinium thiocyanate (3.29 g., 0.0122 mole) in s-tetrachloroethane (50 ml.) was kept at 24.8° for 115 hours. The reaction mixture was dissolved in chloroform (200 ml.), and the solution was extracted three times with a total of 200 ml. of 1:3 hydrochloric acid. The acidic extract was washed twice with ether and once with hexane, and the washings were combined with the chloroform solution. This solution was washed with water, twice with saturated sodium bicarbonate solution and again with water. After drying the solution over magnesium sulfate, the solvents were distilled through a Vigreux column, with vacuum applied to remove the s-tetrachloroethane. The residue was taken up in ethanol and cooled in Dry Ice-acetone to give a first crop of crystals. After two additional concentrations of the mother liquors, the total yield of benzyl thiocyanate was 1.56 g. (85.4%), m.p. $43-45^\circ$, mixed m.p. with authentic benzyl thiocyanate $44-45^\circ$. The acid extract was made basic with cold, concentrated sodium hydroxide solution and extracted with ether. The ether extract was dried over magnesium sulfate, and the ether was removed by distillation. The residue was dissolved in ethanol, and a solution of picric acid (3.5 g.) in ethanol (50 ml.) was added. The yield of dimethylaniline picrate which resulted was 3.9 g. (91.2%), m.p. $157-158^\circ$ dec., mixed m.p. with authentic dimethylaniline picrate $157-158^\circ$ dec.

C. From Chloroform.—A solution of benzyl dimethylanilinium thiocyanate (8.4 g., 0.031 mole) in chloroform (500 ml.) was kept at 24.8° for 118 hours. The reaction mixture was extracted three times with a total of 200 ml. of 1:1 hydrochloric acid solution. The acid extract was washed three times with ether and once with hexane, and the washings were combined with the chloroform solution which was then dried over magnesium sulfate. The residue obtained after removal of the solvents was dissolved in ethanol and cooled in Dry Ice-acetone. This yielded a first crop of product, and a second crop was obtained by concentrating the mother liquors. The total yield of benzyl thiocyanate was 4.17 g. (90%), m.p. $42-44^\circ$. The acid solution was made basic and extracted with ether. The ether was dried over magnesium sulfate, and the residue obtained on distillation was treated with a hot solution of picric acid (8.4 g.) in ethanol (125 ml.). The yield of dimethylaniline picrate that resulted was 9.46 g. (86.6%), m.p. $158-159^\circ$ dec.

D. From Benzyl Alcohol.—Two procedures, A and B, were used in working up the benzyl alcohol solutions. In

a typical example using procedure A, a solution of benzyl dimethylanilinium thiocyanate (10 g., 0.037 mole) in benzyl alcohol (100 ml.) was kept at 50.8° for 69 hours. The benzyl alcohol and dimethylaniline that formed were removed by distillation at 0.75 mm. with the bath temperature not exceeding 70° . The residual oil was taken up in ethanol, and the total yield of product, obtained by cooling in Dry Ice-acetone followed by further concentration, was 2.85 g. (51.6%). The melting point after crystallization from ethanol was $42-43^\circ$. The mixed m.p. with authentic benzyl thiocyanate was $42-44^\circ$. Repetition of this experiment using 300 ml. of benzyl alcohol gave 38.9% of benzyl thiocyanate. It was shown separately that this procedure does not permit a quantitative recovery of benzyl thiocyanate, which codistills in part with the benzyl alcohol.

In an example using procedure B, a solution of benzyl dimethylanilinium thiocyanate (10 g., 0.037 mole) in benzyl alcohol (200 ml.) was kept at 50.8° for 88.5 hours. The reaction mixture was dissolved in chloroform (200 ml.), and the solution was extracted three times with a total of 400 ml. of 1:3 hydrochloric acid solution. The organic layer was washed twice with water, and this was combined with the acid extract. The acidic solution was washed twice with hexane, and the washings were combined with the organic layer. This organic solution was dried over magnesium sulfate; the low-boiling solvents were distilled at the water pump; benzyl alcohol was distilled at 1 mm., b.p. 57° . On cooling the residue in Dry Ice-acetone, the product, dibenzyl disulfide, was obtained; yield 3.91 g. (85%), m.p. $70-71^\circ$ after crystallization from ethanol. The mixed m.p. of the product with authentic dibenzyl disulfide was $70-72^\circ$, and its infrared spectrum was identical with that of dibenzyl disulfide. The acidic solution was made basic with cold, concentrated sodium hydroxide solution and extracted four times with ether. The extract was dried over magnesium sulfate, and the ether was removed by distillation. The residue was dissolved in ethanol and treated with picric acid (12 g.) in ethanol (100 ml.). The yield of dimethylaniline picrate was 9.12 g. (70.4%), m.p. $157-159^\circ$ dec. Repetition of this experiment gave 83% of dibenzyl disulfide and 64.5% of dimethylaniline picrate.

