Nucleophilic Substitutions at Dicoordinated Sulfur. Kinetic Study of the Reaction between Triphenylmethyl Sulfenyl Chloride and *n*-Butylamine in Benzene

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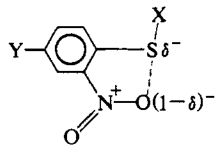
Abstract: The rate of reaction between tritylsulfenyl chloride and *n*-butylamine has been measured in benzene at 25° using a spectrophotometric technique. In the absence of additives the rate depends on the square of the amine concentration. The reaction is markedly accelerated by addition of bases or salts; terms which depend on the concentration of an additive and are first order in amine appear in the kinetic expression. The likelihood that the salts act as bases in the low-polarity medium benzene is discussed. An intermediate complex mechanism is preferred to the kinetically indistinguishable "one-step" reaction between an amine dimer or adducts and the substrate.

It is well known that sulfenyl compounds, RS–X, react with nucleophiles, Y:, according to eq 1. The steric requirements of reaction 1 have been found to be very

$$\text{RS–X} + \text{Y:} \rightarrow \text{RS–Y} + \text{X:} \qquad (1)$$

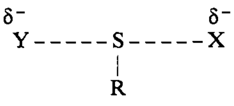
similar to those of nucleophilic substitutions at carbon,[1] thus supporting the conclusion that the transition states for carbon and divalent sulfur have a similar geometry, in that the nucleophile, reaction center, and leaving group lie on the same line. However, if a linear activated complex for nucleophilic displacement at carbon can be justified, since entering and leaving groups occupy the same orbital, sulfur, a second-row element, could in principle use its empty d orbitals to accommodate the electron pair of a nucleophile, thus making possible a nonlinear transition state. The easy availability of sulfur d orbitals for bonding has long been suggested by Parker and Kharasch[2] and is supported by experimental evidence such as the existence of the very stable molecule SF_6 and by analogy with other second-row elements which undoubtedly make use of d orbitals in nucleophilic substitutions: silicon[3] and phosphorus.[4] Very recently Givens and Kwart[5,6] have suggested the formation of a trigonal bipyramidal structure with ten electrons around the sulfur atom for the transition state of the reaction between *o*-nitrobenzensulfenyl chloride and acetate ion. The electronic requirements for this reaction have been found to be almost nil and this would be in contrast with a pentacovalent transition state with a formal negative charge on the sulfur atom. Similar results have been found by Brown and Hogg[7] in the alkaline hydrolysis of *o*-nitrobenzensulfenic esters. However, when *o*-nitro compounds are considered, the ground state may also be stabilized by substituents on the benzene ring due to the strong attractive interaction between S and O (I).[8] Thus, in such cases electronic effects are difficult to assess.



I

In the absence of an *o*-nitro group, larger substituents effects on nucleophilic substitutions at divalent sulfur have been found. For the sulfite–aryl thiosulfite exchange[9] and for the chloride ion catalyzed hydrolysis of sulfenyl chlorides[10] ρ values of 0.85 and 1.04 have been respectively found. Although these values are probably small if a full negative charge on sulfur has to be stabilized, it may well be that the negative charge of the reaction center does not need to be dispersed by electron-withdrawing substituents in the organic moiety since it can be very easily accommodated by low-lying d orbitals.

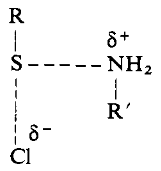
It is worth noting at this point that the steric effects on divalent sulfur have been studied with nucleophiles bearing a negative charge.[1] It is possible in this case that a linear transition state would be favored even in the case of d-orbital participation since entering and leaving groups repel each other and tend to stay as far apart as possible (II).



$$\overset{\delta^-}{\text{Y}}\text{-----}\underset{\substack{|\\ \text{R}}}{\text{S}}\text{-----}\overset{\delta^-}{\text{X}}$$

II

On the other hand, if a neutral nucleophile is used, *e.g.*, an amine, entering and leaving groups are likely to have opposite charge and electrostatics would force them to stay as close as possible (III).[11]



III

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[1] A. Fava and A. Iliceto, *J. Am. Chem. Soc.*, **80**, 3478 (1958).

[2] A. J. Parker and N. Kharasch, *Chem. Rev.*, **59**, 583 (1959).

[3] L. H. Sommer, "Stereochemistry, Mechanism and Silicon," McGraw-Hill Book Co., Inc., New York, N. Y., 1965, p 155.

[4] R. F. Hudson, "Structure and Mechanism in Organo-Phosphorus Chemistry," Academic Press, New York, N. Y., 1965, p 57.

[5] E. N. Givens and H. Kwart, *J. Am. Chem. Soc.*, **90**, 378 (1968).

[6] E. N. Givens and H. Kwart, *ibid.*, **90**, 386 (1968).

[7] C. Brown and D. R. Hogg, *Chem. Commun.*, 38 (1967).

[8] W. C. Hamilton and S. J. LaPlaca, *J. Am. Chem. Soc.*, **86**, 2289 (1964).

[9] A. Fava and A. Ceccon, unpublished data cited in E. Ciuffarin and A. Fava, *Progr. Phys. Org. Chem.*, **6**, 81 (1968).

[10] L. Di Nunno, G. Modena, and G. Scorrano, *Ric. Sci.*, **36**, 825 (1966).

