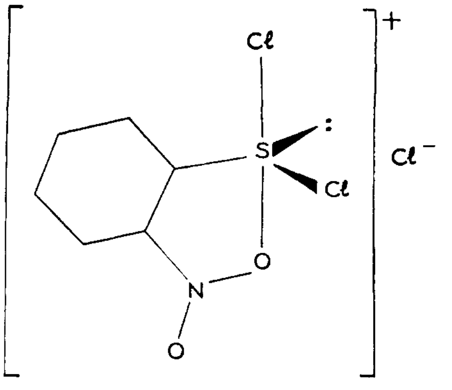
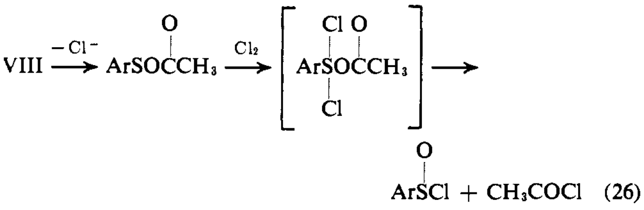


IX

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]

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 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]



$$\mathrm{VIII} \xrightarrow{-\mathrm{Cl}^-} \mathrm{ArSO}\overset{\mathrm{O}}{\overset{|}{\mathrm{C}}}\mathrm{CH_3} \xrightarrow{\mathrm{Cl_2}} \left[\mathrm{Ar}\underset{\underset{\mathrm{Cl}}{|}}{\overset{\overset{\mathrm{Cl}}{|}}{\mathrm{S}}}\mathrm{O}\overset{\mathrm{O}}{\overset{|}{\mathrm{C}}}\mathrm{CH_3}\right] \longrightarrow \mathrm{Ar}\overset{\mathrm{O}}{\overset{|}{\mathrm{S}}}\mathrm{Cl} + \mathrm{CH_3COCl} \quad (26)$$

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(40) E. A. Robinson, Symposium on Hydrocarbon Ions, 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966.

(41) Private communication of unpublished results of A. Fava and E. Ciuffarin, Istituto de Chimica Generale, Pisa, Italy, Oct 1966.

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

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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

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(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. Givens submitted in partial fulfillment of the requirements for the Masters Degree of the University of Delaware, June, 1963.

which could be briefly described as a multistep process in which the initial occurrence is the rapid electrophilic attack by chlorine on the sulfenyl chloride forming in rapid equilibrium an intermediate arylsulfur trichloride. This step is followed by solvent exchange through metathetical ion pairs generated by ionization of the sulfur trichloride. Ion return and splitting off of acetyl chloride lead to product.

On comparing the *o*-nitroarenesulfenyl chloride series with the *para*-substituted series, marked differences in reactivity were observed. Although the chlorination of these *o*-nitrobenzenesulfenyl chlorides has long been known to produce sulfonyl chlorides, some confusion exists as to the necessary reaction conditions. Zincke, *et al.*,[2] reported that *o*-nitrophenyl disulfide reacts as do other disulfides in anhydrous acetic acid to produce the corresponding sulfonyl chloride. On the other hand, Fierz, Schlittler, and Waldman[3] later showed that chlorination of 2-nitrobenzenesulfenyl chloride in aqueous media produced the corresponding sulfonyl chloride in "marked yield." Whether water was indispensable to the attainment of this result, in contradistinction to the earlier work of Zincke and his collaborators,[2] was not made clear. In glacial acetic acid with added sodium acetate, however, we have shown[1a] that 4-chloro-2-nitrobenzenesulfenyl chloride was chlorinated to give an 88% yield of the corresponding sulfonyl chloride. On the basis of detailed kinetic and stoichiometric studies, a mechanism was proposed involving bimolecular SN2 type displacement at bivalent sulfur with chlorine becoming involved only following the rate-determining event.

We are now able to present the results of a systematic study of the chlorination of 4-substituted 2-nitrobenzenesulfenyl chlorides in *aqueous* acetic acid. This appears to be a considerably different process from the reaction occurring in anhydrous acetic acid containing acetate anion, and possesses features that have particular interest for our understanding of mechanisms of chlorination of divalent sulfur compound.[4]

Experimental Section

Sodium acetate, sodium hydrogen phosphate, potassium dihydrogen phosphate, lithium perchlorate, and lithium chloride were commercially available analytical grade reagents. Constant boiling hydrochloric acid (20.22% by weight) was prepared by the method of Hullett and Bonner.[5] Chlorine, supplied by Matheson Coleman and Bell, was dried by passing through concentrated sulfuric acid. Chlorine solutions were standardized by an iodometric procedure.

Sulfenyl chlorides, *i.e.*, 2,4-dinitrobenzene,[6] 2-nitrobenzene,[7] 4-carboxyl-2-nitrobenzene,[8] 4-chloro-2-nitrobenzene,[9] and 4-trifluoromethyl-2-nitrobenzenesulfenyl chlorides,[7] were prepared from commercially available disulfides, mercaptans, or their precursors by known procedures.

Sulfonyl chlorides were prepared by the procedure described here for 4-carboxyl-2-nitrobenzenesulfonyl chloride. Ten grams of 4-carboxyl-2-nitrobenzenesulfenyl chloride was dissolved in 25 ml of acetic acid to which 4 ml of water was added. Chlorine was bubbled through the solution for 30 min after which the reaction mixture was poured onto ice and diluted to 200 ml. The ice was melted and the insoluble precipitate separated by filtration and dissolved in benzene. The solution was washed with dilute sodium bicarbonate and water and dried with sodium sulfate. Hexane was added to the benzene solution until the cloud point was reached. The product was filtered, dried, and recrystallized from benzene-hexane (10.5 g, mp 197–198°).

