The Mechanism of Chlorination of Arenesulfenyl Chlorides. VI[1a-c]

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Abstract: In anhydrous acetic acid, the chlorination of 4-substituted arenesulfenyl chlorides to sulfonyl chlorides has been characterized by the equation rate $= k_1[Cl_2][ArSCl]$. Various hydroxylic components of the reaction medium are found to enter the rate equation with the second power of their respective concentrations. Added neutral salts produce rate effects which are recognized as the largest ever measured for polar reactions in acetic acid. The powerful accelerating influence of added acetate in the medium taken together with a variety of other observations has been reconciled with anion behavior as a nucleophile. A *para* substituent bias of the chlorination rate has also been demonstrated (Hammett $\rho = -2.4$). The kinetic demand for the activity of a proton transfer agent in this reaction has also been established. By contrast, the chlorination of 2-nitrobenzenesulfenyl chlorides does not occur in the absence of water and/or acetate anion in the acetic acid medium. The mechanism of this reaction is clearly differentiated from the "normal" case by virtue of the complete absence of aromatic (*para*) substituent rate effects and lack of dependence of the rate both on chlorine concentration and on the presence of added neutral salts. On the basis of these lines of evidence and taking consideration of the ground-state structures of the normal (ArSCl) and abnormal (*o*-nitro-ArSCl) substrates, suitable mechanisms for their respective chlorination reactions may be proposed.

The following results are from a continuing study of the chlorination of bivalent sulfur compounds, namely the chlorination of sulfenyl chlorides.[1a] The preparative utility of the chlorinations of bivalent sulfur compounds has been demonstrated by several workers.[2] The study of the chlorinations of aliphatic sulfur compounds by Douglass and co-workers has been instrumental in extending the scope of these reactions.

Early studies by Zincke and co-workers[2c] on aromatic disulfides and the later studies of Douglass and co-workers on aliphatic disulfides showed that equimolar ratios of disulfide and chlorine gave the corresponding sulfenyl chloride quantitatively (eq 1).[2e] Failure to

$$CH_3SSCH_3 + Cl_2 \longrightarrow 2CH_3SCl \qquad (1)$$
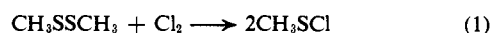
use stoichiometric quantities of reagents results in impure products.

The next step in sulfur chlorination reactions is the formation of the chlorine addition product, a sulfur trichloride. Addition of chlorine to the intensely red methanesulfenyl chloride in an inert solvent at -10 to $-20°$ forms quantitatively the colorless sulfur trichloride (eq 2).[3] Understandably, the formation of
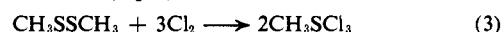
$$CH_3SCl + Cl_2 \longrightarrow CH_3SCl_3 \qquad (2)$$

the trichloride from the disulfide was observed under the same conditions (eq 3). Of several sulfur trichlo-

$$CH_3SSCH_3 + 3Cl_2 \longrightarrow 2CH_3SCl_3 \qquad (3)$$

rides prepared, the most stable, methanesulfur trichloride, had a decomposition temperature of 30°; the arylsulfur trichlorides were less stable. Phenylsulfur trichloride decomposed below 10°. Two major paths of decomposition were evident from the sulfur trichloride reactions: simple aliphatic compounds decompose with accompanying chlorination of the adjacent methylene group (eq 4);[3,4] arylsulfur trichlorides decompose predominately by reverting to starting material (eq 5). Thus, arenesulfenyl

$$RCH_2SCl_3 \longrightarrow R\overset{\overset{\displaystyle Cl}{|}}{C}H{-}SCl + HCl \qquad (4)$$

$$C_6H_5SCl_3 \longrightarrow C_6H_5SCl + Cl_2 \qquad (5)$$

trichloride decomposition demonstrates a reversible reaction. The failure of trichloromethanesulfenyl chloride to form the sulfur trichloride may be regarded as an example of an equilibrium lying far to the left (eq 6).

$$CCl_3SCl + Cl_2 \overset{\longrightarrow}{\longleftarrow} CCl_3SCl_3 \qquad (6)$$

The reactivities of the sulfur trichlorides are apparently very much greater than the precursor sulfenyl chlorides. Douglass and co-workers[5] found that while methanesulfenyl chloride gave no immediate reaction with acetic acid (eq 7), the trichloride reacts immediately giving sulfinyl chloride, acetyl chloride, and hydrogen chloride (eq 8). Other hydroxylic reagents, *i.e.*, benzoic acid (eq 9), water (eq 10), and methanol (eq 11), lead to the appropriate products.

$$CH_3SCl + HOAc \longrightarrow \text{no reaction} \qquad (7)$$

$$CH_3SCl_3 + HOAc \longrightarrow CH_3\overset{\overset{\displaystyle O}{|}}{S}Cl + AcCl + HCl \qquad (8)$$

(1) Papers in this series: III, H. Kwart and R. W. Body, *J. Org. Chem.*, 30, 1188 (1965); (b) IV, H. Kwart, R. W. Body, and D. M. Hoffmann, *Chem. Commun.*, 765 (1967); (c) V. H. Kwart and P. S. Strilko, *ibid.*, 767 (1967); (d) the data in this article are taken in part from the thesis of E. N. Givens submitted in partial fulfillment of the requirements for the Masters Degree of the University of Delaware, June 1963.
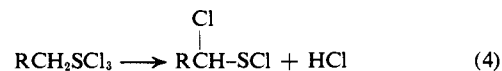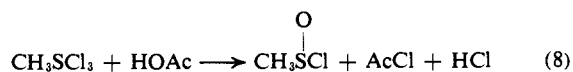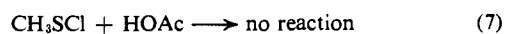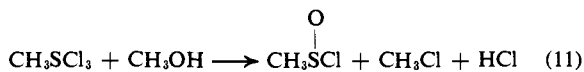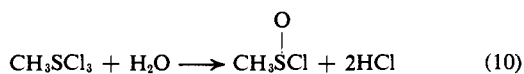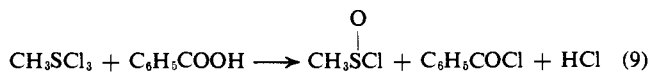
(2) (a) N. Kharasch, S. J. Potempa, and H. L. Wehrmeister, *Chem. Rev.*, 39, 269 (1946); (b) F. Muth in Houben-Weyl's "Methoden der Organishen Chemie," 4th ed, Georg Thieme Verlag, Stuttgart, Germany, 1955, pp 580–584; (c) T. Zincke and W. Frohneberg, *Ber.*, 43, 837 (1910); (d) I. B. Douglass, "Alkanesulfenyl Chlorides in Organic Sulfur Compounds," Vol. I, N. Kharasch, Ed., Pergamon Press Inc., New York, N. Y., 1961, p 350; (e) I. B. Douglass, B. S. Farah, and E. G. Thomas, *J. Org. Chem.*, 26, 1996 (1961); (f) I. B. Douglass, *ibid.*, 30, 633 (1965).

(3) K. R. Brower and I. B. Douglass, *J. Am. Chem. Soc.*, 73, 5787 (1951); I. B. Douglass, K. R. Brower, and F. T. Martin, *ibid.*, 74, 5770 (1952).
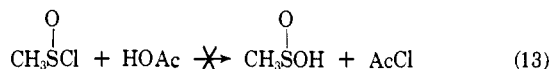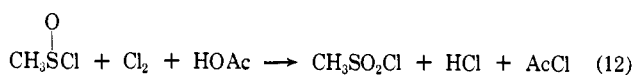
(4) Such α-methyl chlorination is common to bivalent sulfur compounds. See R. Stroh in Houben-Weyl's "Methoden der Organischen Chemie," 4th ed, Georg Thieme Verlag, Stuttgart, Germany, 1962, p 644 ff.