[11] See Ciuffarin and Fava, ref 9.

Table I. Pseudo-First-Order Rate Constant (k') and Second-Order Rate Coefficient ($k_2 = k'/[BuNH_2]$) for the Reaction between RSCl and $BuNH_2$

$[BuNH_2] \times 10^2, M$	$k' \times 10^3, sec^{-1}$	$k_2 \times 10^2, M^{-1} sec^{-1}$
0.0689	0.0018	0.27[a]
0.137	0.0083	0.61[a]
0.344	0.032	0.94[a]
0.683	0.10	1.5[a]
0.784	0.13	1.6[a]
1.34	0.61	4.5[a]
2.68	1.8	6.6
3.18	2.6	8.1
3.33	3.3	9.9
5.37	8.9	16.0
6.36	12.0	18.0
7.40	15.0	20.0
8.22	20.0	24.0
9.13	22.0	25.0

[a] Initial rates.

Table II. Rate Constants in the Presence of $BuNH_3Cl$[a]

$[BuNH_2] \times 10^2, M$	$k' \times 10^3, sec^{-1}$	$k_2 \times 10^2, M^{-1} sec^{-1}$
0.055	0.0095	1.7
0.109	0.021	1.9
0.275	0.055	2.0
0.546	0.13	2.4
1.070	0.40	3.7
2.080	1.40	6.7

[a] $2.8 \times 10^{-5} M$.

In an attempt to elucidate the geometry of the activated complex in such nucleophilic substitutions at sulfur and to shed further light on the question of d-orbital participation, we are now carrying out a systematic study of the reaction between sulfenyl halides and amines.

Results

We report in this paper the reaction between *n*-butylamine ($BuNH_2$) and triphenylmethyl sulfenyl chloride (RSCl) in benzene at 25°. The choice of a particularly bulky organic moiety was dictated by the need of reducing the substitution rate to a manageable range. RSCl reacts quantitatively with $BuNH_2$ to give N-(*n*-butyl)triphenylmethylsulfenamide (RSNHBu) and *n*-butylamine hydrochloride ($BuNH_3Cl$) according to eq 2.

$$RSCl + 2BuNH_2 \rightarrow RSNHBu + BuNH_3Cl \qquad (2)$$

In all kinetic runs the concentration of RSCl was about $1.4 \times 10^{-4} M$. While the sulfenamide is an inert product, the salt revealed itself to be a strong catalytic agent in the low polarity medium benzene. At low amine concentration (less than $2.5 \times 10^{-2} M$) marked autocatalysis was observed; thus initial rates have been measured. However, as the concentration of amine was increased the catalytic effect of the salt became negligible and the pseudo-first-order plots appeared to be linear within experimental error. The experimental data are tabulated in Table I.

The second-order rate coefficient, $k_2 = k'/[BuNH_2]$, where k' is the pseudo-first-order rate constant, varies linearly with the amine concentration (Figure 1) in the 150-fold range investigated and vanishes at zero amine concentration. The value of the intercept calculated by the least-squares treatment is in fact of the same order as its relative error, $k_2^0 = (1.0 \pm 0.6) \times 10^{-3} M^{-1} sec^{-1}$. Thus, the reaction is second order in amine and follows eq 3. The least-squares average value of the third-order rate coefficient (k_3) is $2.6 M^{-2} sec^{-1}$, with a correlation coefficient[12] $r = 0.995$.

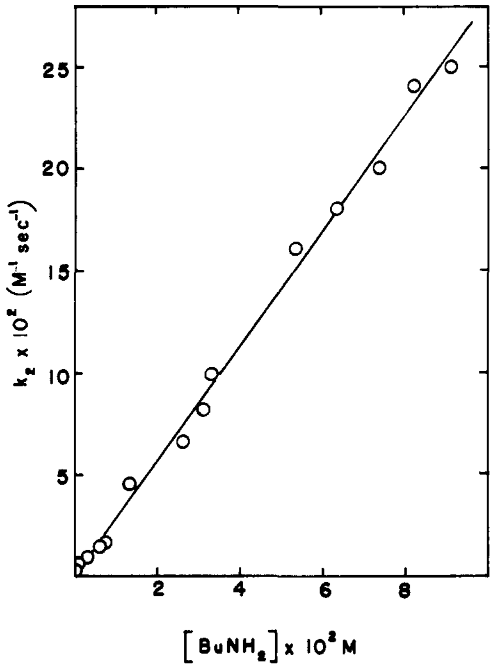

Figure 1. Second-order plot of the rates of reaction of triphenylmethylsulfenyl chloride with *n*-butylamine.

$$k_2 = k_3[BuNH_2] \qquad (3)$$

Salt Effects. Since the minute amount of salt produced during the reaction proved to be an excellent catalyst, the effect of the product salt on the reaction has been investigated. Given the extremely low solubility of *n*-butylamine hydrochloride in benzene, its effect has been measured in a series of runs which showed autocatalysis. When the rate is calculated from the slope of the tangent line to the pseudo-first-order plot at 20% reaction, which corresponds to $2.8 \times 10^{-5} M$ of $BuNH_3Cl$ formed, the second-order rate coefficient still depends linearly on the amine concentration. However, a small but definite intercept emerges. The data are summarized by Table II. They appear to fit eq 4 fairly well. A least-squares treatment gives $k_0 = (1.5 \pm 0.15) \times 10^{-2} M^{-1} sec^{-1}$ and $k_3' = 2.1 M^{-2} sec^{-1}$ ($r = 0.98$).