Anal. Calcd for $C_7H_4ClNO_6S$: C, 31.65; H 1.51; N 5.27. Found: C, 32.13; H, 1.63; N, 5.16.

The spectrophotometric technique was discussed previously.[1a] All of the kinetic runs were made at 29.9°. The pseudo-first-order rate constants observed throughout are referred to as apparent rate constants, k_{app}.

Results and Discussion

The anhydrous acetic acid chlorination of 4-substituted benzenesulfenyl chlorides was observed to have the stoichiometry represented by eq 1. *o*-Nitrobenzenesulfenyl chlorides in anhydrous acetic acid in the presence of chlorine fail to react, but in aqueous acetic acid both substrates react readily with the stoichiometry shown in eq 2. An iodometric procedure used to analyze for unreacted chlorine in the presence of the sulfonyl chloride product was sufficient to establish the stoichiometry of the benzenesulfenyl chloride reaction. The stoichiometry for *o*-nitrobenzenesulfenyl chlorides (eq 2) could not be determined by the iodometric method because of ready oxidation of iodide ion by the 2-nitrobenzenesulfonyl chloride products.[10] Thus, separation of unreacted chlorine from the reaction vessel was necessary. This was achieved by distilling most of the solvent including the chlorine from the presence of the sulfonyl chloride. An iodometric analysis of the distillate thus established the stoichiometry shown in eq 2. The quantitative recovery of sulfonyl chlorides eliminated the occurrence of any possible side reactions from further consideration. In three experiments, 99, 92, and 89% of 2,4-dinitrobenzenesulfonyl chloride was isolated from the corresponding sulfenyl chloride. Correspondingly, excellent yields of crystalline sulfonyl chlorides were isolated from all of the sulfenyl chlorides with the exception of the 4-trifluoromethyl-2-nitrobenzenesulfonyl chloride which had previously been reported to be an oil.[12]

$$\mathrm{ArSCl + 2Cl_2 + 2HOAc \longrightarrow ArSO_2Cl + 2AcCl + 2HCl} \qquad (1)$$

$$\mathrm{ArSCl + 2Cl_2 + 2H_2O \longrightarrow ArSO_2Cl + 4HCl} \qquad (2)$$

Because of the distinct possibility of competing solvolysis reactions of the sulfenyl chlorides in the various solvent systems, an examination was made of the stability of several substrates in anhydrous and aqueous acetic acid. All the *o*-nitrobenzenesulfenyl

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(2) T. Zincke and F. Farr, *Ann.*, **391**, 64 (1912); T. Zincke, *ibid.*, 400, 9 (1913); E. Riesz, A. Lorenz, C. Myschalow, and O. Strakosch, *Monatsch.*, **50**, 267 (1928).

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

(4) For the previously published article in this series see H. Kwart, R. W. Body, and D. M. Hoffman, *Chem. Commun.*, 765 (1967); H. Kwart and P. S. Strilko, *ibid.*, 767 (1967).

(5) G. A. Hullett and W. D. Bonner, *J. Am. Chem. Soc.*, **31**, 390 (1909).

(6) N. Kharasch, G. I. Gleason, and C. M. Buess, *ibid.*, **72**, 1796 (1950).

(7) M. H. Hubacker, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p 455.

(8) N. Kharasch and A. J. Havlik, *J. Am. Chem. Soc.*, **77**, 1150 (1955).

(9) M. B. Sparke, J. L. Cameron, and N. Kharasch, *ibid.*, **75**, 4909 (1953).

(10) *o*-Nitrobenzenesulfonyl chlorides react much more rapidly with iodide solution than benzenesulfonyl chloride. Products from the reaction of benzenesulfonyl chloride and sodium iodide in acetone are sodium sulfinate and diphenyl disulfone.[11]

(11) E. Gebauer-Fulnegg and F. Riesenfeld, *Monatsch.*, **47**, 185 (1926); H. Kroepelin and K. Born, *Arch. Pharm.*, **287**, 561 (1954); *Chem. Abstr.*, **52**, 9005*f* (1954).

(12) C. T. Holdrege, R. B. Babel, and L. C. Cheney, *J. Am. Chem. Soc.*, **81**, 4807 (1959).

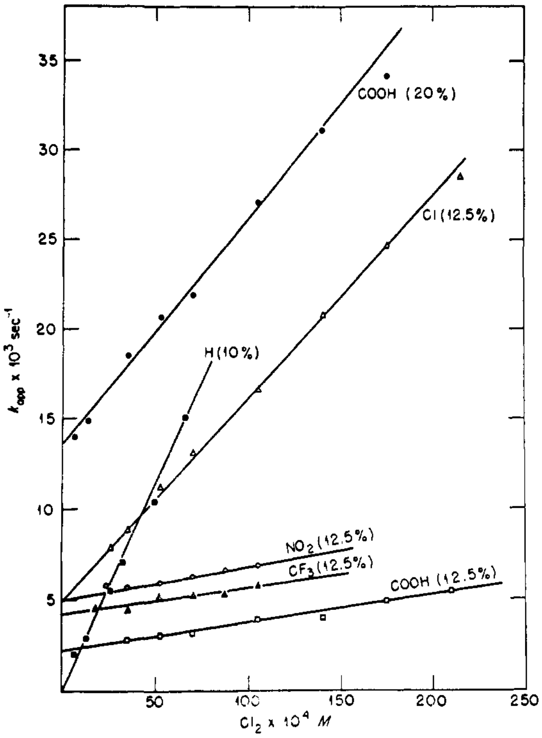

Figure 1. Chlorination of 4-substituted 2-nitrobenzenesulfenyl chlorides in aqueous acetic acid (4 substituent shown with per cent aqueous acid).