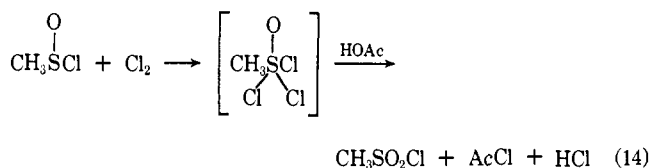(5) I. B. Douglass and D. R. Poole, *J. Org. Chem.*, 22, 536 (1957).

$$CH_3SCl_3 + C_6H_5COOH \longrightarrow CH_3\overset{O}{\underset{}{S}}Cl + C_6H_5COCl + HCl \quad (9)$$

$$CH_3SCl_3 + H_2O \longrightarrow CH_3\overset{O}{\underset{}{S}}Cl + 2HCl \quad (10)$$

$$CH_3SCl_3 + CH_3OH \longrightarrow CH_3\overset{O}{\underset{}{S}}Cl + CH_3Cl + HCl \quad (11)$$

It seems most likely that in acetic acid, the trichloride rather than the sulfenyl chloride or a sulfenium ion, RS^+, reacts directly to form the sulfinyl chloride quantitatively.

The chlorination of sulfinyl chlorides in acetic acid has been shown to produce the corresponding sulfonyl chlorides (eq 12).[2e] Since the sulfinyl chloride was found to be unreactive toward acetic acid (eq 13),

$$CH_3\overset{O}{\underset{}{S}}Cl + Cl_2 + HOAc \longrightarrow CH_3SO_2Cl + HCl + AcCl \quad (12)$$

$$CH_3\overset{O}{\underset{}{S}}Cl + HOAc \overset{}{\not\longrightarrow} CH_3\overset{O}{\underset{}{S}}OH + AcCl \quad (13)$$

Douglass and co-workers[2e] reasoned that the corresponding sulfinic acid is not an intermediate in the reaction; rather a chlorine adduct of the sulfinyl chloride could react with the acetic acid to give the product (eq 14).[6] Physical evidence for this intermediate was not obtained. Thus, Douglass and co-

$$CH_3\overset{O}{\underset{}{S}}Cl + Cl_2 \longrightarrow \left[CH_3\overset{O}{\underset{Cl\quad Cl}{S}}Cl \right] \xrightarrow{HOAc}$$

$$CH_3SO_2Cl + AcCl + HCl \quad (14)$$

workers,[2,3] in a series of very informative articles, have demonstrated by careful experiment the stoichiometric relationships involved. Starting with mercaptan, the corresponding disulfide, sulfinyl chloride, or sulfonyl chloride can be prepared in pure form and in excellent yield. Mechanistically their results suggest an initial formation of the sulfur trichloride when starting with the sulfenyl chloride; hydroxylic reagent then reacts rapidly with this trichloride intermediate giving the observed product.

The structure of the trichloride, whether ionic or covalent, is unresolved. Solubility data strongly suggest an ionic form,[3] although analogous fluorine covalent addition complexes are known to have trigonal-bipyramidal structures with alkyl groups occupying equatorial positions[7] (as shown below).

$$O-\overset{\overset{F}{|}}{\underset{\underset{F}{|}}{S}}\overset{F}{\underset{R}{\diagdown}}$$
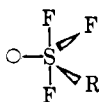
The objectives of the work being presented here were to evaluate and, if possible, to elaborate the ideas discussed above (which have gained some currency) by

(6) It also follows that the alternative displacement of chloride ion to form the mixed anhydride, $ArS(O)OCOCH_3$, and HCl can be excluded as a reaction path in view of the nonoccurrence of the eq 13 step. This affords further support for Douglass' assumption[2e] of an intermediate equivalent to the chlorine adduct depicted in eq 14. However, in other hydroxylic media the eq 13 step may indeed be important.

(7) E. L. Muetterties, W. Mahler, K. J. Packer, and R. Schmutzler, *Inorg. Chem.*, **3**, 1298 (1964).

means of a kinetic technique. The dependence on sulfenyl chloride, chlorine, hydroxylic reagent, and carboxylate anion concentrations have thus been examined, as well as electrostatic considerations and neutral salt effects.

Experimental Section

Sodium acetate and lithium perchlorate were commercially available analytical grade reagents. Chlorine, supplied by Matheson Coleman and Bell, was dried by passing through concentrated sulfuric acid. Chlorine solutions were standardized by an iodometric procedure. Dry acetic acid was prepared by the method of Orr and Kharasch[8] from reagent grade acetic acid which had been previously refluxed over chromic anhydride.[9] Sulfenyl chlorides, *i.e.*, 2- and 4-nitro-,[10] 4-chloro-,[11] 4-chloro-2-nitro,[11] 2,4-dinitro-,[11] 4-methyl-2-nitro-,[11] and unsubstituted[12] benzenesulfenyl chlorides, were prepared from commercially available disulfides, mercaptans, or their precursors by known procedures.

The automatic recording spectrophotometer used in the kinetic studies has been previously discussed.[13a]

The reaction vessel for the ultraviolet studies was a two-stage system described previously.[13] The concentration of reagents was adjusted such that 1.00 ml of substrate was microburetted or pipetted into the lower stage and 7.00 ml was microburetted into the upper stage. The bulb was tightly stoppered and equilibrated 15 or 20 min in a water bath maintained at the appropriate temperature. The vessel was removed, dried, and placed in the cell holder of the instrument to equilibrate an additional 10 min. The vessel was then rapidly inverted several times, and reinserted into the cell chamber. The mixing operation required no more than 6 sec. The absorbency of the reaction solution was traced automatically by the recorder as a function of time. Appropriate points were picked from the trace and treated according to Guggenheim's method.[14]

Several of the more rapid studies were made on an instrument designed and constructed by Fritz and Kwart which will be described by these authors in detail in a future publication.

Results

The 4-substituted benzenesulfenyl chlorides are more reactive than the corresponding 4-substituted 2-nitrobenzenesulfenyl chlorides. The increased reactivity limits the available data since the rates tend to exceed the boundary of simple kinetic measurement.

Chlorine Dependence. The effect of chlorine was studied in anhydrous acetic acid using a varying excess of chlorine. Regardless of the excess of chlorine, first-order kinetic dependence on chlorine was observed for these sulfenyl chlorides. The data plotted in Figures 1 and 2 are listed in Table I. Zero intercepts were found for each of the substrates although the scatter of points for benzenesulfenyl chloride is apparently greater. The low chlorine–sulfenyl chloride molar ratios for these first points were a consequence of the extremely high rates of reaction. The first-order dependence on chlorine established by plots like those in Figures 1 and 2 confirm that chlorine enters the reaction sequence either prior to, or in the rate-

(8) W. L. Orr and N. Kharasch, *J. Am. Chem. Soc.*, **75**, 6030 (1953).

(9) L. F. Fieser, "Experiments in Organic Chemistry," 3rd ed. D. C. Heath and Co., Boston, Mass., 1955, p 281.

(10) M. H. Hubacker, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p 455; T. Zincke, *Ann.*, **400**, 9 (1913).