$$k_2 = k_3'[BuNH_2] + k_0 \qquad (4)$$

The salt effect has been studied in greater detail by using a more soluble salt, tetra-*n*-butylammonium perchlorate, Bu_4NClO_4. The single runs do not show any detectable autocatalysis even at concentrations in Bu_4NClO_4 as low as $1.4 \times 10^{-5} M$. The data are collected in Table III. Three concentrations of salt have

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[12] H. S. Mickley, T. K. Sherwood, and C. E. Reed, "Applied Mathematics in Chemical Engineering," 2nd ed, McGraw-Hill Book Co., Inc., New York, N. Y., 1957, Chapter 2.

Table III. Rate Constants in the Presence of Salts

$[BuNH_2] \times 10^2, M$	Added salt	Concn $\times 10^4, M$	$k' \times 10^3, sec^{-1}$	$k_2 \times 10^2, M^{-1} sec^{-1}$
0.258	Bu_4NClO_4	0.142	0.13	5.0
0.661	Bu_4NClO_4	0.142	0.50	8.2
1.31	Bu_4NClO_4	0.142	1.1	8.9
2.58	Bu_4NClO_4	0.142	2.7	10.0
0.783	Bu_4NClO_4	5.00	2.5	32.0
1.25	Bu_4NClO_4	5.00	4.7	38.0
2.01	Bu_4NClO_4	5.00	9.1	45.0
3.21	Bu_4NClO_4	5.00	16.6	52.0
5.14	Bu_4NClO_4	5.00	32.2	63.0
0.244	Bu_4NClO_4	21.1	1.71	70.0
0.781	Bu_4NClO_4	21.1	5.95	76.0
1.56	Bu_4NClO_4	21.1	12.3	80.0
3.13	Bu_4NClO_4	21.1	30.5	98.0
5.00	Bu_4NClO_4	21.1	52.7	105.0
0.782	Bu_4NClO_4	0.00	0.12	1.5[a]
0.782	Bu_4NClO_4	0.935	1.2	15.0
0.782	Bu_4NClO_4	2.85	2.0	26.0
0.782	Bu_4NClO_4	3.74	2.5	32.0
0.782	Bu_4NClO_4	5.71	3.0	39.0
0.782	Bu_4NClO_4	7.18	3.2	40.0
0.782	Bu_4NClO_4	8.56	3.4	44.0
0.782	Bu_4NClO_4	9.98	3.9	50.0
0.782	Bu_4NClO_4	11.4	4.2	54.0
0.782	Bu_4NClO_4	15.0	4.6	59.0
0.782	Bu_4NClO_4	20.0	5.3	68.0
0.201	Bu_4NCl	2.88	3.3	164.0
0.770	Bu_4NCl	2.88	13.0	169.0
1.58	Bu_4NCl	2.88	26.0	165.0
3.14	Bu_4NCl	2.88	52.0	167.0
0.782	Bu_4NCl	0.815	4.5	58.0[a]
0.782	Bu_4NCl	1.63	7.9	101.0[a]
0.782	Bu_4NCl	3.26	14.0	180.0
0.782	Bu_4NCl	8.70	34.0	430.0

[a] Initial rate.

been studied at varying amine concentration and in all cases the reaction follows the rate law expressed by eq 4. The value of the intercept (Figure 2, curves a, b, and c) increases at increasing salt concentrations and so does the slope. The salt effect on k_3' is much smaller than that on k_0 (eq 4) and they have different mechanistic origin (see Discussion). At the smallest concentration of salt, $1.42 \times 10^{-5} M$, the value of the third-order rate coefficient ($2.5 M^{-2} sec^{-1}$) is indistinguishable within experimental error from that observed in absence of salt ($2.6 M^{-2} sec^{-1}$), but it is three times as large at a concentration in salt $2.1 \times 10^{-3} M$. An analysis of the dependence of the rate on the concentration of salt shows that in the range investigated (9.35×10^{-5}–$2.00 \times 10^{-3} M$) a square-root relationship is followed (Figure 3). Thus the order in salt is 0.5 and k_0 of eq 4 becomes $k_s[salt]^{0.5}$. A one-half order in salts in low polarity solvents is generally accounted for as an effect of the free ions.[13,14]

In order to check which ion is responsible for the catalysis and the occurrence of a "special" salt effect,[14] experiments have been performed in the presence of tetra-*n*-butylammonium chloride Bu_4NCl. A very peculiar phenomenon came to light. The first-order rate plot which was convex in absence of additives, due to autocatalysis, became concave upon addition of Bu_4NCl: the

