Catalysis by Added Salts in the Reaction of Benzenesulfonyl Chloride with *N*-Methylaniline in Chloroform and in Acetone

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The rate of reaction of benzenesulfonyl chloride with *N*-methylaniline in chloroform and in acetone at 24.4 ± 0.1° is strongly accelerated by added salts such as *N*-methylaniline hydrochloride, benzyltriethylammonium chloride, benzyltriethylammonium nitrate, and tetraethylammonium perchlorate. It is proposed that the observed rate increases are due to base catalysis, with the ion pair from the salt actually participating in the rate-determining transition state, rather than to a neutral salt effect.

Reactions in which a proton is transferred somewhere along the reaction path from reactants to products are capable of exhibiting base catalysis under appropriate conditions. Such catalysis has been demonstrated for the reaction of 2,4-dinitrochlorobenzene with *n*-butylamine in chloroform[1] and for the ethanolysis of benzoyl chlorides in acetone and chloroform.[2] In both of these reactions an intermediate addition complex is formed, the rate-determining process involves only bond formation, and the observed catalysis is catalysis of intermediate formation. A reconsideration of presumed salt effects in the reaction of phenacyl bromide with *N*-ethylaniline in chloroform[3] indicates that these results, too, are better explained by invoking base catalysis. This last reaction is of the S_N2 type and does not involve an addition intermediate.

The rates of reaction of substituted benzenesulfonyl chlorides with various substituted anilines have been measured in methanol.[4] Substituent effects in the sulfonyl chloride and aniline were correlated by Hammett and Brønsted equations, respectively, and the conclusion was reached that the reaction is a one-step, nucleophilic substitution on sulfur. This interpretation, although further supported by the finding that phenyl benzenesulfonate shows no ^{18}O exchange during either basic[5] or acidic[6] hydrolysis, is arguable.

Ciuffarin, Senatore, and Isola[7] have measured the leaving group mobilities for the reactions of the benzenesulfonyl halides with aniline, *n*-butylamine, and hydroxide ion. The leaving group mobilities of iodide, bromide, and chloride proved to be very similar for each nucleophile, and the authors have buttressed this finding with carefully reasoned arguments in support of a mechanism involving an intermediate complex with bond forming as the rate-limiting step.

In the present study the rates of reaction of benzenesulfonyl chloride with *N*-methylaniline in chloroform and in acetone were determined at 24.4 ± 0.1°. Since the conversion of these reactants to the *N*-methylanilide involves a proton transfer, special attention was given to the possibility of observing base catalysis in this reaction. The study also included measurements of the effect of added salts on the reaction rate.

Results

The reaction of benzenesulfonyl chloride with *N*-methylaniline proved to be autocatalytic, and second-order plots were strongly concave upward. The initial addition of *N*-methylbenzenesulfonylanilide had only a trivial effect on the observed rates, but the initial addition of *N*-methylaniline hydrochloride resulted in a strong acceleration of the reaction rate, and with the initial amine hydrochloride at one-fifth the initial concentration of the benzenesulfonyl chloride or higher, second-order plots were linear to beyond 60% reaction and permitted the determination of apparent second-order rate constants. These have been tabulated in Table I.

In the first four experiments shown in Table I both the initial benzenesulfonyl chloride concentrations and the initial amine hydrochloride concentrations were kept constant, and the initial *N*-methylaniline concentrations were varied. The rate constants that resulted were constant, well within experimental error. The average of the value obtained was 2.44×10^{-2} l. mol^{-1} min^{-1} and the maximum deviation from this average value was only slightly more than 3%.

In the last four experiments in Table I, the amine and acid chloride concentrations were constant and the amounts of added amine hydrochloride were varied. In these experiments the values of the second-order rate constants increase with increasing initial amine hydrochloride concentration. Since a plot of log k_2^* *vs.* $\mu_0^{1/2}$, where μ_0 is the initial ionic strength, is linear, the observed rate accelerations might be attributed to a salt effect. However, a plot of k_2^* *vs.* the initial amine concentration is also linear, as shown in Figure 1. The results presented to this point, can, therefore, be accommodated equally well by assuming that the aminolysis reaction is catalyzed by the amine hydrochloride. The experimental results will be presented on the basis of this latter assumption, and the assertion that a salt effect is not significantly involved will be justified in the subsequent discussion.