chlorides were found to be completely stable, showing no apparent decomposition in anhydrous acetic acid for periods up to several days. Benzenesulfenyl chloride reacted slowly in acetic acid with a k_{app} of 2.0×10^{-5} sec^{-1}. In aqueous acetic acid, 2,4-dinitrobenzenesulfenyl chlorides were shown by Kharasch, King, and Bruice[13] to give disulfide, sulfonyl chloride, thiolsulfonate, sulfenic anhydride, and sulfonic acid. The rate of hydrolysis, however, is so much slower than the chlorination reaction that the latter can be studied without fear of kinetic complications.

For example, in 12.5% aqueous acetic acid, the relative rates of chlorination *vs.* hydrolysis for 2-nitro- and 4-chloro-2-nitrobenzenesulfenyl chlorides were 90:1 and 60:1, respectively (Table I); in 0.40 *M* lithium perchlorate the relative rates for the latter were 50:1.

Table I. Chlorination and Hydrolysis Rates of 4-X-2-Nitrobenzenesulfenyl Chlorides in 12.5% Aqueous Acetic Acid at 29.9°

X	[ArSCl] × 10^4[a]	[Cl$_2$] × 10^3[a]	[LiClO$_4$][a]	k_{app} × 10^3 sec^{-1}
H	1.75	6.60		29.8
	1.75	...		0.32
Cl	1.75	3.50		8.84
	1.75	...		0.14
	1.75	3.50	0.40	50.0
	1.75	...	0.40	0.98[b]
NO$_2$	1.75	3.50	...	5.66
	1.75	3.50	0.20	11.4

[a] Concentrations in moles/l. [b] For the hydrolysis reaction, b = 15 (see eq 8).

Ultraviolet Absorption Spectra. The ultraviolet spectral characteristics for the arenesulfenyl chlorides in the 300–400-mμ region are presented in Table II. Included is the wavelength at which the reaction rate data are obtained. Reasons for the absorption in this region have been discussed.[14] All of the sulfenyl chlorides included in this study are colored and the corresponding sulfonyl chlorides are colorless. Other data would suggest that the sulfinyl chloride and sulfur trichloride intermediates are colorless,[15] and probably have little absorption in the 390-mμ region, therefore. The loss of both visible and ultraviolet absorption during the reaction is most probably due to the disappearance of sulfenyl chloride.

Table II. Ultraviolet Spectra of 4-X-2-Nitrobenzenesulfenyl Chlorides in Acetic Acid

4 Substituent	λ_{max}, mμ	ϵ, (cm moles)/l.	$\lambda_{kinetics}$, mμ
H	390	2840	390
Cl	398–400	2520	390
COOH	382	2440	380
CF$_3$	381	4270	390
NO$_2$	314	8240	390

In any reaction sequence the sulfur trichloride must be considered as a possible intermediate.[15] If the sulfur trichloride intermediate does exist to any degree in acetic acid, addition of chlorine to the sulfenyl chloride should cause an immediate decrease in absorption until an equilibrium concentration is reached. There is, however, no spectral evidence for such a change suggesting that the equilibrium lies far to the left (as shown for eq 3) as determined for trichloromethanesulfenyl chloride.[16]

$$\mathrm{ArSCl} + \mathrm{Cl_2} \rightleftharpoons \mathrm{ArSCl_3} \qquad (3)$$

Dependence on Chlorine. The kinetic data were obtained by pseudo-first-order techniques used in earlier studies.[1a] Chlorine dependence in aqueous acetic acid was obtained from plots of k_{app} *vs.* chlorine concentrations for several substrates. The data demand that the rate equation must have two terms, one which is first order in chlorine concentration and the second which is chlorine independent as in eq 4. The

$$\text{rate} = k_{app}[\mathrm{ArSCl}] = k_1[\mathrm{Cl_2}][\mathrm{ArSCl}] + k_2[\mathrm{ArSCl}] \qquad (4)$$

intercepts and slopes are directly dependent on water concentration. This is clearly apparent, for instance, in the case of 4-carboxyl-2-nitrobenzenesulfenyl chloride from data listed in Table III and plotted in Figure 1 at two different water concentrations.

Dependence on Water. The effect of water concentration for several substrates was obtained from log–log plots of k_{app} *vs.* water concentration (Figure 2, plotted from data in Table III). The approximate value of 4 for each slope indicates the rate equation must

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(13) N. Kharasch, W. King, and T. C. Bruice, *J. Am. Chem. Soc.*, 77, 932 (1955).

(14) E. Gebauer-Fulnegg, *ibid.*, **49**, 2270 (1927).

(15) I. B. Douglass, B. S. Farah, and E. G. Thomas, *J. Org. Chem.*, **26**, 1996 (1961); I. B. Douglass, "Organic Sulfur Compounds," Vol. I, N. Kharasch, Ed., Pergamon Press Inc., New York, N. Y., 1961, 350; K. R. Brower and I. B. Douglass, *J. Am. Chem. Soc.*, **73**, 5787 (1951).