(11) M. B. Sparke, J. L. Cameron, and N. Kharasch, *J. Am. Chem. Soc.*, **75**, 4909 (1953); N. Kharasch, G. I. Gleason, and C. M. Buess, *ibid.*, **72**, 1796 (1950); T. Zincke and H. Rose, *Ann.*, **406**, 110 (1914).

(12) J. Goerdeler and J. Vitt, *Ber.*, **92**, 2563 (1959).

(13) (a) H. Kwart and I. M. Sarasohn, *J. Am. Chem. Soc.*, **83**, 917 (1961); (b) H. Kwart and M. M. Baevsky, *ibid.*, **80**, 580 (1958).

(14) E. A. Guggenheim, *Phil. Mag.*, **2**, 538 (1936); see A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1961, p 49.
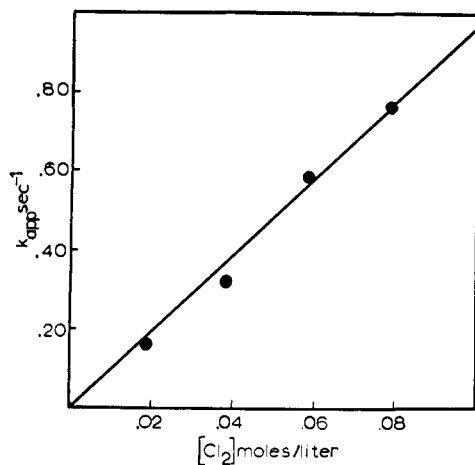
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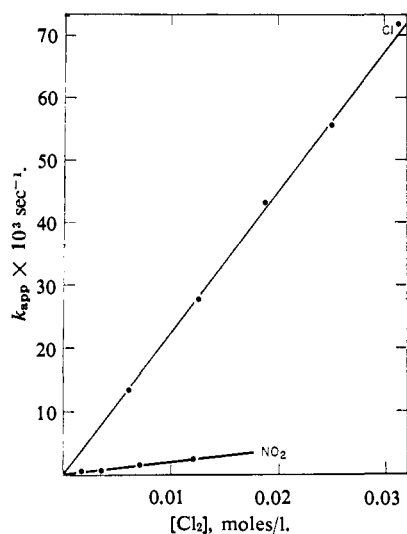Figure 1. Effect of chlorine concentration on the chlorination of benzenesulfenyl chloride in acetic acid.

Figure 2. Effect of chlorine concentration on the chlorination of 4-substituted benzenesulfenyl chlorides in acetic acid.
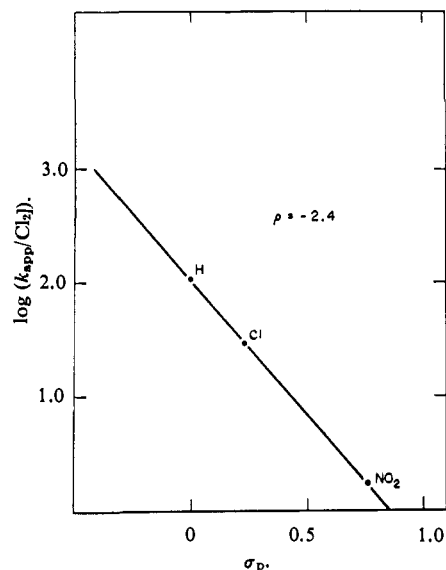

Figure 3. Hammett plot for the chlorination of 4-substituted benzenesulfenyl chlorides in acetic acid.

In the second solvent system, the order with respect to acetic acid was determined with use of acetic acid–carbon tetrachloride solutions. Large variations in solvent composition were necessary in order to

determining step as expressed in eq 15 (k_{app}, observed first-order rate constant).

$$\text{rate} = k_{app}[\text{ArSCl}] = k_1[\text{Cl}_2][\text{ArSCl}] \quad (15)$$

A Hammett σ–ρ correlation (Figure 3) of the second-order rate constants (k_1) taken from the slopes of these plots gives a ρ of -2.4. The large negative ρ value is suggestive of a transition state in which increased electron density on sulfur enhances the role of chlorine in the reaction, or, expressed alternatively, increases the capacity of sulfur to tolerate positive charge.

Hydroxylic Medium and Neutral Salt Dependence. The hydroxylic solvent effect was studied in three systems. The first utilizing solvent composed of methyl alcohol in carbon tetrachloride manifested a second-order dependence on methyl alcohol. Low concentrations of alcohol did not seem to alter the solvent characteristics appreciably. The 30-fold span in rate constants (Table II), corresponding to a ca. fivefold change in methanol concentration, appears to support a second-order dependence on alcohol (eq 16).

$$\text{rate} = k_{app}[\text{ArSCl}] = k_2[\text{Cl}_2][\text{MeOH}]^2[\text{ArSCl}] \quad (16)$$

Table I. Rates of Chlorination of 4-Substituted Benzenesulfenyl Chlorides in Acetic Acid at 29.9° [a]

X[b]	[4-XC₆H₄SCl]	[Cl₂] × 10²	[H₂O] × 10²	[LiClO₄] × 10³	[AcONa] × 10²	k_{app} × 10² sec⁻¹
H	3.87 × 10⁻³	1.98				16.2
		3.95				31.4
		5.92				58.9
		7.90				76.5
Cl	1.25 × 10⁻³	0.625				1.30
		1.25				2.80
		1.87				4.29
		2.50				5.58
		3.12				7.21
		0.625	6.94			1.43
		0.625	13.9			1.77
		0.625	20.8			2.01
		0.625	34.5			2.88
		0.625	41.6			3.39
		0.625	48.6			3.71
		0.601	...	0.312		1.31
		0.601	...	0.625		1.50
		0.601	...	3.12		2.17
		0.601	...	6.25		2.84
		0.601	...	12.5		3.75
		0.601	...	18.8		5.81
		0.601	...	25.0		7.48
	5.53 × 10⁻³	2.66	...	...	0.621	47.1
		2.66	...	..	1.24	139
		2.66	...	...	2.48	328
NO₂	1.75 × 10⁻⁴	0.175	...	...	...	0.0677
		0.35	...	...	...	0.107
		0.70	...	...	...	0.159
		1.22	...	...	...	0.264

[a] Concentrations in moles/l. [b] X = 4 substituent.

obtain a significant range of rate data. Solvent compositions with only small amounts of carbon tetrachloride showed a significant drop in k_{app} compared to 100% acetic acid reactions; successive dilutions did not affect the rate as dramatically as the

Table II. Effect of Methanol Concentration on the Chlorination of 4-Chlorobenzenesulfenyl Chloride in Carbon Tetrachloride–Methanol Solution at 29.9°[a]

[CH₃OH], M	$k_{app} \times 10^3$ sec⁻¹	$k_{app}/[CH_3OH]^2$, l.²/mole² sec
0.495	98.7	0.403
0.403	57.5	0.354
0.301	44.1	0.460
0.248	27.2	0.433
0.124	5.17	0.334
0.087	3.25	0.416
		Av 0.40 ± 0.04

[a] [4-ClC₆H₄SCl] = 0.00133 mole/l.; [Cl₂] = 0.0272 mole/l.

first dilution. A plot of log k_{app} vs. log [HOAc] was linear with a slope of 2.16 indicating a second-order dependence on acetic acid (Table III).