Assuming, as we have, that the observed rate increases are due to catalysis and not to a salt effect, the rate expression wil be given by eq 1, where A is the benzenesulfonyl chloride, B is the amine, C is the amine hydrochloride, and X is the product (*A*, *B*, *C*, and *X* are their concentrations, respectively). Since an increase in the initial amine concentration does not result in an increase in the experimental second order rate constant, k_2 must be equal to zero. The values of k_1 and k_3 can be obtained from the intercept and slope, respectively, of the plot of k_2^* *vs.* C_0 shown in Figure 1, and a least-squares treatment led to a value of 1.83×10^{-2} l. mol^{-1} min^{-1} for k_1 and a value of 0.543 l.^{2} mol^{-2} min^{-1} for k_3.

$$dx/dt = k_1AB + k_2AB^2 + k_3ABC \qquad (1)$$

The ratio of k_3 to k_1 above is 29.7 l. mol^{-1}. This is sufficiently large so that at a high initial concentration of the amine hydrochloride the rate of the uncatalyzed reaction will be negligible with respect to that of the catalyzed reaction. The simplified rate expression, eq 2, becomes

$$\frac{dx}{dt} \cong k_3(A_0 - X)(B_0 - 2X)(C_0 + X) \qquad (2)$$

appropriate, and this can be integrated to give eq 3.

Table I
Rates of Reaction of Benzenesulfonyl Chloride and *N*-Methylaniline in the Presence of Initially Added *N*-Methylaniline Hydrochloride in Chloroform at 24.4 ± 0.1°

$C_6H_5SO_2Cl$, mol l.$^{-1}$	$C_6H_5NHCH_3$, mol l.$^{-1}$	$C_6H_5N^+H_2CH_3$, Cl^-, mol l.$^{-1}$	$k_2^* \times 10^2$, l. mol^{-1} min^{-1}
0.05015	0.1217	0.01026	2.45
0.05026	0.1834	0.01016	2.36
0.05023	0.2754	0.01020	2.52
0.05134	0.3677	0.01022	2.41
0.05026	0.1834	0.01016	2.36
0.05050	0.1833	0.02482	3.22
0.05001	0.1832	0.05019	4.52
0.04993	0.1830	0.07915	6.14

$$k_3t = \frac{(B_0 + 2C_0)\ln\dfrac{A_0 - X}{A_0} - 2(A_0 + C_0)\ln\dfrac{B_0 - 2X}{B_0} + (2A_0 - B_0)\ln\dfrac{C_0 + X}{C_0}}{(2A_0 - B_0)(A_0 + C_0)(B_0 + 2C_0)} \quad (3)$$

Equation 3 in conjunction with the data for the last run shown in Table I was used to obtain a value for k_3. A plot of t *vs.* the right side of eq 3 was linear, with all eight experimental points on the line, and the slope, equal to k_3, was 0.506 l.^{2} mol^{-2} min^{-1}, in good agreement with the value obtained from the plot of k_2^* *vs.* C_0.

A more general rate expression, containing terms for both the uncatalyzed and the catalyzed reactions, is given by eq 4. Equation 4 can be integrated in a useful form by

$$dx/dt = k_1(A_0 - X)(B_0 - 2X) + k_3(A_0 - X) \times (B_0 - 2X)(C_0 + X) \quad (4)$$

making the substitution $D_0 = C_0 + k_1/k_3$. The integrated expression that results is eq 5. Using the previously obtained estimates for k_1 and k_3, which gave a value of 0.0337 mol l.$^{-1}$ *for the ratio* k_1/k_3, eq 5 was used in conjunction with the data for the last four experiments in Table I to calculate additional values for k_3.