The following experiments were performed as controls on the work-up procedure: (1) a mixture of benzyl thiocyanate, benzyl alcohol, hydrogen chloride and chloroform was vacuum distilled and benzyl thiocyanate was recovered from the residue. (2) A solution of equimolar quantities of benzyl thiocyanate and dimethylaniline in benzyl alcohol was distilled by procedure A and benzyl thiocyanate was recovered. (3) A solution of equimolar quantities of benzyl thiocyanate and dimethylaniline was subjected to the work-up of procedure B, and benzyl thiocyanate was recovered.

Reaction of Benzyl Thiocyanate and Dimethylaniline in Benzyl Alcohol.—A solution of benzyl thiocyanate (5 g., 0.0335 mole) and dimethylaniline (4.06 g., 0.0335 mole) in benzyl alcohol (25 ml.) was kept at 50.8° for 190 hours. The reaction mixture was dissolved in chloroform (60 ml.), and the solution was extracted three times with a total of 100 ml. of 1:1 hydrochloric acid. The acid extract was washed with hexane, and the hexane was combined with the chloroform solution, which was then washed with water, twice with saturated sodium bicarbonate solution and again with water. After the solution was dried over magnesium sulfate, the solvents were removed *in vacuo*, the benzyl alcohol boiling at 52° at 1 mm. The residue was dissolved in methanol and cooled in Dry Ice-acetone, yielding 4.27 g. (100%) of crude dibenzyl disulfide. After three crystallizations from ethanol, the m.p. was $69-72^\circ$, and its infrared spectrum was identical with that of authentic dibenzyl disulfide. A separate experiment showed that benzyl thiocyanate can be recovered in at least 82% yield from a concentrated solution of benzyl thiocyanate in benzyl alcohol (in the absence of dimethylaniline) which had been kept at 50.8° for 15 days.

The question of why procedure A permits the isolation of benzyl thiocyanate whereas procedure B results in dibenzyl disulfide has not been resolved by these experiments. There must be some facile path for converting one of these products into the other which we have not succeeded in identifying.

Discussion

For the reaction of benzyl dimethylanilinium thiocyanate to form benzyl thiocyanate and di-

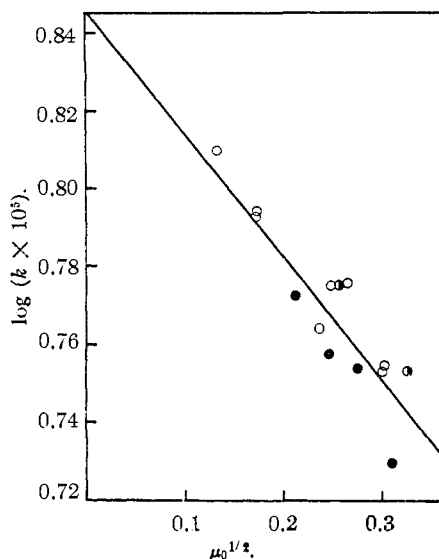


Fig. 1.— $\log(k \times 10^5)$ vs. $\mu_0^{1/2}$ for the reaction of benzyl-dimethylanilinium thiocyanate in N-methylpropionamide at $50.8 \pm 0.1^\circ$. The open circles are for the reaction without neutral salt added. The half-filled circles are for the reaction with lithium nitrate added, and the solid circles are with benzyl-dimethylanilinium nitrate added.

methylaniline, the most straightforward situation is the one in which the salt is completely ionized and the products result from a nucleophilic displacement by thiocyanate ion on the benzylic carbon atom of the quaternary ammonium ion. For this limiting case, the reaction would be second order over-all and first order in each individual ion. Moreover, both the magnitude and direction of the variation of the rate as a function of the ionic strength should be predictable from the Brønsted theory of salt effects, whence it may be shown that, for the reaction between a univalent positive ion and a univalent negative ion

$$\log k = \log k_0 - \frac{2N^2\epsilon^2(2\pi)^{1/2}}{(2.3026)(DRT)^{3/2}(1000)^{1/2}} \mu^{1/2} \quad (13)$$

where k is the experimental second-order rate constant, k_0 is the rate constant at zero ionic strength, N is the Avogadro number, ϵ is the unit charge, μ is the ionic strength and D is the dielectric constant of the solvent at the reaction temperature, T , in $^\circ\text{K}$.¹²