(16) I. B. Douglass, K. R. Brower, and F. T. Martin, *ibid.*, **74**, 5770 (1952).

Table III. Chlorination Rates of 4-Substituted 2-Nitrobenzenesulfenyl Chlorides in Aqueous Acetic Acid at 29.9°[a]

X[b]	[4,2-X-$NO_2C_6H_3SCl$]	$[Cl_2] \times 10^3$	$[H_2O]$	$k_{app} \times 10^3$ sec^{-1}	$\frac{k_{app}}{[H_2O]^4} \times 10^{-6}$ [c]
H	1.75×10^{-4}	0.66	5.56	2.02	2.11
		1.32	5.56	2.88	3.01
		2.64	5.56	5.54	5.80
		3.30	5.56	7.14	7.48
		4.95	5.56	10.4	10.9
		6.62	5.56	15.1	15.8
		7.00	2.78	1.09	18.3
		7.00	4.17	4.98	16.0
		7.00	6.95	29.8	12.8
Cl	1.75×10^{-4}	2.62	6.95	7.89	3.38
		3.50	6.95	8.84	3.79
		5.25	6.95	11.2	4.80
		10.5	6.95	16.6	7.12
		14.0	6.95	20.8	8.92
		17.5	6.95	24.7	10.6
		21.0	6.95	28.5	12.2
		7.00	4.17	1.87	6.25
		7.00	5.56	5.26	5.50
		7.00	6.95	13.6	5.84
		7.00	8.34	30.7	6.35
		7.00	9.73	48.2	5.38
COOH	1.75×10^{-4}	0.70	11.1	13.9	0.92
		1.40	11.1	14.8	0.98
		3.50	11.1	18.5	1.22
		5.25	11.1	20.7	1.37
		7.00	11.1	21.9	1.45
		10.5	11.1	27.1	1.80
		14.0	11.1	31.2	2.06
		17.5	11.1	34.2	2.26
		3.50	6.95	2.80	1.21
		5.25	6.95	3.03	1.30
		7.00	6.95	3.18	1.36
		10.5	6.95	3.90	1.67
		14.0	6.95	3.96	1.70
		17.5	6.95	4.90	2.11
		21.0	6.95	5.52	2.37
		7.00	5.56	1.28	1.34
		7.00	8.34	6.30	1.30
		7.00	9.73	11.4	1.27
NO_2	1.75×10^{-4}	2.40	6.95	5.80	2.49
		3.50	6.95	5.66	2.42
		5.25	6.95	5.92	2.54
		7.00	6.95	6.28	2.70
		7.85	6.95	6.52	2.80
		10.5	6.95	6.87	2.94
	1.20×10^{-4}	2.40	2.78	0.170	2.84
		2.40	4.17	0.688	2.30
		2.40	5.56	2.48	2.60
		2.40	8.34	10.7	2.21
		2.40	9.73	19.1	2.13
		2.40	11.1	35.3	2.34
		2.40	12.5	69.0	2.84
CF_3	1.75×10^{-4}	1.80	6.95	4.62	1.98
		3.50	6.95	4.44	1.91
		5.20	6.95	5.20	2.23
		7.00	6.95	5.22	2.24
		8.70	6.95	5.32	2.28
		10.5	6.95	5.81	2.49
		3.50	5.56	2.06	2.16

[a] Concentrations in moles/l. [b] X = 4 substituent. [c] $l.^4$ $moles^{-4}$ sec^{-1}.

have a fourth-order dependence on water concentration in each term (eq 5).

$$\text{rate} = k_3[H_2O]^4[ArSCl] \tag{5}$$

Combining eq 4 and 5 gives

$$\text{rate} = k_4[Cl_2][H_2O]^4[ArSCl] + k_5[H_2O]^4[ArSCl] \tag{6}$$

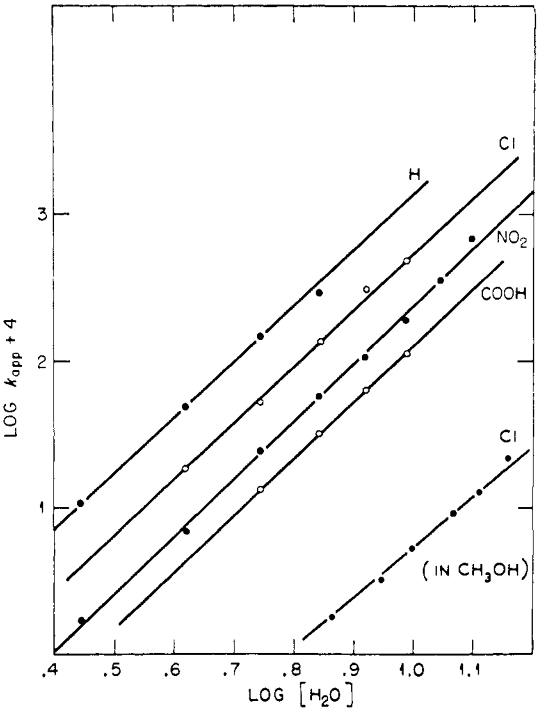

Figure 2. Effect of water concentration on the chlorination of 4-substituted 2-nitrobenzenesulfenyl chloride in aqueous acetic acid.