$$k_3t = \frac{\ln[A_0/(A_0 - X)]}{(B_0 - 2A_0)(D_0 + A_0)} + \frac{2\ln[B_0/(B_0 - 2X)]}{(2A_0 - B_0)(2D_0 + B_0)} - \frac{\ln[D_0/(D_0 + X)]}{(A_0 + D_0)(B_0 + 2D_0)} \quad (5)$$

All four of the experiments gave good linear plots, and the k_3's that resulted ranged from 0.44 to 0.50 l.^{2} mol^{-2} min^{-1}, with the average value being 0.48 l.^{2} mol^{-2} min^{-1}. Increasing the ratio k_1/k_3 to 0.0355 mol l.$^{-1}$ led to a lower average value, 0.45 l.^{2} mol^{-1} min^{-1}, for k_3, and decreasing the ratio to a value lower than 0.0337 mol l.$^{-1}$ would presumably result in higher values for k_3. The fit, although not ideal, is still sufficient to provide some confidence in the validity of the treatment.

The presumed catalysis due to *N*-methylaniline hydrochloride could be either acid catalysis, with hydrogen bonding to the departing chlorine atom of the benzenesulfonyl chloride facilitating reaction, or base catalysis, with chloride ion or the *N*-methylaniline hydrochloride ion pair assisting in the proton transfer from the *N*-methylaniline. To permit a choice between these two alternatives, the reaction rates with initially added benzyltriethylammonium chloride and benzyltriethylammonium nitrate were measured. These two salts would be expected to be effective in base catalysis *via* hydrogen bonding to the hydrogen of *N*-methylaniline but would be ineffective in acid catalysis. The results are shown in Table II.

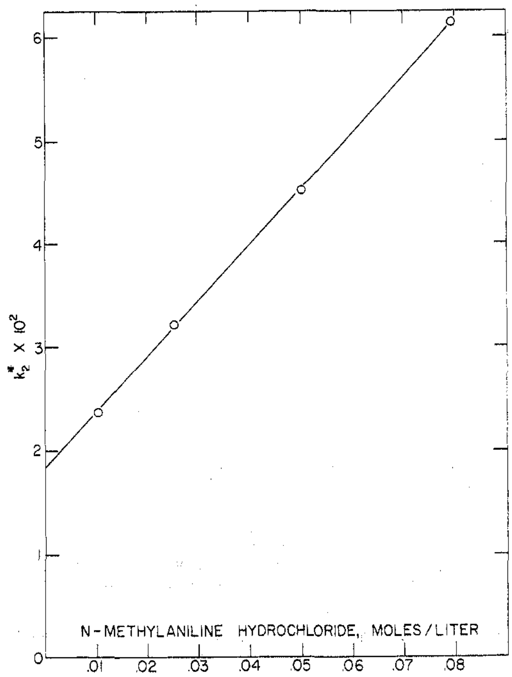


Figure 1. k_2^* *vs.* the initial concentrations of *N*-methylaniline hydrochloride in chloroform at 24.4 ± 0.1°.

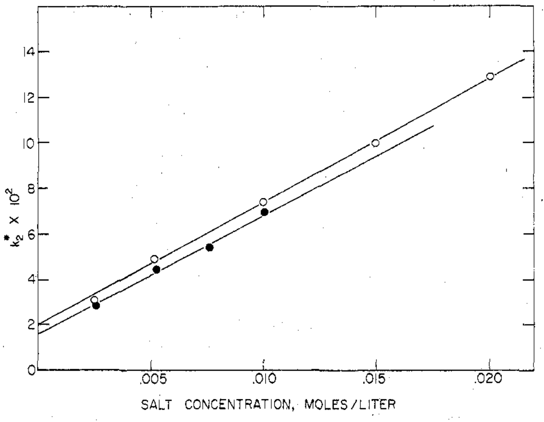


Figure 2. k_2^* *vs.* the initial concentrations of benzyltriethylammonium chloride (lower line) and benzyltriethylammonium nitrate (upper line) in chloroform at 24.4 ± 0.1°.