N-Methylpropionamide was chosen as a solvent, since its high dielectric constant, almost twice that of water at $50.8 \pm 0.1^\circ$, makes it reasonable to expect complete ionization of the salt, benzyl-dimethylanilinium thiocyanate. The reaction products, benzyl thiocyanate and dimethylaniline, were isolated in better than 70% yield, and the reverse reaction, although measurable, was slow with respect to the forward reaction. The conformity to the bimolecular rate law was excellent over the entire range of reaction for each of the measurements in Table II. In accordance with eq. 13 a plot of $\log k$ vs. $\mu^{1/2}$ for the reaction in N-methylpropionamide at $50.8 \pm 0.1^\circ$ should be a straight line with intercept, $\log k_0$, and slope, -0.413 . Such a plot is shown in Fig. 1, which

(12) K. J. Laidler, "Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1950, pp. 124-127.

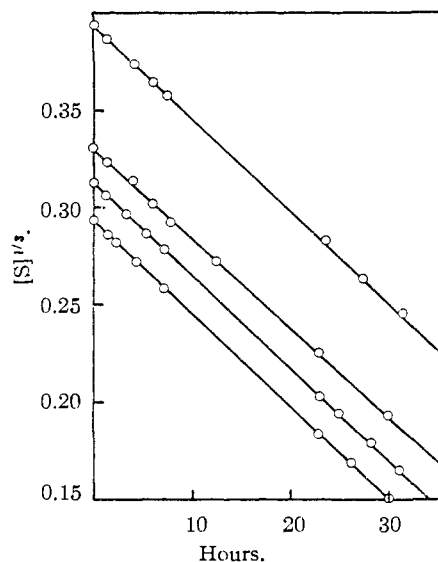


Fig. 2.—Two-thirds order plots for the reaction of benzyl-dimethylanilinium thiocyanate in chloroform at $24.8 \pm 0.1^\circ$. The initial concentrations, reading from top to bottom, are 0.0612 M, 0.0363 M, 0.0308 M and 0.0254 M.

includes all of the measurements of Table II. The straight line shown is that determined by the method of least squares using all of the experimental points. The line has a slope of -0.314 and the maximum deviation of any experimental point from this line is less than 3%.

This agreement is probably all that should be anticipated particularly when it is noted that the solutions were as concentrated as 0.09 molar and that the ionic strengths were changing during the course of a run. It is, therefore, reasonable to conclude that in N-methylpropionamide complete ionization is closely approached and that variations in rate with ionic strength are attributable to a Brønsted salt effect.

It is next of interest to consider this same reaction in the most non-polar solvent which was studied, chloroform. From this solvent, both products could be isolated in yields exceeding 85%, and the reverse reaction was too slow to be measurable. When the bimolecular rate equation was applied to the data, the rate constants varied strongly with time over the course of a single set of measurements. It might be argued that this variation is due to a salt effect, which would be large in this low dielectric constant medium. That this is not the case may be shown by calculating instantaneous rate constants, obtained from the slopes at particular times of the product vs. time curves and the known reactant concentrations at those times, and plotting these against the corresponding square roots of the ionic strengths. The result was a curve, not a straight line, and even in dilute solution this curve does not approach the slope calculated for chloroform from eq. 13. The first-order rate equation was equally unsatisfactory, since the experimental points deviated sharply from a first-order plot, particularly at high percentage reactions.

However, the data could be fitted exactly as a two-thirds-order reaction for which the rate equa-

tion is

$$[S]^{1/3} = [S_0]^{1/3} - (k/3)t \quad (14)$$

The rate constants for four sets of measurements, with the initial salt concentrations varying from 0.0254 to 0.0612 *M*, are shown in Table IV. The average value for the rate constant is 3.92×10^{-6} mole^{1/3} l.^{-1/3} sec.⁻¹, and the maximum deviation from this average value is 2.04%. The experimental data for all four runs are plotted in Fig. 2. It is to be noted that the fit is excellent over the entire course of each run.