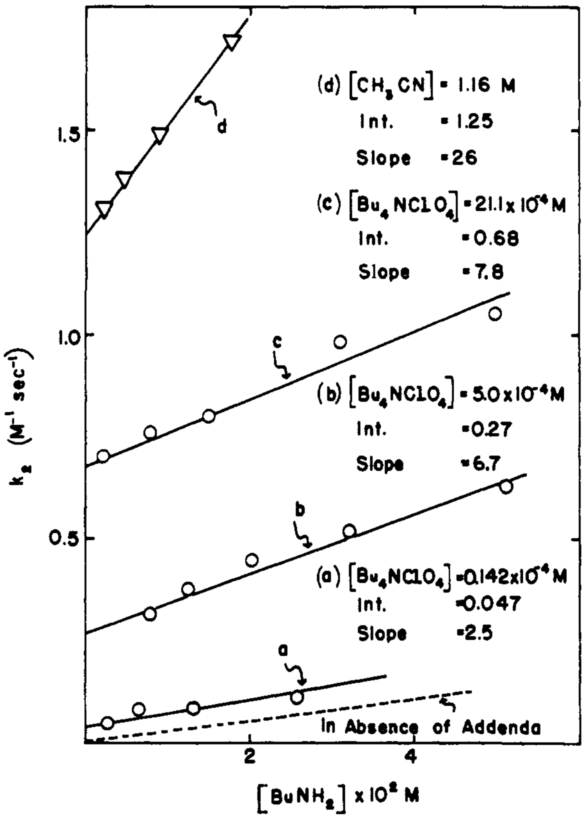

Figure 2. Second-order plots of the rates of reaction of triphenylmethylsulfenyl chloride with *n*-butylamine in the presence of tetra-*n*-butylammonium perchlorate (○) or acetonitrile (▽).

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(13) E. D. Hughes, C. K. Ingold, S. F. Mok, S. Patai, and Y. Pocker, *J. Chem. Soc.*, 1265 (1957).

(14) S. Winstein, P. E. Klinedinst, and G. C. Robinson, *J. Am. Chem., Soc.*, **83**, 885 (1961).

Table IV. Effect of Combined Salts[a]

$[Bu_4NClO_4] \times 10^4$, M	$[Bu_4NCl] \times 10^4$, M	$[(C_7H_{15})_4NClO_4] \times 10^4$, M	$k_2 \times 10^2$, M^{-1} sec^{-1}
	1.74		160
10.2			55
10.2	1.74		93
	1.53		140
		4.68	51
	1.53	4.68	160

[a] $[BuNH_2] = 1.2 \times 10^{-2}$ M.

Table V. Effect of Triethylamine, Pyridine, and Acetonitrile

$[BuNH_2] \times 10^2$, M	Additive	Concn $\times 10^2$, M	$k' \times 10^3$, sec^{-1}	$k_2 \times 10^2$, M^{-1} sec^{-1}
3.34	Et_3N	0.00	3.3	9.9
3.34	Et_3N	5.10	5.5	17.0
3.34	Et_3N	10.30	8.3	25.0
3.34	Et_3N	20.60	13.0	39.0
13.00	Pyridine	0.00	43.0	33.0
13.00	Pyridine	1.28	44.0	34.0
13.00	Pyridine	5.00	51.0	39.0
13.00	Pyridine	7.35	52.0	40.0
0.888	Pyridine	3.40	0.55	6.2
1.76	Pyridine	3.40	1.3	7.6
4.50	Pyridine	3.40	7.7	17.0
9.00	Pyridine	3.40	26.0	29.0
3.40	Acetonitrile	0.0	3.10	9.2
3.40	Acetonitrile	8.1	4.30	13.0
3.40	Acetonitrile	16.1	6.91	20.0
3.40	Acetonitrile	32.3	12.1	36.0
3.40	Acetonitrile	64.7	24.4	78.0
0.234	Acetonitrile	116.0	3.05	131.0
0.465	Acetonitrile	116.0	6.44	139.0
0.914	Acetonitrile	116.0	13.6	149.0
1.77	Acetonitrile	116.0	30.5	172.0

reaction rate slowed down while the reaction proceeded. At increasing salt concentration, the concavity was flattened out until it disappeared completely (see Discussion). Thus, at low salt concentrations initial rates have been measured. The data in Table III show that Bu_4NCl is a stronger catalyst than Bu_4NClO_4, its reportedly smaller dissociation constant notwithstanding.[15]

The order in Bu_4NCl has been found to be approximately 0.75. A plot of $(k_2 - k_2^0)/[\text{salt}]^{0.5}$, where k_2^0 is the rate constant at zero salt concentration, *vs.* $[\text{salt}]^{0.5}$ has been found to be linear. Thus, in the presence of Bu_4NCl the kinetic expression is

$$k_2 = k_2^0 + k_4[\text{salt}]^{0.5} + k_4'[\text{salt}] \qquad (5)$$

The greater catalytic efficiency of Bu_4NCl compared to that of Bu_4NClO_4 supports the view that the anion is the effective catalyst. Further support of this is given by experiments performed in the presence of a combination of salts (Table IV). In fact, addition of Bu_4NClO_4 to a reaction mixture containing Bu_4NCl depresses the rate because of common ion effect which reduces the concentration of Cl . On the contrary, addition of tetra-*n*-heptylammonium perchlorate, $(C_7H_{15})_4NClO_4$, which does not possess a common ion, does not depress the rate.