Both sets of data in Table II gave linear plots of k_2^* *vs.* the salt concentrations, as shown in Figure 2. The intercepts and slopes of these lines result in two additional values for k_1 and the rate constants for the reactions catalyzed by the quaternary ammonium chloride and the nitrate, k_4 and k_5, respectively. The values obtained, using the method of least squares, for k_1 were 1.64 × 10^{-2} l. mol^{-1} min^{-1} from the chloride and 2.00 × 10^{-2} l. mol^{-1} min^{-1} from the nitrate. The k_4 and k_5 obtained from the slopes of the two straight lines were 5.33 and 5.47 l.^{2} mol^{-2} min^{-1}, respectively. Since the quaternary ammonium chloride is ten times more effective in accelerating the reaction rate than the amine hydrochloride, it can be concluded that acid catalysis is not involved.

In acetone as solvent the reaction does not exhibit the strong autocatalytic characteristics observed in chloroform. Individual runs give linear second-order plots to beyond 60% reaction. However, at constant initial concentrations of the sulfonyl chloride, the rate constants obtained increase with increasing initial *N*-methylaniline concentrations. The observed increases in k_2^* are small

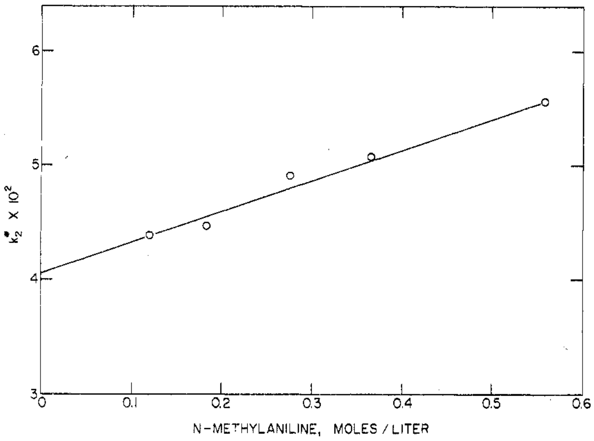


Figure 3. k_2* *vs.* the initial *N*-methylaniline concentrations in acetone at 24.4 ± 0.1°.

Table II
Rates of Reaction of Benzenesulfonyl Chloride and *N*-Methylaniline in the Presence of Initially Added Benzyltriethylammonium Chloride and Benzyltriethylammonium Nitrate in Chloroform at 24.4 ± 0.1°

$C_6H_5SO_2Cl$, mol l.$^{-1}$	$C_6H_5NHCH_3$, mol l.$^{-1}$	Added salt, mol l.$^{-1}$	$k_2^* \times 10^2$, l. mol^{-1} min^{-1}
A. Benzyltriethylammonium Chloride			
0.05040	0.1821	0.002507	2.88
0.05072	0.1843	0.005115	4.59
0.05069	0.1827	0.007569	5.51
0.05011	0.1847	0.01008	7.04
B. Benzyltriethylammonium Nitrate			
0.05042	0.1843	0.002442	3.18
0.05007	0.1829	0.005108	4.92
0.04985	0.1839	0.009952	7.50
0.05024	0.1829	0.01491	10.1
0.05025	0.1853	0.02010	13.0

Table III
Rates of Reaction of Benzenesulfonyl Chloride and *N*-Methylaniline with and without Added *N*-Methylaniline Hydrochloride and Benzyltriethylammonium Nitrate in Acetone at 24.4 ± 0.1°