Table III. Effect of Solvent Composition on the Chlorination of 4-Chlorobenzenesulfenyl Chloride in Acetic Acid–Carbon Tetrachloride Mixtures at 29.9°[a]

[CH₃COOH], vol. %	$k_{app} \times 10^3$ sec⁻¹	[CH₃COOH], vol. %	$k_{app} \times 10^3$ sec⁻¹
100	56.7	50.0	6.47
87.5	25.0	37.5	3.06
75.0	17.4	25.0	1.90
62.5	9.30		

[a] [4-ClC₆H₄SCl] = 1.25 mmoles/l.; [Cl₂] = 0.0260 mole/l.

In the third solvent system studied, the dependence of reaction rate on water concentration in acetic acid solution was examined in the case of 4-chlorobenzenesulfenyl chloride. A linear relationship (Table IV) was found with a positive intercept comparable in magnitude to the rate in anhydrous acetic acid. This is clearly consistent with a situation in which there are two competing reactions, one which has a first-order dependence on water and one which is independent of water concentration.

Table IV. Effect of Water Concentration on the Chlorination of 4-Chlorobenzenesulfenyl Chloride in Aqueous Acetic Acid at 29.9°[a]

[H₂O], M	$k_{app} \times 10^3$ sec⁻¹	[H₂O], M	$k_{app} \times 10^3$ sec⁻¹
0.0694	14.3	0.345	28.8
0.139	17.7	0.416	33.9
0.208	20.1	0.486	37.1

[a] [4-ClC₆H₄SCl] = 1.25 mmoles/l.; [Cl₂] = 6.25 mmoles/l.

Medium effects are possible in these solvents and are, indeed, expected, but the magnitude of these effects and the consistent mathematical relationship correlating such rate influences permit a kinetic interpretation both here and in other work[15] which strongly suggests a role for the hydroxyl component apart from what may be designated as a "medium effect."

Sodium acetate was observed to accelerate the reaction sharply, so much so that the extent of increase restricted the obtainable data by tending to go beyond

(15) E. N. Givens and H. Kwart, J. Am. Chem. Soc., 90, 386 (1968).
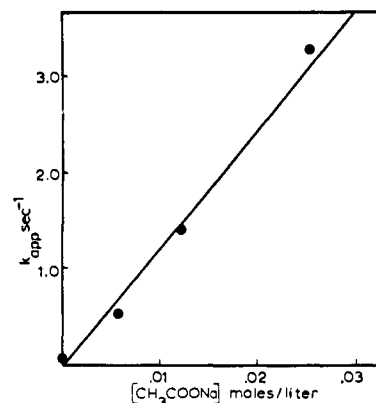
Figure 4. Effect of sodium acetate concentration on the chlorination of 4-chlorobenzenesulfenyl chloride in acetic acid.

the limits of simple measurement. Moreover, the relative rates of the acetate and the acetic acid reactions were so different that the acetate-independent reaction was not affected by the acetic acid reaction (Figure 4, from data listed in Table I). The second-order rate constants for these runs were 107 ± 21 l./mole sec. These values, approximated from initial rates, are intended to demonstrate the tremendous accelerating effect of acetate ion. The linear dependence measured in this system is in excellent accord with a corresponding observation made in the 2-nitrobenzenesulfenyl chloride series (see below). This might be interpreted as an indication of the fact that in the presence of acetate the need for another hydroxylic reagent to act as proton acceptor is obviated. The following equation expressed the rate dependencies for this system of two competing nucleophiles.

$$\text{rate} = k_{app}[\text{ArSCl}] = k_3[\text{Cl}_2][\text{NaOAc}][\text{ArSCl}] + k_1[\text{Cl}_2][\text{ArSCl}] \quad (17)$$

A large acceleration by lithium perchlorate on 4-chlorobenzenesulfenyl chloride is plotted as k_{app} vs. [LiClO₄] in Figure 5, from the data listed in Table I. A 225-fold rate increase due to the presence of 0.10 M perchlorate may be estimated from the slope of this linear relationship.

Chlorination of o-Nitrobenzenesulfenyl Chlorides. When compared to the above results which apply for the case of ArSCl possessing nothing more than a para substituent, the following evidence demonstrates that the presence of a nitro substituent ortho to the sulfenyl chloride causes a change in the chlorination mechanism. It has previously been reported by Fierz and co-workers[16] that chlorination in aqueous media of 2-nitrobenzenesulfenyl chloride does result in the sulfonyl chloride. However, it has now (here) been confirmed that this reagent does not react after an extended period of standing at 25° in anhydrous acetic acid solutions of chlorine under normal conditions. Moreover, it is also clear that the addition of sodium acetate induces an extremely rapid chlorination reaction. For instance, an 88% yield of 4-chloro-2-nitrobenzenesulfonyl chloride was isolated readily from the chlorination of the corresponding substituted sulfenyl chloride in anhydrous acetic acid containing

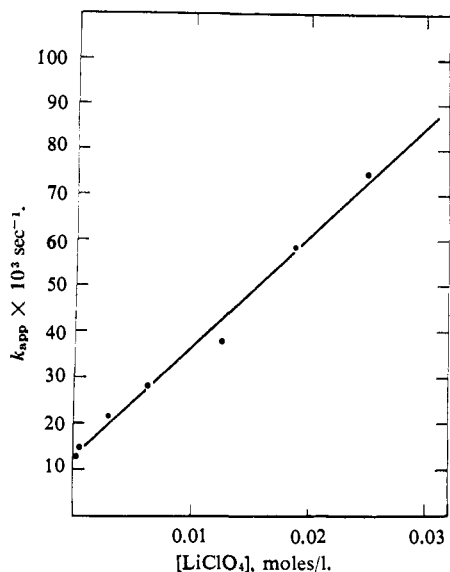(16) E. H. Fierz, E. Schlittler, and H. Waldman, Helv. Chim. Acta, 12, 667 (1929).

Figure 5. Effect of lithium perchlorate concentration on the chlorination of 4-chlorobenzenesulfenyl chloride in acetic acid.

Figure 6. Effect of sodium acetate concentration on the chlorination of 4-chloro-2-nitrobenzenesulfenyl chloride in acetic acid.

a small amount of anhydrous sodium acetate. When this reaction was pursued kinetically by the method discussed earlier, a rate equation (eq 18) could be

$$\text{rate} = k_4[\text{CH}_3\text{COONa}][\text{ArSCl}] \qquad (18)$$

deduced describing a zero-order dependence on chlorine (see Table V) and first-order dependence on sodium acetate confirmed by a plot (Figure 6) passing through the origin.

Table V. Rates of Chlorination of 4-Chloro-2-nitrobenzenesulfenyl Chloride in Acetic Acid–Sodium Acetate Solution[a]

[CH₃COONa]	[Cl₂]	[LiClO₄]	$k \times 10^3$ sec⁻¹	k, l./mole sec
0.0175	0.0158	...	5.29	0.302
0.0422	0.0158	...	13.4	0.318
0.0492	0.0158	...	15.7	0.317
0.0810	0.0158	...	26.8	0.331
0.0810	0.0158	0.100	15.2	0.188
0.103	0.0158	...	33.1	0.322
0.154	0.0158	...	47.8	0.311
0.205	0.0158	...	64.4	0.314
0.0422	0.0235	...	13.1	0.311
0.0422	0.0313	...	13.8	0.328
0.0422	0.0391	...	13.5	0.320
0.0422	0.0470	...	13.5	0.320
0.0422	0.0548	...	14.0	0.332
0.0422	0.0157	0.0500	11.2	0.266
0.0422	0.0157	0.100	8.40	0.199
0.0422	0.0157	0.200	7.97	0.189
0.0422	0.0157	0.300	8.19	0.194
0.0422	0.0157	0.400	8.94	0.212
0.0422	0.0157	0.100	8.81[b]	0.209
0.0422	0.470	0.100	9.36	0.222
0.148	0.0548	...	50.6	0.292

[a] [4-Cl-2-NO₂C₆H₃SCl] = 4.00 × 10⁻⁴ M, λ 390 mμ, 29.7°. [b] Contains 0.080 M LiCl.