Values of k_4 are 25 and 15 $M^{-1.5}$ sec^{-1} for chloride and perchlorate ions, respectively. These figures do not

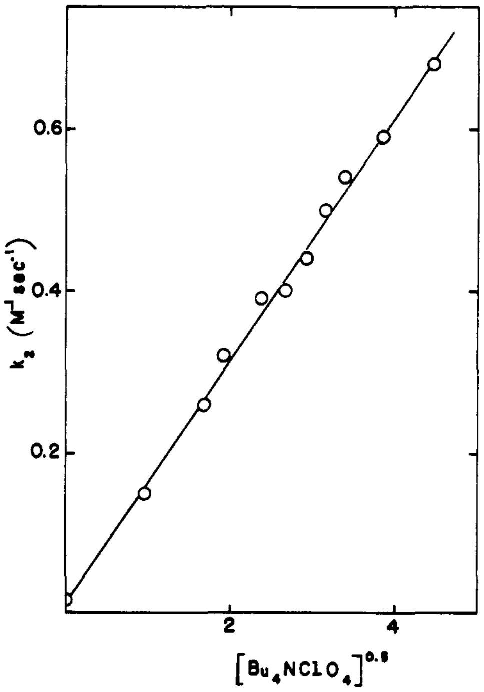

Figure 3. Second-order rate constants for the reaction of triphenylmethylsulfenyl chloride with *n*-butylamine (at constant concentration, 7.82×10^{-3} M) as a function of the square root of tetra-*n*-butylammonium perchlorate concentration.

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(15) E. D. Hughes, C. K. Ingold, S. Patai, and Y. Pocker, *J. Chem. Soc.*, 1206 (1957).

represent the true catalytic power of the anions since the dissociation constant of the salts should be taken into account. When this is done by using Ingold's data,[15] Cl^- is found to be about four times as effective as ClO_4^-. The value of k_4' is 4.300 M^2 sec^{-1} for the chloride and too small to be measured for the perchlorate.

Effect of Added Bases. The clean second-order dependence on amine found in the absence of additives suggests that the reaction may be base catalyzed. To check on this, experiments have been performed in the presence of tertiary amines. The reaction is indeed catalyzed by triethylamine and pyridine. The data are summarized in Table V.

The presence of the tertiary amine does not swamp out the catalytic effect of the salt formed in the reaction. In the presence of triethylamine an even more marked autocatalysis than in its absence is observed. A reasonable explanation may be that, because triethylamine is a stronger base than $BuNH_2$, triethylamine hydrochloride is predominantly formed. That it proves to be a better catalyst than $BuNH_3Cl$ is probably due to a greater dissociation constant. On the other hand, in the presence of pyridine the autocatalysis is similar to that found in its absence. Pyridine being a weaker base than $BuNH_2$, only $BuNH_3Cl$ is formed. Initial rates had to be measured. The second-order rate constant depends linearly on the concentration of triethylamine and pyridine (eq 6) (Table V). The value of k_B is 1.4 and 1.0 M^{-2} sec^{-1} for

$$k_2 = k_3'[\mathrm{BuNH_2}] + k_\mathrm{B}[\mathrm{B}] \qquad (6)$$

triethylamine and pyridine, respectively. The value of k_3', calculated from the four entries at constant pyridine concentration of Table V, is equal to 2.9 M^{-2} sec^{-1}, very close to that found in absence of additives.

Addition of acetonitrile increases the rate and produces effects qualitatively similar to those observed upon addition of salts or tertiary amines. However, no definite order in acetonitrile was observed (Table V).

Acetonitrile can affect the rate as a weak base or by increasing the polarity of the medium. A plot of k_2 *vs.* acetonitrile concentration shows an upward curvature, suggestive of a strong medium effect. However, acetonitrile also exerts a specific effect since at constant acetonitrile concentration and varying amine concentrations a linear plot is observed (Figure 2, curve d) with a definite intercept which can be attributed to a base-catalyzed step. The catalytic constant of acetonitrile, calculated by the slope of the tangent at the intercept of the curve obtained by plotting k_2 *vs.* acetonitrile concentration (Table V), is $\leqslant 0.2\ M^{-2}$ sec^{-1}.

Discussion

The clean second-order dependence on amine which has been found in absence of additives, points to the specific involvement of two molecules of amine in the rate-determining step. When salts, tertiary amines, or acetonitrile are added to the reaction mixture, the rate equation is modified and, besides the term which is second order in amine, other terms which are first order in amine and function of the concentration of additive become important (eq 4). Hence, new paths are possible for the reaction to occur, which require in the transition state a molecule of amine and a molecule of additive. While this does not define the transition state, base catalysis seems to be a general phenomenon. The order of decreasing efficiency of various bases on the reaction is: $BuNH_2$, 2.6; Et_3N, 1.4; Pyr, 1.0; CH_3CN, $\leqslant 0.2\ M^{-2}$ sec^{-1}. Although the differences in catalytic power are not very pronounced, the order is that of decreasing basicity.[16] Hence, hydrogen abstraction by a base seems to play an important role.