$C_6H_5SO_2Cl$, mol l.$^{-1}$	$C_6H_5NHCH_3$, mol l.$^{-1}$	Added salt, mol l.$^{-1}$	$k_2^* \times 10^2$, l. mol^{-1} min^{-1}
0.05074	0.1201		4.39
0.05042	0.1837		4.47
0.05044	0.2757		4.91
0.05087	0.3640		5.08
0.05054	0.5575		5.57
A. *N*-Methylaniline Hydrochloride			
0.05050	0.1831	0.01005	5.09
0.05037	0.1820	0.01759	5.43
0.05040	0.1832	0.02515	5.84
0.05044	0.1829	0.03776	6.49
B. Benzyltriethylammonium Nitrate			
0.05022	0.1819	0.00510	6.28
0.05080	0.1834	0.01010	7.83
0.05057	0.1839	0.02008	11.1
C. Tetraethylammonium Perchlorate			
0.05002	0.1835	0.00498	5.05
0.05055	0.1849	0.01009	5.46
0.05012	0.1831	0.01972	6.06

but beyond possible experimental error. With initially added *N*-methylaniline hydrochloride the observed increases in k_2* are larger, and with initially added benzyltriethylammonium nitrate the k_2*'s are larger still. These results are assembled in Table III.

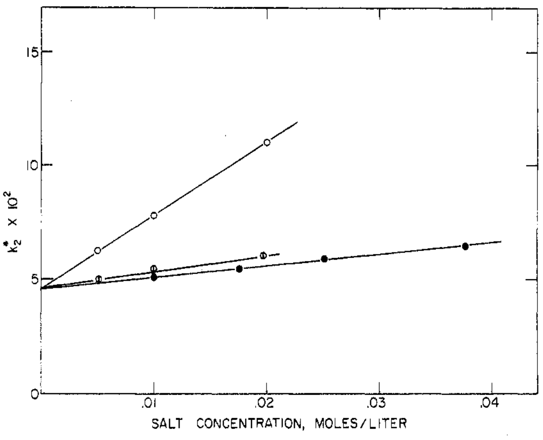


Figure 4. k_2* *vs.* the initial concentrations of *N*-methylaniline hydrochloride (lower line), tetraethylammonium perchlorate (middle line), and benzyltriethylammonium nitrate (upper line) in acetone at 24.4 ± 0.1°.

Table IV
Rate Constants for the Uncatalyzed and Catalyzed Reactions of Benzenesulfonyl Chloride and *N*-Methylaniline in Chloroform and in Acetone at 24.4 ± 0.1°

	Chloroform	Acetone
$k_1 \times 10^2$, l. mol^{-1} min^{-1} Uncatalyzed reaction	1.83	4.05
$k_2 \times 10^2$, l.^{2} mol^{-2} min^{-1} Catalysis by *N*-methylaniline	0	2.79
k_3, l.^{2} mol^{-2} min^{-1} Catalysis by *N*-methylaniline hydrochloride	0.543	0.529
k_4, l.^{2} mol^{-2} min^{-1} Catalysis by benzyltriethylammonium chloride	5.47	
k_5, l.^{2} mol^{-2} min^{-1} Catalysis by benzyltriethylammonium nitrate	5.33	3.28
k_6, l.^{2} mol^{-2} min^{-1} Catalysis by tetraethylammonium perchlorate		0.677
k_2/k_1, l. mol^{-1}	0	0.69
k_3/k_1, l. mol^{-1}	29.7	13.1
k_4/k_1, l. mol^{-1}	299	
k_5/k_1, l. mol^{-1}	291	81.0
k_6/k_1, l. mol^{-1}		16.7

A plot of k_2* *vs.* the initial amine concentrations for the first five runs in Table III is linear, as shown in Figure 3. The intercept of this line is equal to k_1, the rate constant for the uncatalyzed reaction in acetone, and the slope is equal to k_2, the rate constant for the reaction catalyzed by *N*-methylaniline. The constants obtained were 4.05 × 10^{-2} l. mol^{-1} min^{-1} for k_1 and 2.79 × 10^{-2} l.^{2} mol^{-2} min^{-1} for k_2.