The role of acetate ion (in eq 18) as a nucleophile, and not merely as a proton acceptor (base), is consistent with the following observation. Addition of sodium hydrogen phosphate (Na₂HPO₄) to anhydrous acetic acid causes chlorination to occur, but the addition of

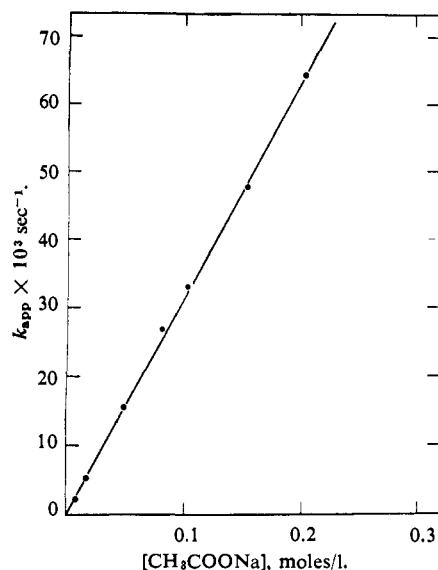KH₂PO₄ to anhydrous acetic acid does not effect chlorination. The former is a source of acetate ion, while the latter is too weak a base to form acetate ion. If the role of acetate ion were the neutralization of the HCl product, H₂PO₄⁻ should also serve such a function since it is a sufficiently strong base to neutralize HCl.

The absence of a Hammett substituent effect (see Table

Table VI. Rates of Chlorination of 4-Substituted 2-Nitrobenzenesulfenyl Chlorides[a]

X[b]	25.8°	29.7°	35.2°
CH₃		12.4	
H		7.16	
H[c]		14.3	
Cl	10.4	14.4	20.3
NO₂		9.17	

[a] λ 390 mμ; rates × 10³ sec⁻¹. [b] 4 substituent, 4.0 × 10⁻⁴ mole/l.; [Cl₂] = 0.0152 mole/l.; [CH₃COONa] = 0.0440 mole/l. [c] [CH₃COONa] = 0.0844 mole/l.

VI) in the chlorination of 4-substituted 2-nitrobenzenesulfenyl chlorides suggests that a change in electron density at the sulfur atom has little affect on the reaction process. Nucleophilic displacement at the sulfur atom in the 2-nitrobenzenesulfenyl system has been reported to have a substituent effect. For instance, in the addition of a series of 4-substituted 2-nitrobenzenesulfenyl chlorides to cyclohexene in glacial acetic acid, where the olefin is regarded as the nucleophile,[17] a ρ value of −0.71 has been determined.[18,19] Olefin addition differs from the reaction discussed here since it involves uncharged reactants and products and

(17) A. J. Parker and N. Kharasch, Chem. Rev., 59, 583 (1959).
(18) C. Brown and D. R. Hogg, Chem. Commun., 358 (1965).
(19) Substituent effects on nucleophiles displacing on sulfur have been reported: ArAsO(OH)⁻ on disulfide, ρ = −0.25;[20] 2,4-(NO₂)₂-C₆H₃SCl addition to 4-substituted styrenes, ρ = −2.20.[21]
(20) O. Foss in "Organic Sulfur Compounds," Vol. 1, N. Kharasch, Ed., Pergamon Press Inc., New York, N. Y., 1961, p 93; H. H. Jaffé, Chem. Rev., 53, 191 (1953); A. Cohen, H. King, and W. I. Strangeways, J. Chem. Soc., 2866 (1932).
(21) W. L. Orr and N. Kharasch, J. Am. Chem. Soc., 75, 6030 (1953).

ionic intermediates.[21,22,24] The fundamental reaction here apparently involves ionic reactants and products and uncharged intermediates. The absence of a measurable rate acceleration due to added lithium perchlorate (see Table V) and the absence of a common ion effect may be held to be in consonance with this inference.

Discussion

The Normal Chlorination Process. The recorded observations of Douglass and co-workers on the color of the various compounds they studied[2d] provides a basis for the kinetic technique. These workers found that alkane and arenesulfenyl chlorides are intensely colored compounds, an observation corresponding to our results on strictly aromatic sulfenyl chlorides. In contrast, the sulfur trichlorides prepared by Douglass and co-workers were colorless, except for benzenesulfur trichloride which retains a slight coloration, although of a completely different magnitude compared to that of the corresponding sulfenyl chlorides.[3] These authors believe this is due to a slight amount of remaining sulfenyl chloride in the product. Observations on sulfinyl chlorides reported by these workers, on the other hand, show they are faintly yellow, while the sulfonyl chlorides are colorless. Consequently, qualitative estimates concerning absorptions at 400 mμ of the different sulfur chlorides can be made with some confidence, as shown in Table VII.

Table VII

	Color	ϵ at 400 mμ
RSCl	Intensely colored	Very significant
RSCl$_3$	Colorless	Negligible
O ‖ RSCl	Faint yellow	Negligible
RSO$_2$Cl	Colorless	Negligible

Since the kinetic method used in this study involves following the loss in optical density at about 400 mμ, it seems safe to presume that the color loss is due to disappearance of sulfenyl chloride since a corresponding loss in visible color also occurs. The reaction can be expressed kinetically by a rate equation having a first-order dependence on chlorine concentration (eq 19).

$$\text{rate} = k[\text{Cl}_2][\text{ROH}]^2[\text{ArSCl}] \qquad (19)$$

This dependence on chlorine allows chlorine to enter the reaction in a rapid step prior to the rate-determining event which will agree with the existence of a sulfur trichloride species or its equivalent in the reaction series.

The second-order dependence on hydroxylic component apparently holds for both acetic acid and methanol. Aqueous acetic acid requires two terms

in the rate equation, one following the normal acetic acid reaction and one having a first-order dependence on water and a predicted first-order dependence on acetic acid. Therefore, some mechanistic alternatives may be considered which fulfill these requirements as expressed in eq 19, where ROH may be either water, methanol, or acetic acid.

In a sequence of steps beginning with the attack by ROH on the sulfenyl chloride as the first step (eq 20), the kinetic demands are met only by a subsequent slow step, since chlorine has not played a role in the reaction. If methanol were the hydroxylic reagent, the product of the first step would be the sulfenate ester. The chlorination would occur in the ester (step 2a in eq 20). A study of several sulfenate esters has shown, however, that the chlorination of the ester is many times more rapid than that of the corresponding sulfenyl chloride.[25] Thus, the slow step must precede the formation of a sulfenate ester. In cases where R is hydrogen or acyl, we can assume for purposes of this interpretation the occurrence of the same reaction sequence.

Another mechanistic possibility would be an ionization of the sulfenate ester (step 2 in eq 20). This mechanism would conform to the rate equation if

$$\text{ArSCl} + \text{ROH} \xrightarrow{1} \text{ArSOR} \xrightarrow[2]{-R^+} \text{ArSO}^- \xrightarrow[3]{\text{Cl}_2} \overset{\text{O}}{\underset{‖}{\text{ArSCl}}} \qquad (20)$$

step 3 or a succeeding step were rate determining since, in this fashion, the necessary kinetic dependence on chlorine and hydroxyl component would be met. However, the sulfenate ester is again the product of the first step; the rate-determining step would have to follow step 2 for this mechanism to be valid. Clearly, for the reason mentioned above, namely, the rapidity of the sulfenate ester chlorination, this mechanism is excluded.