The chloride ion has been calculated to be about four times as effective as the perchlorate ion (see above). The high specificity of ionic chloride suggests that the catalysis by salts cannot be accounted for by Winstein's "special" salt effect.[14] The strong catalytic effect displayed by quaternary ammonium salts can also be accounted for in terms of base catalysis. Once the occurrence of a normal salt effect or Winstein's "special" salt effect[14] are ruled out, the specificity of the anions (see Results) leaves base catalysis as the most likely explanation. Chloride ion has already been considered as a hydrogen acceptor in many nucleophilic substitutions in polar[18–21] and nonpolar[10,21,22] solvents. Although perchlorate ion is a very poor base in polar solvents, it does not seem unreasonable to assume that in low polarity media, where solvation effects are not expected to decrease the anion nucleophilicity, ClO_4^- can act as a base. Very recently Kevill[23] has in fact suggested that ClO_4^- acts as a hydrogen acceptor in the methanolysis of methyl perchlorate in benzene.

It turned out that charged anions were more effective catalysts than neutral bases. It may well be that the interaction of the increasingly positive hydrogen (as the new N–S bond is formed) becomes greater with a charged than with a neutral base. Hence, if free ions are such effective bases because of their charge, they should display their basicity also as ion pairs, the reactivity of the paired nucleophile being reduced in proportion to its electrostatic interaction with the counterion.[24] As it turned out, in the case of Bu_4NCl, two terms have been found in the rate equation (eq 5), which depend on the concentration of salt. The first term, k_4, can be ascribed to the free ion and the second (k_4') to the ion pair. In the case of the perchlorate salt, only the first term was detected. Thus either the ion pair is ineffective or its catalytic efficiency is relatively too small to be measured within experimental error. However, a discussion on this point requires a more thorough investigation of the effect of different tetraalkyl ammonium salts, a topic which we are currently investigating. The catalytic efficiency of the various hydrochlorides cannot be discussed because of the uncertainties in the data. Their relatively low catalytic power could be ascribed to their very low dissociation constant and probably the hydrochlorides exert their small effect as ion pairs. The downward drift in rate observed in the presence of small amounts of Bu_4NCl while the reaction proceeded can be easily explained by the forma-

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(16) Triethylamine has a slightly greater basicity than butylamine. However, steric effects make it a weaker catalyst in many base-catalyzed reactions.[17]

(17) G. S. Hammond, "Steric Effects in Organic Chemistry," M. S. Newmann, Ed., John Wiley & Sons, Inc., New York, N. Y., 1956, p 457.

(18) D. N. Kevill and F. D. Foss, *Tetrahedron Letters*, 2837 (1967).

(19) R. F. Hudson and G. Moss, *J. Chem. Soc.*, 2982 (1964).

(20) M. W. Williams and G. T. Young, *ibid.*, 3701 (1964).

(21) A. D. Allen and G. Modena, *ibid.*, 3671 (1957).

(22) L. Di Nunno, G. Modena, and G. Scorrano, *Ric. Sci.*, **35**, 1423 (1965).

(23) D. N. Kevill and H. S. Posselt, *Chem. Commun.*, 438 (1967).

(24) N. N. Lichtin, M. S. Puar, and B. Wassermann, *J. Am. Chem. Soc.*, **89**, 6677 (1967).

tion of $(BuNH_3Cl_2)^-$. In such a form the chloride ion is very slightly basic, being already hydrogen bonded, while free ions are subtracted from the dissociation equilibrium of Bu_4NCl.

Addition of salts can influence the reaction also by a change in polarity of the solvent medium. That this effect turns out to be a relatively minor one may be seen from Figure 2 (curves a, b, and c). In such plots, the slope corresponds to the term in the rate equation which is second order in amine. Thus the value of k_3 can be calculated in different media. Addition of 2×10^{-3} M Bu_4NClO_4 increases k_3 nearly threefold while the over-all rate increase which is mostly due to the specific effect of the salt, is of the order of 10 to over 100 times, depending on the amine concentration. A comparable medium effect on k_3 is observed in the presence of acetonitrile (1.16 M) where k_3 is about 10 times greater than in benzene.

From the available evidence, base catalysis seems to be the most likely explanation for the second order in amine and the response of the reaction to various additives. However, more than one mechanism can be associated with it.

First, a scheme of mechanism can be drawn which assumes the preformation of an adduct between the nucleophile and a base, followed by the rate-determining step as shown by eq 7a and 7b.

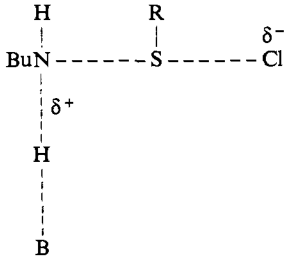
$$BuNH_2 + B \rightleftarrows (BuNH_2 \text{-----} B) \tag{7a}$$

$$RSCl + (BuNH_2 \text{-----} B) \rightarrow \text{products} \tag{7b}$$

Alternatively the data can be explained in terms of a scheme which also accounts for base catalysis. It assumes a fast equilibrium between the substrate and the nucleophile to form an intermediate which afterwards suffers hydrogen abstraction in a rate-limiting step (eq 8). The

$$RSCl + BuNH_2 \rightleftarrows I \xrightarrow{B} \text{products} \tag{8}$$

first of these mechanisms is essentially that which has been proposed by Hudson[25] and Kevill[23] in nucleophilic substitutions at saturated carbon in benzene with neutral nucleophiles, since a favorable dispersal of the positive charge developing on the initially neutral nucleophile would make the adduct much more reactive than the unassociated nucleophile. In this mechanism the transition state can be pictured as in IV, where bond breaking and making are simultaneous with hydrogen removal.