It is not surprising that these data can be fitted equally well with a rate equation having two terms, one of lower order than two-thirds and one of higher order than two-thirds. One such equation, of pertinence to the present study, is eq. 15

$$-d[S]/dt = k_1[S] + k_2[S]^{1/2} \quad (15)$$

in which one term is first order and the other is half order. The integrated form of 15 is eq. 16

$$-\log \left([S]^{1/2} + \frac{k_2}{k_1} \right) = -\log \left([S_0]^{1/2} + \frac{k_2}{k_1} \right) + \frac{k_2}{(2)(2.3026)} t \quad (16)$$

In fitting the data to eq. 16, the ratio, k_2/k_1 , was varied by a trial and error process until an optimum fit was obtained. The best value for k_2/k_1 proved to be 0.190 mole^{1/2} l.^{-1/2}, and the data are plotted in Fig. 3 using this value. That a satisfactory fit

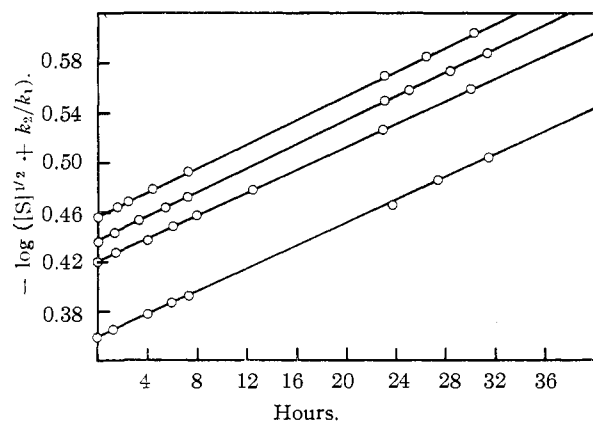


Fig. 3.—The reaction of benzyldimethylanilinium thiocyanate in chloroform at $24.8 \pm 0.1^\circ$ plotted according to eq. 16. The initial concentrations, reading from top to bottom, are 0.0254 *M*, 0.0308 *M*, 0.0363 and 0.0612 *M*.

is obtained is indicated by the facts that all experimental points for each individual run fall on a straight line and that the slopes are constant, within experimental error, for the four sets of measurements. From the slopes shown in Fig. 3, the values for the rate constants, k_1 and k_2 , can be calculated, and these are given in Table V.

Either of these two treatments of the experimental data in chloroform indicate that species more highly associated than free ions predominate in this solution. In terms of our introductory treatment of the effect of ion association on re-

TABLE V

RATES OF REACTION OF BENZYLDMETHYLANILINIUM THIOCYANATE, S, IN CHLOROFORM AT $24.8 \pm 0.1^\circ$

S, mole l. ⁻¹	$k_1 \times 10^6$, sec. ⁻¹	$k_2 \times 10^6$, mole ^{1/2} l. ^{-1/2} sec. ⁻¹
0.0254	6.24	1.19
.0308	6.26	1.19
.0363	5.99	1.14
.0612	6.01	1.14

action order, the fit to eq. 14 suggests that the most abundant species in the solution are the triple ions, whereas the fit to eq. 16 points to ion pairs and quadrupoles, interrelated by an equilibrium, predominating in the system. The present results do not permit a choice between these two alternatives, and, in fact, they do not completely rule out the possibility that the observed rates may be attributable to some other combination of associated species. They do, however, point strongly to the need for interpreting rates in non-polar solvents in terms of ion association equilibria and specific rates for associated and non-associated reactants.

It remains now to consider this reaction in two solvents of intermediate polarity. The intention in these experiments was to find a solvent in which the salt would exist almost entirely as ion pairs. For this situation we have predicted that the rate of disappearance of the salt should be first order. The abundant measurements of ion-pairing equilibria available in the literature suggest that ion pairs are favored in media of dielectric constant close to ten. Our first experiments were done in *s*-tetrachloroethane. In this solvent the two individual runs (Table III) gave good first-order plots, but the run at the higher initial salt concentration resulted in an appreciably lower rate constant. The reaction is, therefore, not truly first-order, and species more highly associated than ion pairs are probably important in this solvent.

The reaction was next studied in a solvent of slightly higher dielectric constant, benzyl alcohol. There is some ambiguity about the product in this solvent, and this has been described in detail in the Experimental section. There is, however, no ambiguity about the rate of disappearance of the salt in this system. As shown in Table III, it is unequivocally first-order, and we would conclude that the ion pair is the predominant species in benzyl alcohol.

Thus many of the expectations of our initial analysis have been realized. In solvents of very high dielectric constant, where complete ionization is approached, the rate is second-order, and the Brønsted salt effect is important. In solvents of low or intermediate dielectric constant, it is the degree of association of the salt which determines the reaction order. It is this latter finding which is significant in the present study for, in agreement with other results in the literature,¹⁻⁶ it points to ion association equilibria rather than salt effects as the proper explanatory concept in these solvents.