The rate constants k_4 and k_5 apply to the chlorine-dependent and -independent reactions, respectively. Values of k_4 and k_5 (Table IV) are obtained from plots of $k_{app}/H_2O]^4$ *vs.* $[Cl_2]$ (Figure 3 plotted from data in Table III). The two lines for 4-carboxyl-2-nitrobenzenesulfenyl chloride in Figure 1, which represent 12.5 and 20% aqueous acetic acid reactions, become virtually identical in Figure 3. The relative competition of the chlorine-dependent and-independent reactions at a particular chlorine concentration can be obtained from an expression such as R (eq 7). As an

$$R = (k_4/k_5)[Cl_2] \tag{7}$$

example values for R at 1.0×10^{-2} M chlorine concentration are given in Table IV.

Table IV. Rate Constants of Chlorine-Dependent and -Independent Reactions[a]

4 Substituent[b]	$k_4 \times 10^5$ [c]	$k_5 \times 10^6$ [d]	R[e]
H	24.9	0	∞
Cl	4.87	2.0	2.4
COOH	0.78	0.9	0.87
CF_3	0.82	1.9	0.46
NO_2	1.20	2.3	0.52

[a] Defined by eq 6. [b] For 4-substituted 2-nitrobenzenesulfenyl chloride. [c] $l.^5/mole^5$ sec. [d] $l.^4/mole^4$ sec. [e] Relative rates of chlorine-dependent and -independent reaction at 1.0×10^{-2} M chlorine concentration calculated from $R = k_4[Cl_2]/k_5$ (eq 7).

The strong differences in *para*-substituent influence on the magnitude of k_4 and k_5 are at once apparent from study of these data (Table IV). The chlorine-dependent reaction (k_4) has a rate sensitivity to *para* substitution approximately equal to that of the electrophilic reaction mechanism of substrates without the *o*-nitro group (Hammett $\rho = -2.5$).[1a] The

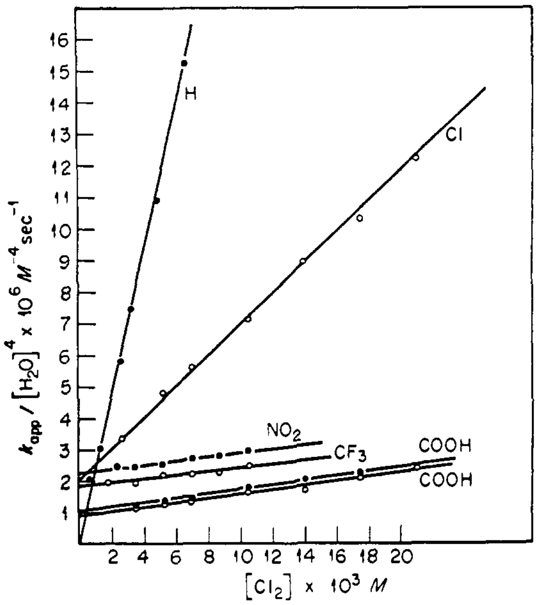

Figure 3. Effect of chlorine concentration on the chlorination of 4-substituted 2-nitrobenzenesulfenyl chlorides in aqueous acetic acid.

rate of the chlorine-independent reaction (k_5) is clearly unbiased by *para* substitution, as found previously[1a] for the nucleophilic chlorination mechanism of *o*-nitro substrates.

Dependence on Methanol. From *a priori* considerations the dependence on methanol and water would be expected to be different in a situation where four water molecules were known to be involved in the rate equation. Chlorination of 2,4-dinitrobenzenesulfenyl chloride at rather high concentrations of methanol in acetic acid, which were necessary to obtain rates conducive to our methods of measurement, yielded data indicative of a fourth-order dependence on methanol (Figure 2 plotted from data in Table V). Again, each term in the rate equation contains a fourth-order dependence on methanol concentration.

"Medium effects" cannot be directly excluded in these systems as a basis for explaining solvent rate influence. However, the consistent rate correlations observed here with both water and methanol concentrations, as well as those effects observed earlier,[1a] demands a mechanistic relationship with greater definition than is usually implied by the term "medium effect." For example, we observe for 2,4-dinitrobenzenesulfenyl chloride chlorination a 14-fold rate enhancement on increasing the water component from 5 to 10% in acetic acid. In the case of 4-chlorobenzenesulfenyl chloride a nearly twofold rate increase results for approximately doubling (0.38% → 0.88%) the concentration of water in this medium.

Chlorination of 2,4-dinitrobenzenesulfenyl chloride in 50% by volume acetic acid-*t*-butyl alcohol was very slow; a k_{app} of 2.7×10^{-5} sec^{-1} at 0.0035 *M* chlorine was observed. This result cannot be compared to chlorination in methanol-acetic acid solution since different substrates were used. The slow rate of chlorination of 2,4-dinitrobenzenesulfenyl chloride in *t*-butyl alcohol (containing) solution is particularly significant by comparison to the chlorination of *t*-butyl 2,4-dinitrobenzenesulfenate in anhydrous acetic acid. The latter reaction is exceedingly rapid.[17]