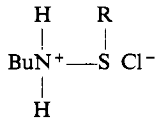


$$\overset{H}{\underset{\overset{\delta^+}{\vdots}\,H\,\vdots\,B}{BuN}}\text{------}\overset{R}{S}\text{------}\overset{\delta^-}{Cl}$$

IV

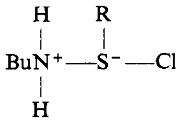
While we cannot disregard the above mechanism, we consider it very unlikely in our case due to the very low concentration of amine used. At a stoichiometric concentration as low as 5×10^{-4} M the amount of dimer would be so small compared to that of the monomer that, if it were responsible for the second order in amine, its reactivity would be so much greater than that of the monomer to make base catalysis a general phenomenon in nucleophilic substitutions, which is not the case.[26]

As far as the second mechanism is concerned, it does not define the nature of the intermediate. Two types of intermediates can be fitted in such a scheme: either an ion pair[27] (V) or a pentacovalent intermediate (VI) through the use of sulfur d orbitals. In both cases the intermediate



$$\overset{H}{\underset{H}{BuN^{+}}}\text{—}\overset{R}{S}\ Cl^{-}$$

V



$$\overset{H}{\underset{H}{BuN^{+}}}\text{—}\overset{R}{S^{-}}\text{—}Cl$$

VI

cannot go to products before hydrogen is abstracted by a base because an amino group bearing a formal positive charge is a very good leaving group and the intermediate is likely to return to reagents.

Experimental Section

Materials. Reagent grade benzene was refluxed over sodium for 1 day and fractionated. Acetonitrile was dried over Drierite, refluxed over phosphorus pentoxide, and distilled. From the redistillation over anhydrous potassium carbonate the fraction boiling at 81.5–81.6° was collected. Reagent grade triethylamine, pyridine, and *n*-butylamine were refluxed over sodium and fractionated.

Tetra-*n*-butylammonium chloride and perchlorate were prepared by neutralization of an aqueous solution of tetra-*n*-butylammonium hydroxide with hydrochloric and perchloric acid. After evaporation of the solvent the salts were recrystallized once from dry ethyl acetate and once from benzene and dried under vacuum at 60°. Tetra-*n*-heptylammonium perchlorate was prepared in a similar way from tetra-*n*-heptylammonium hydroxide.

Triphenylmethylsulfenyl chloride was prepared by addition of sulfuryl chloride to the corresponding thiol dissolved in ethyl ether containing a few drops of sulfuric acid and recrystallized twice from benzene–petroleum ether, yield 90%, mp 136–137°.[28]

Anal. Calcd for $C_{19}H_{15}SCl$: C, 73.41; H, 4.86. Found: C, 73.4; H, 4.8.

N-(*n*-Butyl)triphenylmethylsulfenamide. To 3 g of triphenylmethylsulfenyl chloride suspended in 40 ml of petroleum ether, 1.5 g (5% excess) of *n*-butylamine was added while stirring. The mixture was washed three times with 1 N HCl and three times with water and dried over anhydrous sodium sulfate. After cooling at −80°, the precipitate thus obtained was filtered off and washed twice with petroleum ether (bp 30–60°), keeping the temperature at −80°, yield 84%, mp 52–53°.

Anal. Calcd for $C_{23}H_{25}NS$: C, 79.49; H, 7.25; N, 4.03; S, 9.22. Found: C, 79.6; H, 7.2; N, 4.1; S, 9.1.

Kinetics. The reaction kinetics were followed by measuring the decrease in optical density with time at 280 mμ. A Beckman DU spectrophotometer equipped with a thermostated cell compartment was used. In all cases the experimental infinity was identical with that calculated from the concentrations and extinction coefficients of the products. The appropriate solution of *n*-butylamine (100–300 μl) was injected directly into 3 ml of the reaction mixture contained in a 10-mm stoppered quartz cuvette by means of a micropipet and a syringe. The cuvette was then vigorously shaken. In case of fast reactions mixing was ensured by an air stream produced by discharging into the reaction mixture the excess of air contained in the syringe.

The reactions followed good first-order kinetics except in cases when autocatalysis or rate depression was observed. In such cases initial rates have been measured.

Since in some cases up to 8000-fold excess of reagents with respect to the sulfenyl chloride was used, the purity of reagents was checked by vpc. No contamination was observed. Moreover, alcohols,[29] more bulky amines[29] and water[10] react much more

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[25] R. F. Hudson and I. Stelzer, *J. Chem. Soc., B*, 775 (1966).

[26] For a discussion on this point see: J. F. Bunnett and G. T. Davis, *J. Am. Chem. Soc.*, **82**, 665 (1960).

[27] L. Goodman and N. Kharasch, *ibid.*, **77**, 6541 (1955).

[28] D. Vorländer and E. Mittag, *Chem. Ber.*, **52**, 413 (1919).

[29] E. Ciuffarin, unpublished results.

slowly than primary amines. Primary amines, *e.g.*, *n*-butylamine and *n*-heptylamine, react approximately at the same rate.[29] Thus the possibility that undetected amounts of nucleophiles could disturb the kinetics was ruled out.