Plots of k_2* vs. the initial *N*-methylaniline hydrochloride concentrations (lower line in Figure 4), k_2* *vs.* the initial tetraethylammonium perchlorate concentrations (middle line in Figure 4), and k_2* *vs.* the initial benzyltriethylammonium nitrate concentrations (upper line in Figure 4) are also linear. In these three cases the intercepts are equal to k_2* for the reaction with 0.05 *M* chloride and 0.18 *M* amine, rather than to k_1, because of the slight catalysis by *N*-methylaniline. The slopes, however, do provide estimates of the rate constant, k_3, for the reaction catalyzed by *N*-methylaniline hydrochloride, the rate constant, k_6, for the reaction catalyzed by tetraethylammonium perchlorate, and the rate constant, k_5, for the reaction catalyzed by benzyltriethylammonium nitrate, and the constants obtained were 0.529, 0.677, and 3.28 l.^{2} mol^{-2} min^{-1}, respectively.

To facilitate comparisons between the two solvents, all of the rate constants obtained have been assembled in Table IV. Also included are ratios of each catalyzed rate constant to the uncatalyzed rate constant. These afford a direct indication of the relative importance of the uncatalyzed and catalyzed reactions in product formation and, in general, highlight the fact that catalysis is more important in chloroform than in acetone.

Experimental Section

Materials. Eastman Kodak Co. White Label benzenesulfonyl chloride was distilled at 0.2-0.3 mm and a middle cut, bp 60-62°, was retained.

N-Methylaniline was distilled two times under nitrogen from 20 *mesh zinc and a few pieces of mossy zinc,* a middle cut being taken each time, bp 84-86° (12 mm). The amine was stored under nitrogen when not in use.

Reagent grade chloroform, containing 0.50% ethanol as stabilizer, from the J. T. Baker Co. was used without purification.

Reagent grade acetone was shaken with calcium chloride and then permitted to stand for several hours over calcium chloride. The drying agent was removed by filtration, and the acetone was distilled, with a sizable forerun and residue being discarded.

N-Methylaniline hydrochloride was prepared by standard methods and crystallized two times from methanol-ether, mp 124-126°.

Anal. Calcd for $C_7H_{10}NCl$: Cl, 24.68. Found: Cl, 24.69.

Benzyltriethylammonium nitrate and benzyltriethylammonium chloride were prepared by methods previously described.[8]

Eastman Kodak Co. White Label tetraethylammonium perchlorate was crystallized from water and dried *in vacuo* at 100°, mp 350-351° dec.

Rate Measurements. Separate, determinate solutions of the benzenesulfonyl chloride and the amine were made up at the temperature of the measurements. When salts were used, these were added to the amine solution rather than to the sulfonyl chloride solution. The solutions were mixed at zero time, and 10-ml aliquots were withdrawn at appropriate time intervals and quenched by shaking with a mixture of 50 ml of benzene and 50 ml of 1:4 nitric acid. The acid layer was separated and the benzene layer was extracted two times with 25-ml portions of water. The water extracts were added to the acid extract, and the combined extracts were analyzed for chloride ion by the Volhard method.

Product Isolation Experiments. *N*-Methylbenzenesulfonanilide. *N*-Methylaniline (9.89 g, 0.0923 mol) was added to a solution of benzenesulfonyl chloride (4.13 g, 0.234 mol) in chloroform (100 ml). The solution was left standing at room temperature for 40 hr and diluted with chloroform (150 ml). The diluted solution was washed with water (50 ml) and two times with 100-ml portions of 1:1 hydrochloric acid and finally with water again. The solution was dried over magnesium sulfate. The solvent was removed with the water pump, and the crude product was crystallized from methanol, yield 5.65 g (97.6%), mp 77-78°. A second crystallization raised the melting point to 78-79°.

When the reaction was run in acetone, the reaction mixture was left standing as above. The acetone was then removed, and benzene (250 ml) was added. The subsequent procedure was as already described. The yield of product was 96.3%. A repetition of the experiment with initially added benzyltriethylammonium nitrate in an amount equivalent to the benzenesulfonyl chloride gave an 80.3% yield of *N*-methylbenzenesulfonanilide.