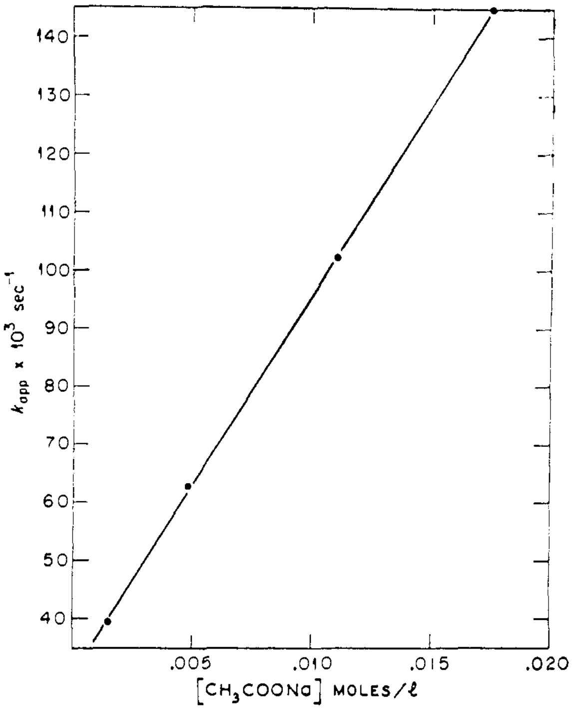

Figure 4. Effect of sodium acetate concentration on the chlorination of 4-chloro-2-nitrobenzenesulfenyl chloride in aqeuous acetic acid (12.5%) in the presence of 0.10 *M* $LiClO_4$.

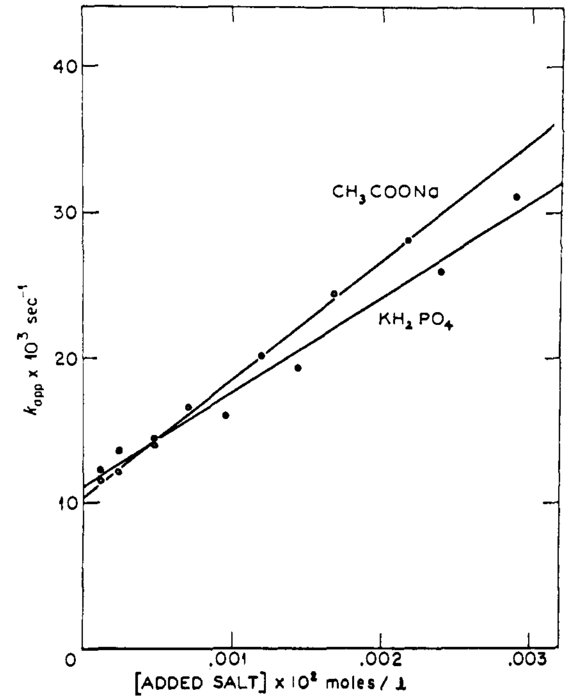

Figure 5. Effect of base concentration on the chlorination of 2,4-dinitrobenzenesulfenyl chloride in 15% aqueous acetic acid.

Added Salts. The chlorination of the 4-chloro- and 4-nitro-substituted 2-nitrobenzenesulfenyl chlorides in aqueous acetic acid was accelerated by the presence of sodium acetate (Figures 4 and 5, plotted from data in Table V), the former also with 0.10 *M* lithium perchlorate present. Both reactions, that is, with and

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(17) H. Kwart and E. N. Givens, unpublished results.

Table V. Effect of Added Salt on the Chlorination Rates of 4-Substituted 2-Nitrobenzenesulfenyl Chlorides in Aqueous Acetic Acid[a]

X[b]	[4,2-X-$NO_2C_6H_3SCl$]	[Cl_2] × 10^3	[H_2O]	[$LiClO_4$] × 10^2	[LiCl] × 10^3	[CH_3OH]	[AcONa] × 10^3	[HCl] × 10^3	[KH_2PO_4] × 10^4	k_{app} × 10^3 sec^{-1}
H	1.75 × 10^{-4}	3.48	5.56	0.10						9.61
		3.48	5.56	0.20						9.52
		3.48	5.56	0.30						10.1
		3.48	5.56	2.0						14.8
		3.48	5.56	3.0						16.3
		3.48	5.56	6.0						25.4
		3.48	5.56	10.0						32.8
		3.48	5.56	15.0						39.9
		3.48	5.56	18.0						55.2
		3.48	5.56	21.0						61.5
	5.00 × 10^{-4}	3.50	5.56							8.16
		3.50	5.56		2.50					9.40
		3.50	5.56		5.00					8.39
		3.50	5.56		7.50					8.78
		3.50	5.56		10.0					7.98
Cl	1.75 × 10^{-4}	3.50	6.95	0.25						9.33
		3.50	6.95	1.25						12.0
		3.50	6.95	7.50						17.4
		3.50	6.95	10.0						21.2
		3.50	6.95	20.0						29.2
		3.50	6.95	30.0						40.1
		3.50	6.95	40.0						50.0
		3.62				7.34				1.48
		3.62				8.80				2.88
		3.62				10.3				5.12
		3.62				11.7				8.78
		3.62				13.2				13.3
		3.62				14.7				18.4
	4.00 × 10^{-4}	7.90	6.95	0.00102			1.60			16.0
		7.90	6.95	0.0102			1.60			17.8
		7.90	6.95	0.102			1.60			17.4
		7.90	6.95	0.500			1.60			19.1
		7.90	6.95	1.00			1.60			22.3
		7.90	6.95	5.00			1.60			33.5
		7.90	6.95	10.0			1.60			39.6
		7.90	6.95	20.0			1.60			51.5
		7.90	6.95	30.0			1.60			60.1
		7.90	6.95	40.0			1.60			72.3
		7.90	6.95	10.0			4.80			63.2
		7.90	6.95	10.0			11.1			102.3
		7.90	6.95	10.0			17.5			145
NO_2	1.75 × 10^{-4}	3.50	6.95	20.0						11.4
		3.50	8.34		1.00					10.3
		3.50	8.34		5.00					11.4
		3.50	8.34		10.0					11.5
		3.50	8.34		50.0					13.0
		3.50	8.34		100					13.0
	1.20 × 10^{-4}	2.42	8.34				0.060			11.5
		2.42	8.34				0.120			11.5
		2.42	8.34				0.240			12.1
		2.42	8.34				0.480			13.9
		2.42	8.34				0.720			16.6
		2.42	8.34				1.20			20.1
		2.42	8.34				1.68			24.4
		2.42	8.34				2.16			28.1
		2.42	8.34					1.20		9.40
		2.42	8.34					1.68		8.30
		2.42	8.34					2.16		7.02
		2.45	8.34						1.20	12.1
		2.45	8.34						2.40	13.6
		2.45	8.34						4.80	14.5
		2.45	8.34						9.60	16.1
		2.45	8.34						14.4	19.4
		2.45	8.34						24.0	26.0
		2.45	8.34						28.8	31.2