Still another mechanism may be proposed, as outlined in eq 21. This sequence of steps would conform

$$\text{ArSCl} + \text{Cl}_2 \underset{1}{\rightleftharpoons} \text{ArSCl}_3 \underset{2}{\overset{\text{ROH}}{\rightleftharpoons}} \text{ArSCl}_2(\text{OR}) \xrightarrow{3}$$

$$\overset{\text{O}}{\underset{|}{\text{ArSCl}}} + \text{RCl} \qquad (21)$$

to the rate equation were the second step or a succeeding step rate controlling. If, as previously considered, the sulfur trichloride intermediate exists in equilibrium with the sulfenyl chloride, this would not alter the over-all kinetic dependence of the reaction on chlorine. Further, equilibria (eq 22) between covalent and

$$\text{ArSCl} + \text{Cl}_2 \rightleftharpoons \underset{\underset{\text{covalent}}{\underbrace{\quad\quad}}}{\overset{\text{Cl}}{\underset{|}{\text{ArSCl}}}} \rightleftharpoons \underset{\underset{\text{ionic}}{\underbrace{\quad\quad}}}{\overset{\text{Cl}}{\underset{+}{\text{ArSCl}}} \text{Cl}^-} \qquad (22)$$

ionic sulfur trichlorides would still fit the kinetic requirement. The negative ρ value suggests that greater electron density on sulfur increases the capacity of the sulfur–chlorine complex to ionize by increasing the ability of sulfur to tolerate positive charge. Con-

(22) N. Kharasch and C. M. Buess, *J. Am. Chem. Soc.*, **71**, 2724 (1949); D. J. Cram, *ibid.*, **71**, 3884 (1949). Presumably the small normal salt effects for displacement by styrene on 2,4-(NO$_2$)$_2$C$_6$H$_3$SCl in acetic acid [*b* values are 3.9 (NaClO$_4$) and 2.7 (LiCl)] result from the ionic intermediate. We have calculated these values using the familiar relationship[23] $k = k'$ (1 + *b*[salt]).
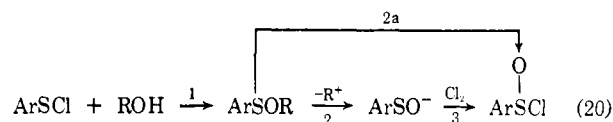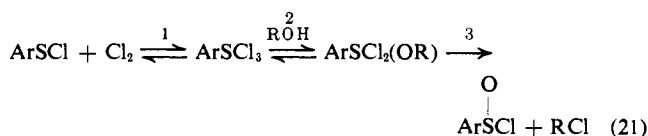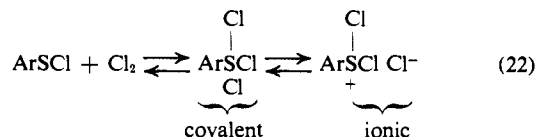
(23) S. Winstein, E. Clippinger, A. H. Fainberg, and G. C. Robinson, *ibid.*, **76**, 2597 (1954).

(24) H. Kwart and L. J. Miller, *ibid.*, **83**, 4552 (1961).

(25) Unpublished results from these laboratories to appear in a future article.

sequently, since ionization seems likely to be important in the rate-controlling process, the substituents will be a factor in determining the energy level of the transition state. The increase in electron density also will facilitate the formation of the trichloride intermediate, thereby shifting the equilibrium (eq 22) to the right yet having no direct influence on the activation energy.

Step 2 of this mechanism (eq 21) would involve displacement of chloride ion by the hydroxylic component, thus resulting in oxidative electron exchange (eq 23).

$$ArSCl_3 + ROH \xrightarrow[-HCl]{2} ArSCl_2(OR) \longrightarrow product \qquad (23)$$
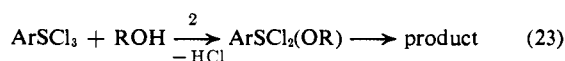
The product would be the chlorinated sulfenate ester, where R is methyl, or the mixed anhydride, where R is acetyl. Referring again to the work on these esters,[25] the intermediate postulated to undergo cleavage of the carbon–oxygen bond in the slow step of the ester chlorination reaction is the chlorine ester adduct in eq 23, but, as noted above, the slow step in the ester reaction is much more rapid than the sulfenyl chloride chlorination reaction itself. Therefore, the slow step in the sulfenyl chloride chlorination must precede step 3 in eq 21 and follow upon the formation of the chlorine addition product (step 1). It is to be assumed that where R is acyl or hydrogen the same reaction path is utilized, in this, the "kinetically most eligible" mechanism among all the proposed possibilities.

Effects of added salts, such as lithium perchlorate, on ionic reactions are well known and have been extensively studied.[26] The accelerating effect of added salt on the chlorination reaction affords convincing support for the ionic characteristic delineated by eq 22. The linear dependence of reaction rate on added lithium perchlorate (Figure 5) appears to describe a strong "normal" salt effect.[27] A value of $b = 180$ calculated from eq 24 is considerably larger than normally found in acetic acid.[28]

$$k = k_0(1 + b[\text{LiClO}_4]) \qquad (24)$$

"Salt-assisted ionization"[30] conceivably gives rise to ion-pair metathesis as discussed by Winstein and co-workers.[31] An analogous scheme would represent the initially formed chlorine adduct by equilibria involving covalent and ionic structures (Scheme I). Exchange of ion pairs III_{Cl} and IV_{Cl} with solvent leads to metathetical ions II_Y, III_Y, and IV_Y and the corresponding covalent structure I_Y. Formation of product from I_Y may proceed by two pathways, one involving ionic and the other covalent structures.

(26) S. Winstein, E. Clippinger, A. H. Fainberg, and G. C. Robinson, *J. Am. Chem. Soc.*, **76**, 2597 (1954); C. A. Bunton, "Nucleophilic Substitution at a Saturated Carbon Atom," Elsevier Publishing Co., New York, N. Y., 1963, p 126; A. Fava, A. Iliceto, A. Ceccon, and P. Koch, *J. Am. Chem. Soc.*, **87**, 1045 (1965); D. Darwish and E. A. Preston, *Tetrahedron Letters*, 113 (1964).

(27) A. H. Fainberg and S. Winstein, *J. Am. Chem. Soc.*, **78**, 2763 (1956).

(28) The maximum *b* value reported for reactions in acetic acid is 38 for *exo*-norbornyl *p*-bromobenzenesulfonate acetolysis at 25°.[29] Values up to 2×10^6 have been reported in other solvents.[30]

(29) A. H. Fainberg and S. Winstein, *J. Am. Chem. Soc.*, **78**, 2780 (1956); S. Winstein and E. Clippinger, *ibid.*, **78**, 2784 (1956).
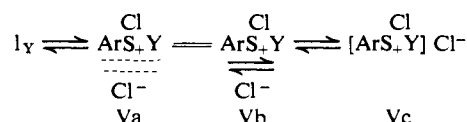
(30) S. Winstein, E. C. Friedrich, and S. Smith, *ibid.*, **86**, 305 (1964); S. Winstein, S. Smith, and D. Darwish, *ibid.*, **81**, 5511 (1959).