Discussion

Benzenesulfonyl chloride and *N*-methylaniline react cleanly in both chloroform and acetone to give *N*-methylbenzenesulfonanilide and *N*-methylaniline hydrochloride. The exact mechanism of this reaction is uncertain, since the available evidence does not distinguish fully between an SN2 reaction having a transition state close to reactants and a mechanism involving an intermediate addition complex with bond forming as the rate-limiting step.[4-7] In terms of either possible mechanism the rate constants reported herein reflect the bond-making process and are relatively unperturbed by the bond-breaking process.

Although a salt, *N*-methylaniline hydrochloride, is a product of the reaction, the rate-determining transition state can have only modest dipolar characteristics, since bond breaking is either slight or absent at the transition state. Moreover, the starting reagents are neutral molecules, not ions, and a reaction of this type would be expected to show some increase in rate with an increase in the dielectric constant of the solvent but would also be expected to be insensitive to the ionic strength of the medium.[9]

The two solvents chosen for this study were chloroform and acetone. Chloroform has a dielectric constant of 4.81 at 20°.[10-12] It can function as a donor in hydrogen bonding but not as an acceptor. Acetone has a dielectric constant of 20.7 at 25°.[13-16] It, in contrast, can function as an acceptor in hydrogen bonding but is relatively ineffective as a donor. The overall reaction rates were, as anticipated, somewhat faster in the solvent of higher dielectric constant, acetone, but the observed accelerations in reaction rate on addition of salts greatly exceeded those that might have been expected as a result of increasing the ionic strength of the medium.

Plots of k_2^* *vs.* the square root of the ionic strength, $\mu^{1/2}$, are linear for the experiments with added salts, but the significance of this observation is questionable. The reactants are not ions, and the Brønsted-Bjerrum theory of salt effects,[17,18] which is valid only for dilute solution reactions between ions at small μ (below 0.01 *M* for 1:1 electrolytes), does not properly apply.[19] Moreover, the salts are only very slightly dissociated in the solvents used, whereas the μ's used in the linear plots of k_2^* *vs.* $\mu^{1/2}$ assumed complete dissociation. Fuoss and Kraus[20] have studied ion-pair formation as a function of the dielectric constant by measuring the equilibrium constants for ion-pair dissociation for tetraisoamylammonium nitrate in dioxane-water mixtures at 25°. Using these results, which covered dielectric constants ranging from 2.38 to 53.0, as a guide, it can be estimated that the equilibrium constants for ion-pair dissociation for quaternary ammonium salts in chloroform and in acetone have values of the order of 10^{-8} and 10^{-2}, respectively. In chloroform, therefore, the salts are present almost entirely as ion pairs and higher aggregates, and even in acetone no more than 10% of the salt is dissociated to free ions.

The foregoing considerations make it improbable that the observed accelerations in rate are attributable to a kinetic salt effect. Further support for this contention is afforded by the results in acetone, shown in Table III and Figure 4. Benzyltriethylammonium nitrate and tetraethylammonium perchlorate would be expected to result in very nearly equivalent salt effects, but in the present system, the rate constant for the reaction catalyzed by the nitrate (k_5 in Table IV) is almost five times as large as the rate constant for the reaction catalyzed by the perchlorate (k_6 in Table IV).

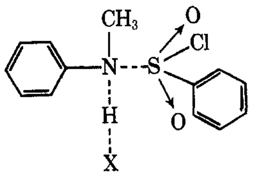
The special case of one or more neutral molecules reacting *via* a strongly dipolar transition state to form oppositely charged ions has also been treated theoretically.[21] A typical case would be the hydrolysis of *tert*-butyl bromide in 90% acetone-10% water, and the treatment leads to a linear relationship between the logarithm of the rate constants and the ionic strength. This treatment is, however, inappropriate for the reactions of present concern, both because the above linear relationship is not observed and because in the absence of extensive bond breaking in the transition state the rate-determining transition state does not have the requisite strong dipolar character.