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

without $LiClO_4$, were first order in sodium acetate. Apparently, the water reaction continues to operate as a competition with acetate ion for substrate. We have noted previously the absence of any reaction of 2,4-dinitrobenzenesulfenyl chloride in glacial acetic acid–chlorine solution with added KH_2PO_4.[1a] Such is not the case with aqueous acetic acid–chlorine systems where the presence of KH_2PO_4 accelerates the reaction giving a linear rate increase with a positive intercept. The rate equation has two terms: one a KH_2PO_4-dependent term (first order) and the other a KH_2PO_4-independent term (Figure 5 plotted from data

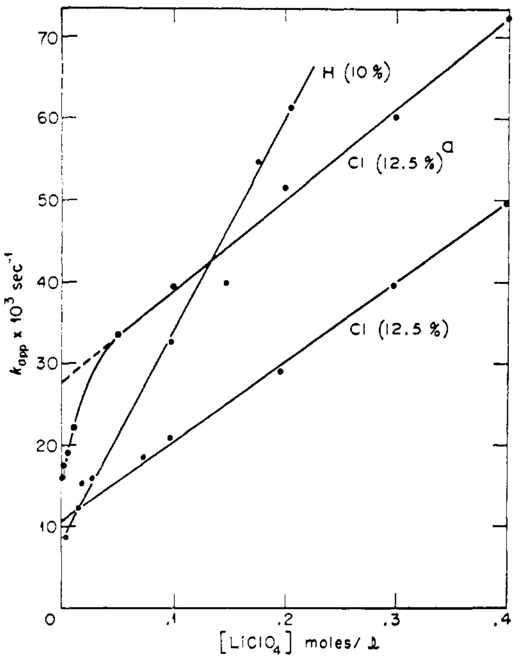

Figure 6. Effect of lithium perchlorate concentration on the chlorination of 4-substituted 2-nitrobenzenesulfenyl chloride in aqueous acetic acid. Per cent water by volume shown; a, contains 1.60 × 10^{-3} M sodium acetate.

in Table V). Obviously, the role of $H_2PO_4^-$ is not the formation of acetate ion since the conjugate acid, H_3PO_4, is a stronger acid than acetic acid itself, but HPO_4^{2-} would form acetate ion and cause thereby the observed substrate reactivity. The inactivity of $H_2PO_4^-$ in glacial acetic acid compared to its activity in aqueous acetic acid argues against assigning it the role of a nucleophile. The nearly equal acceleration due to acetate and $H_2PO_4^-$ ions suggests a mode of reactivity, that is, a proton-transfer step, common to both ions. The rate of reaction of 2,4-dinitrobenzenesulfenyl chloride in the presence of added hydrochloric acid is slightly decelerated (Table V) which is consistent with an observed insensitivity of the (pseudo) first-order kinetic pattern of the reaction to hydrogen chloride product formed during the course of reaction. Thus, the $H_2PO_4^-$ ion does more than merely deplete the hydrogen chloride produced in the reaction. It must be more closely related to the rate-determining process.

The effect of added lithium chloride on the chlorination rate is quite small; indeed, the kinetic measurement is not sufficiently accurate to ascertain from the small change whether an increase or decrease in rate occurs (Table V). Nonetheless, the significance to be inferred, namely, the absence of a common ion rate depression,[18] must be taken into consideration in any mechanistic proposal.

The addition of lithium perchlorate to the aqueous acetic acid media causes acceleration to both the hydrolysis and chlorination reactions. Treatment of the hydrolysis data of 4-chloro-2-nitrobenzenesulfenyl chloride as a "normal salt effect"[19] according to eq 8

$$k = k^0(1 + b[\mathrm{LiClO_4}]) \qquad (8)$$

gives b = 15 (Table I).[20] The chlorination reaction showed linear acceleration by lithium perchlorate for 4-chloro-2-nitro- and 2-nitrobenzenesulfenyl chlorides (Figure 6 plotted from data listed in Table V). Acceleration of 2,4-dinitrobenzenesulfenyl chloride was also measured (Table I). The calculated b values for various 4 substituents are: H, 24.5; Cl, 10; NO_2, 5. Because there are two competing reactions, eq 8 can be expanded to take into consideration the accelerative effect of lithium perchlorate on the individual chlorine-dependent and chlorine-independent terms (eq 9).

$$k_{app}/[\mathrm{H_2O}]^4 = k_4[\mathrm{Cl_2}](1 + b_1[\mathrm{LiClO_4}]) + k_5(1 + b_2[\mathrm{LiClO_4}]) \qquad (9)$$

The b_1 and b_2 values are assigned to the chlorine-dependent (k_4) and -independent (k_5) terms, respectively.