(31) S. Winstein, E. Clippinger, A. H. Fainberg, R. Heck, and G. C. Robinson, *ibid.*, **78**, 328 (1956).
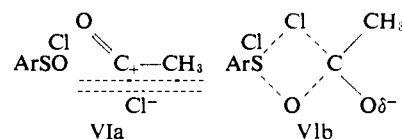
Scheme I

ArSCl + Cl₂ ⇌
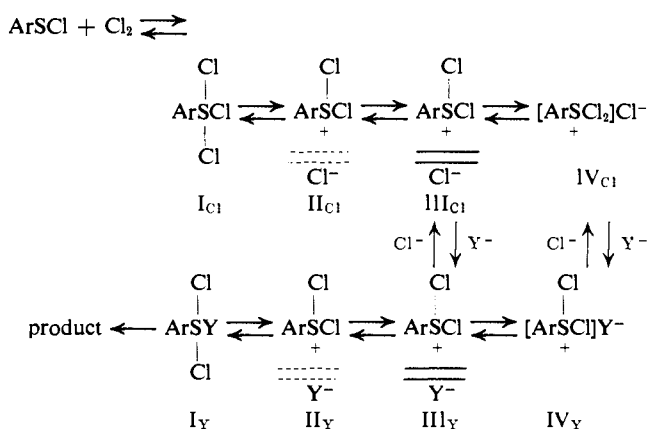
Ionization could lead to ions such as Va, Vb, and Vc

or it may revert to ions II_Y, etc. The covalent structure I_Y constitutes a pivotal point for exchange between these two groups of ions. Collapse to product may result from ions V where ejection of a neutral sulfinyl chloride molecule leaves an acylium chloride ion pair such as in VIa, or product may result from a concerted collapse and ejection of acetyl chloride

from an activated complex such as VIb derived from the covalent structure I_Y. A second hydroxyl component is necessary in this scheme to act as proton-transfer agents in the initial formation of IV_Y or its equivalent. Evidence for ion pairs of the nature of V has been noted in analogous sulfur chlorination reactions[1b,c] manifesting (in general) salt effects of comparable magnitude.

The absence of common ion rate depression,[31,32] as described in the succeeding article,[15] suggests that either IV_{Cl} is not formed or else it reacts directly with solvent to give product without return to external ion pair III_{Cl}.[31] Moreover, the absence of external ion-pair return, *i.e.*, a special salt effect,[1b,c,33] requires that III_{Cl} either react directly with solvent or dissociate to IV_{Cl}. The perchlorate probably assists the reaction by facilitating formation of acetate ion pairs with subsequent collapse to product. Alternatively, the assistance to dissociation of external ion pairs may facilitate attack by hydroxylic reagent.

Assuming a second-order rate dependence on hydroxylic reagent and not some fortuitous correlation of "medium effect" with kinetic dependence on hydroxylic solvent concentration suggests that the second molecule is acting as a proton acceptor prior to or in the rate-determining step. The unimolecular dependence of the rate on small amounts of water shows

(32) S. Winstein, P. E. Klinedinst, and G. C. Robinson, *ibid.*, **83**, 885 (1961).

(33) A. H. Fainberg and S. Winstein, *ibid.*, **78**, 2767(1956).

that water may be acting in one role only, namely as the proton transfer agent favoring either acetate formation or proton removal in the transition state. The bimolecular activity of methanol is in accord with joint activity as nucleophile and proton acceptor. The unlikely existence of sufficient methoxide ion (presumed from the unfavorable autoprotolysis equilibrium eq 25) implies that proton acceptor activity

$$2CH_3OH \rightleftharpoons CH_3O^- + CH_3O^+H_2 \qquad (25)$$
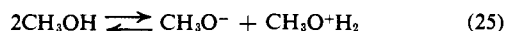
occurs in the transition state. Furthermore, in a more nucleophilic solvent such as methanol, a multiplicity of ion pairing is clearly less important,[29,33,34] being supplanted by more direct nucleophilic displacement. Metathetical ions where $Y = OCH_3^-$ are less likely.

The first-order rate dependence on sodium acetate gives further (indirect) support to the preference of bimolecular dependence on hydroxylic solvent component in the absence of an added base to assist in the proton transfer. The proton removal step is clearly important with regard to the total sequence of steps. It seems likely that it occurs at a point very near to the rate-determining event in the over-all reaction, which is consistent with the ion-pair exchange phenomenon characterizing this mechanism. Acetate ion, conceivably, reacts much more rapidly because it does not require this rate-retarding, proton-transfer step.

The Abnormal Mechanism of Chlorination of o-Nitro Substrates. In arriving at some understanding of the mechanism by which o-nitro-substituted ArSCl undergoes chlorination, the following distinction from the "normal" reaction (discussed above) may be summarized for consideration. (1) The "abnormal" chlorination exhibits a rate which is independent of chlorine (eq 18) in contrast to the normal first-order dependence of the rate on halogen concentration (eq 19). (2) para substitution produces no bias ($\rho \cong 0$) on the chlorination rate of the abnormal reaction where normally electron-releasing substituents exert a strong accelerating influence ($\rho = -2.4$). (3) The abnormal reaction does not occur in the absence of water or stronger nucleophiles such as acetate anion. (4) The normal reaction is characterized by an extraordinarily large (positive) neutral salt effect while the abnormal case shows almost no response. In fact, a ca. 0.6-fold rate depression is experienced in the presence of lithium perchlorate (see Table V). Conceivably, this deceleration could be attributed to the occurrence of equilibria in which lithium acetate is not as completely dissociated as sodium acetate; or, alternatively, the slight negative salt effect may merely be a reflection of the influence of a higher medium dielectric on a transition state experiencing charge dispersion. In either case the effect is of secondary nature and serves only to emphasize the contrast with the corresponding normal reaction characteristics.

For the chlorination of 4-chloro-2-nitrobenzenesulfenyl chloride, the activation parameters (as computed from data listed in Table VI) are $\Delta H^{\ddagger} = 12.0 \pm 1.0$ kcal/mole and $\Delta S^{\ddagger} = -23 \pm 2$ eu. The negative entropy of activation value suggests that the reacting molecule undergoes some restrictive trans-

formation in going to the transition state. Fortunately, the ground state of these sulfenyl chlorides are quite well defined. The ground-state structure proposed by Kharasch, Buess, and King[35] has been strongly supported by the recent X-ray crystallographic analysis of the related ester.[36] The ground state may be represented by a trigonal-bipyramid VII in which the nitro-oxygen and chlorine atoms are axial and the aryl group is equatorial, displaced from the trigonal plane by 20° due to ring restrictions. The two pairs of lone electrons occupy the other equatorial positions.