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Substitution Reactions at Sulfenyl Sulfur. The Extremely Rapid Exchange Reaction between Dimethyl Sulfide and a Dimethylmethylthiosulfonium Salt[1]

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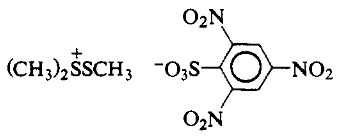
Abstract: The nmr spectra of methyl sulfide, $MeSS^+Me_2$, and mixtures of the two in acetonitrile-d_3 show that the exchange reaction $Me_2S + MeSS^+Me_2 \rightarrow Me_2S^+SMe + Me_2S$ takes place extremely rapidly, k_s being at least $10^5\ M^{-1}\ sec^{-1}$. This is several orders of magnitude faster than the exchange of MeS^- with the corresponding disulfide, and, since MeS^- is a considerably better nucleophile than Me_2S, must be due entirely to the fact that Me_2S^+– is a very much better leaving group than MeS– in a substitution at sulfenyl sulfur. The rate for k_s is also compared to that for an appropriate nucleophilic displacement by Me_2S on an sp^3 carbon, and it is concluded that the displacement at the sulfenyl sulfur of $MeSS^+Me_2$ is at least 10^9–10^{10} faster. Some general implications for organosulfur mechanisms are briefly discussed.

Dialkylalkylthiosulfonium ions, R_2S^+SR', are thought to play a key role as reactive intermediates in a number of alkyl sulfide catalyzed reactions of disulfides[2] and thiolsulfinates (sulfenic anhydrides).[3,4] The successful preparation and purification of dimethylmethylthiosulfonium 2,4,6-trinitrobenzenesulfonate (**1**)



1

by Helmkamp, *et al.*,[5] makes it possible for one to study a number of important aspects of the chemistry of such thiosulfonium ions directly. In the present paper we

$$(CH_3)_2S + CH_3S\overset{+}{S}(CH_3)_2 \rightarrow (CH_3)_2\overset{+}{S}SCH_3 + (CH_3)_2S \quad (1)$$

will show that the rate constant for the exchange reaction in eq 1 is orders of magnitude larger than the rate con-

$$CH_3S^- + CH_3SSCH_3 \rightarrow CH_3SSCH_3 + CH_3S^- \quad (2)$$

stant[6] for the exchange in eq 2 and that thiosulfonium ions such as Me_2S^+SMe can undergo nucleophilic substitution reactions incredibly rapidly.

Results and Discussion

Curve A in Figure 1 shows the nmr spectrum of **1** in CD_3CN at 0°. The largest singlet corresponds to the resonance of the two methyl groups attached to the sulfonium sulfur, the smaller singlet at higher field to the resonance of the methyl attached to the sulfenyl sulfur. Curve B in the same figure is the nmr spectrum of dimethyl sulfide in CD_3CN. Curve C is the spectrum of a 1:1 mixture of **1** and dimethyl sulfide in CD_3CN at 0° with both sulfide and thiosulfonium salt present at a concentration of 0.15 *M*. One sees that the separate resonances due to the methyl groups of the sulfide and the sulfonium methyl groups, $(CH_3)_2S^+$–, have collapsed into a single very sharp resonance centered exactly halfway between the original positions of the $(CH_3)_2S^+$– and $(CH_3)_2S$ resonances. Obviously the methyl groups of the sulfide and those attached to the sulfonium sulfur are undergoing exchange of environment *via* eq 1 at a rate which is rapid on the nmr time scale. Since the original resonances of the Me_2S and Me_2S^+– protons are separated by 60 cps, and since the width at half-height of the collapsed peak in curve C is *only 1 cps*, the average time required for exchange to occur must be very short, no more than 7×10^{-5} sec.[7] This means that the first-order rate constant for the exchange reaction, k_1, has a value of $k_1 \geqq 1.5 \times 10^4\ sec^{-1}$.

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(1) This research supported by the National Science Foundation, Grant GP-6952.

(2) J. L. Kice and E. H. Morkved, *J. Am. Chem. Soc.*, **86**, 2270 (1964).

(3) J. L. Kice, C. G. Venier, and L. Heasley, *ibid.*, **89**, 3557 (1967).

(4) (a) J. L. Kice and G. B. Large, *ibid.*, **90**, 4069 (1968); (b) *J. Org. Chem.*, **33**, 1940 (1968).

(5) G. K. Helmkamp, H. N. Cassey, B. A. Olsen, and D. J. Pettitt, *ibid.*, **30**, 933 (1965).

(6) A. Fava, A. Ilceto, and E. Camera, *J. Am. Chem. Soc.*, **79**, 833 (1957).

(7) This represents an *upper limit* on the average lifetime before exchange. The actual lifetime is almost certainly shorter than this because the figure of 7×10^{-5} sec was calculated using the equation given by Allerhand, Gutowsky, Jonas, and Meinzer[8] (eq 6 of ref 8) assuming that the line width at half-maximum intensity in the absence of exchange was 0.6 cps. Since it seems highly likely that the line width in the absence of exchange is larger than this,[9] 2τ is almost certainly smaller than 7×10^{-5} sec, although by how much one cannot say at this time.

(8) A. Allerhand, H. S. Gutowsky, J. Jonas, and R. A. Meinzer, *J. Am. Chem. Soc.*, **88**, 3185 (1966).