If the observed rate accelerations due to added salts are not the result of a salt effect, an alternative explanation must be sought. The first suggestion of a possible explanation was provided in an earlier study of rates and salt effects in the reactions of phenacyl bromide with *N*-ethylaniline and triethylamine in chloroform.[3] In the reaction with *N*-ethylaniline the initial addition of 0.057 *M* benzyltriethylammonium nitrate increased k_2^* more than sevenfold, but with triethylamine the addition of the same amount of salt resulted in only a 60% increase in k_2^*. In the first reaction a proton is transferred at some point along the reaction path, and base catalysis is possible. In the reaction with triethylamine, where the product is a quaternary ammonium bromide, this is not the case.

The possibility that a neutral salt can serve as a catalyst, facilitating proton transfer, was explored in greater detail for the reaction of 2,4-dinitrochlorobenzene and *n*-butylamine in chloroform.[1] The initial addition of benzyltriethylammonium nitrate resulted in increases in k_2^* comparable with those observed in the system of present interest. The accelerations in rate were attributed to catalysis of intermediate formation, and the catalysis mode was formulated as involving the formation, in the transition state for intermediate formation, of a hydrogen bond, in which the amine hydrogen acted as the donor and the salt served as the acceptor. Such hydrogen bonding both facilitates the proton transfer and mobilizes the available electrons on the nitrogen, thus making it a more effective nucleophile.

If the rate-determining step in the reaction of benzenesulfonyl chloride with *N*-methylaniline reflects primarily the formation of the new S-N bond, the reaction is analogous for present purposes to the reaction of 2,4-dinitrochlorobenzene with *n*-butylamine, which was studied previously. This is equally the case whether or not an addition intermediate is actually involved. A hydrogen bond, from the amine hydrogen to an appropriate acceptor, in the transition state of this reaction will also promote proton transfer and enhance the nucleophilicity of the amine. It is, therefore, pertinent to explore the possibility that the added salts are functioning as true catalysts and to determine whether or not the available experimental observations are consistent with this hypothesis.

Simply stated, this hypothesis amounts to an assertion to the effect that the salt or some component thereof is actually involved in the rate-determining transition state and more specifically that it is present as the acceptor in hydrogen bonding to the amine nucleophile. Such a possible transition state might be depicted as in I, where X represents the necessary salt component.



I

The formation of this transition state does not necessarily require an intermolecular collision, since the hydrogen bond may be formed in a prior equilibrium between the amine and the salt component. The anion from the salt would be effective as X, and the ion pair, with the negative end of the dipole oriented toward the amine hydrogen, might also be suitable.

Species, other than those derived from the salt, which are capable of functioning as acceptors in hydrogen bonding could also be involved in the transition state of this reaction. The amine nucleophile is a candidate as is the acetone solvent, but not chloroform, which is ineffective as an acceptor. The extent to which acetone is involved in transition states such as I is not directly determined by our experiments. However, to the extent that acetone is so involved the effectiveness of other possible catalytic species would be diminished. The proper measure for the catalytic efficiency of a given species is not the absolute magnitude of the derived rate constant but the ratio of the rate constants for the catalyzed and uncatalyzed reactions. These rate ratios are listed in Table IV, where it is apparent that the observed results are in accord with the above expectations. For catalysis by *N*-methylaniline hydrochloride the rate ratio in chloroform is more than twice the ratio in acetone, and for catalysis by benzyltriethylammonium nitrate the rate ratio in chloroform is almost four times as large as in acetone.

The present results do permit a decision as to the salt species responsible for the observed catalytic effects. As already noted, in the solvents used the salts are present predominantly in the ion-pair form. The concentration of the free anion is proportional not to the concentration of the added salt, but to the square root of the concentration. The ion-pair concentration is, however, directly proportional to the salt concentration. The rates that have been measured are in every case linear with the salt concentrations but not with the square roots of the salt concentrations. The proper species in the transition state is, therefore, the ion pair rather than the anion.

Registry No. Benzenesulfonyl chloride, 98-09-9; *N*-methylaniline, 100-61-8; *N*-methylaniline hydrochloride, 2739-12-0; benzyltriethylammonium chloride, 56-37-1; benzyltriethylammonium nitrate, 2484-08-4; *N*-methylbenzenesulfonanilide, 90-10-8.

References and Notes

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