VII   VIII
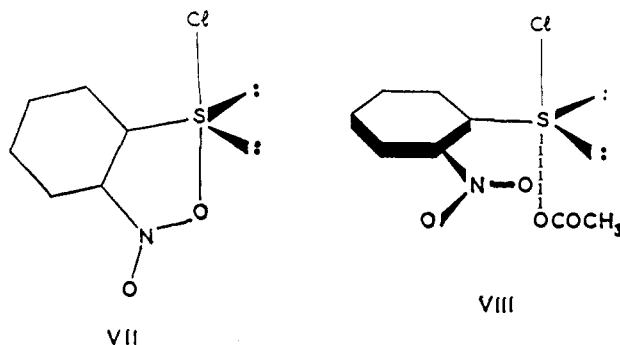
If the approaching group (acetate ion) must become almost completely bonded to the sulfur atom prior to departure of the leaving group, as suggested by Parker and Kharasch[17] for nucleophilic displacement on a sulfur atom, essentially 12 electrons would surround the sulfur atom. This assumes, of course, that the nitro group had not rotated out of the plane of the benzene ring and the trigonal-bipyramidal structure still prevails. Analogous cases involving 12 electrons around sulfur with one unshared electron pair are not known and have been considered unlikely.[37] However, one may correlate both the magnitude and sign of $\Delta S^{\ddagger}$ with rotation of the NO_2 group or the S–Cl group from the plane of the benzene ring. When both groups rotate, a structure VIII is generated in which the axial position is opened for attack by acetate ion and accommodates the stereochemical requirement for "three atoms in a line" proposed by Fava and Iliceto for S_N2 displacements at sulfur.[38] Similar trigonal-bipyramidal structures have been invoked to explain stereochemical observations in nucleophilic displacements on sulfoxides.[39] In the latter case a pseudocyclic structure has been presumed which pictures the entering and leaving groups as occupying the equatorial positions.

The intermediacy of VIII provides a good fit to the kinetic observations. The o-nitro effect favoring bimolecular nucleophilic displacement in preference to the electrophilic chlorine addition reaction observed in the absence of the o-nitro group likely results from the stereochemical requirement for substitution onto an addition complex such as IX which resembles the

(34) H. L. Goering, T. D. Nevitt, and E. F. Silversmith, *J. Am. Chem. Soc.*, 77, 5026 (1955).

(35) N. Kharasch, C. M. Buess, and W. King, *ibid.*, 75, 6035 (1953); N. Kharasch, "Organic Sulfur Compounds," Vol. I, N. Kharasch, Ed., Pergamon Press Inc., New York, N. Y., 1961, p 375.

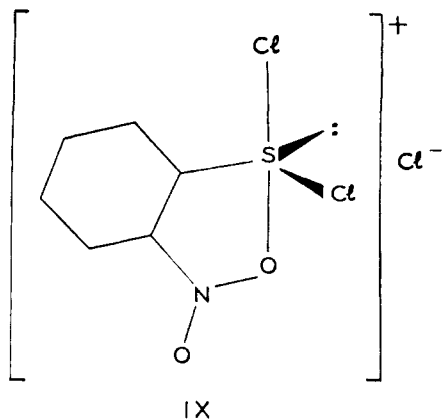(36) W. C. Hamilton and S. J. LaPlaca, *J. Am. Chem. Soc.*, 86, 2290 (1964).

(37) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1962, p 307.

(38) A. Fava and A. Iliceto, *J. Am. Chem. Soc.*, 80, 3478 (1958); W. A. Pryor, "Mechanisms of Sulfur Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 62.

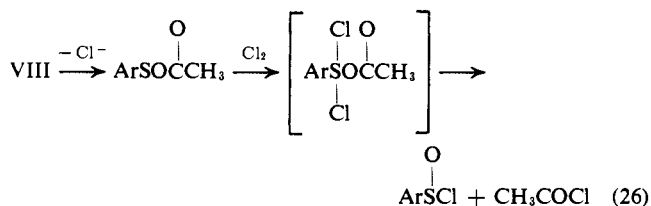(39) J. Day and D. J. Cram, *J. Am. Chem. Soc.*, 87, 4398 (1965).

IX

ground-state structure VII of the substrate. Hence, the additional chlorine atom added to VII blocks the sulfur atom to further attack. Moreover, unlike the 4-substituted benzenesulfenyl chloride chlorination, ion pairs are apparently unimportant here, as attested by the lack of neutral salt effects (which are of extraordinary magnitude in the normal chlorination reaction). Thus, an alternative SN1 type mechanism involving sulfenium ions (ArS⁺) is unacceptable. Further, recent evidence[40] questions the existence of sulfenium ions, i.e., 2,4-dinitrobenzenesulfenium ion[35] in strong sulfuric acid. Instead of the sulfenium ion a protonated sulfenyl chloride, ArS(H)Cl⁺, is the species presumably generated.[40]

(40) E. A. Robinson, Symposium on Hydrocarbon Ions, 152nd

A mechanism of bimolecular nucleophilic displacement on sulfur which is convincingly supported by the data is also consistent with the absence of a *para* substituent rate effect. Similar mechanisms have been previously characterized by negligible Hammett ρ values, a case in point being the reaction of sulfenyl halides with amines in solvents of low polarity.[41]

After loss of chloride ion from VIII, a mixed anhydride results (eq 26). Rapid chlorine addition to the mixed anhydride and subsequent cleavage of the acyl

$$\text{VIII} \xrightarrow{-\text{Cl}^-} \text{ArSOCCH}_3 \xrightarrow{\text{Cl}_2} \left[\begin{array}{c} \text{Cl O} \\ | \ | \\ \text{ArSOCCH}_3 \\ | \\ \text{Cl} \end{array} \right] \longrightarrow$$

$$\text{ArSCl} + \text{CH}_3\text{COCl} \quad (26)$$

oxygen bond could explain the sulfinyl chloride and acetyl chloride products and fit the kinetic requirements. Some support for rapid mixed anhydride cleavage comes from the results of sulfenate ester chlorination.[1c,25] Presumably, like the ester, the mixed anhydride reaction would be very rapid. The sulfonyl chloride product could arise by sulfinyl chloride chlorination.[2d,e]

The Solvolysis and the Abnormal Mechanism of Chlorination of 2-Nitrobenzenesulfenyl Chlorides. VII[1a]

Edwin N. Givens[1b] and Harold Kwart

Contribution from the Department of Chemistry, University of Delaware, Newark, Delaware 19711. Received March 30, 1967

Abstract: The kinetics of the chlorination of various *para*-substituted *o*-nitrobenzenesulfenyl chlorides in solvolytic media such as aqueous acetic acid have been studied in detail. The stoichiometry of these reactions has been established. Chlorine-dependent and -independent terms in the rate equation appear to correspond to electrophilic and nucleophilic reactions at bivalent sulfur. Electron-releasing *para* substituents enhance the electrophilic reaction which has a Hammett ρ value equal to that of the corresponding reaction of substrates without the 2-nitro group.[1a] The chlorine-independent term in the rate equation, on the other hand, shows no rate response with change of the *para* substituent of the 2-nitro substrate. Dependence on methanol and/or water concentration in the rate equation is uniformly fourth order. In the aqueous acetic acid medium dependence of the rate on acetate and/or dihydrogen phosphate anion has been determined to be first order with specific catalytic constants of nearly the same magnitude. A strong normal salt effect[19] was observed for the electrophilic reaction ($b = 24.5$) for added lithium perchlorate. The chlorine-independent reaction, however, showed no rate change with neutral salt whereas the hydrolysis reaction showed moderate acceleration characteristic of the normal salt effect. Neither lithium chloride nor hydrochloric acid added to the reaction medium had any influence on rate. The unusual pattern of reactivity observed for these substrates has been explained by invoking reaction intermediates possessing a trigonal-bipyramid structure of sulfur valencies in which the *o*-nitro oxygen atom and a chlorine occupy apical positions.

The chlorinations of *o*-nitrobenzenesulfenyl chlorides have been studied as a part of a continuing program to elucidate the mechanisms of bivalent sulfur

chlorination reactions. The chlorination of various *para*-substituted benzenesulfenyl chlorides was discussed previously.[1a] A mechanism was proposed

(1) (a) E. N. Givens and H. Kwart, *J. Am. Chem. Soc.*, 90, 378 (1968). (b) Part of this article was abstracted from the thesis of E. N.