Since for 2-nitrobenzenesulfenyl chloride k_5 = 0, b_1 = 24.5. It is not unlikely that b_2 is zero for all of these substrates since in the chlorination of 4-substituted 2-nitrobenzenesulfenyl chlorides in sodium acetate–acetic acid solution, which kinetically is chlorine independent, lithium perchlorate was found to have a small decelerating effect on the reaction rate. In the present chlorine-independent reaction, added salt might be expected to have an even smaller effect in the more ionizing aqueous acetic acid solvent used here. Thus, the rate-retarding effect might disappear giving a b_2 value of zero.

The b_1 values of other substrates may be assumed to be close to the observed b = 24.5 for 2-nitrobenzenesulfenyl chloride.[21] Therefore, using these values, apparent rate constants (k_{app}) in lithium perchlorate solutions can be predicted (see Table VI). Agreement between calculated and observed apparent rate constants appears to support the projected values of b_1 and b_2.

Table VI

4 Substrate	[LiClO$_4$]	—k_{app} × 10^3 sec^{-1}— Calcd	Obsd
Cl	0.20	28.8	29.5
NO_2	0.20	9.8	11.4

The normal salt effect of lithium perchlorate is straightforward (Figure 6). The same reaction but with 0.0016 M sodium acetate, a concentration equivalent to the stoichiometric amount of hydrogen chloride formed in the reaction (eq 2), showed an initial sharp increase in reaction rate like a "special salt effect"[20] (k^0_{ext}/k^0 = 1.75, $[\mathrm{LiClO_4}]_{0.5}$ = 1.0 × 10^{-3} M) fol-

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(18) S. Winstein, E. Clippinger, A. H. Fainberg, R. Heck, and G. C. Rosinson, *J. Am. Chem. Soc.*, **78**, 328 (1956).

(19) A. H. Fainberg and S. Winstein, *ibid.*, **78**, 2763 (1956).

(20) S. Winstein, E. Clippinger, A. H. Fainberg, and G. C. Robinson, *ibid.*, **76**, 2597 (1954); A. Streitwieser, "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 168.

(21) Substituent effects on b values for lithium perchlorate are generally small in sulfonate acetolysis. Values for 4-bromo- and 4-methylbenzenesulfonic acid esters of three alcohols are respectively: neophyl, 15 and 12;[19] α-methylneophyl, 24 and 34;[22] cholesteryl, 30 and 28.[23] The b values for neophyl and p-methoxyneophyl p-toluenesulfonates are 15 and 12,[19] respectively. For more removed substituents p-methoxy-2-phenyl, o-methoxy-2-phenyl, and 2-phenylethyl p-toluenesulfonates, b values are 11, 13, and 14, respectively.[24]

(22) A. H. Fainberg and S. Winstein, *J. Am. Chem. Soc.*, **78**, 2780 (1956).

(23) S. Winstein and E. Clippinger, *ibid.*, **78**, 2784 (1956).

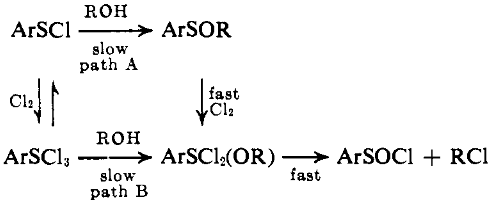
(24) A. H. Fainberg and S. Winstein, *ibid.*, **78**, 2767 (1956).

lowed by a normal salt effect ($b = 5$) (Figure 6 plotted from data in Table V). The slope of the normal salt effect is the same as that without added sodium acetate.

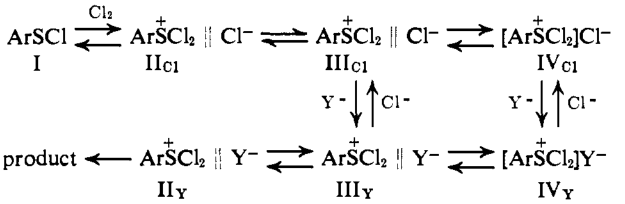
Since the appearance of a special salt effect was detected only in aqueous acetic acid in the presence of sodium acetate and lithium perchlorate combined, but not in the presence of either salt separately or in glacial acetic acid,[1a] an interaction between these two salts is the probable cause. One possible explanation might be that the increasing concentration of lithium perchlorate increases the polarity of the solvent medium and permits further dissociation of the sodium acetate ion pairs. The equilibrium is soon satisfied and further dissociation is negligible with increasing perchlorate.

Considerations Pertinent to the Reaction Mechanism. The two different sulfenyl chloride chlorination mechanisms identified earlier[1a] seem to merge in the aqueous acetic acid chlorination of *o*-nitrobenzenesulfenyl chlorides. The competition of electrophilic and nucleophilic reactions at bivalent sulfur is evident from the first- and zero-order chlorine-dependent terms, respectively, in the rate equation (eq 6). In Scheme I the nucleophilic reaction (path A) is formulated as a rate-determining SN2 substitution on the sulfenyl chloride, followed by rapid chlorine addition and sulfinyl chloride formation. The electrophilic reaction at bivalent sulfur (path B) is represented as a rapid and reversible chlorine addition to the sulfenyl chloride, followed by a rate-determining substitution on tetravalent sulfur by a hydroxylic component of the medium in an SN1 type process involving ionic intermediates (Scheme II).

Scheme I



Scheme II

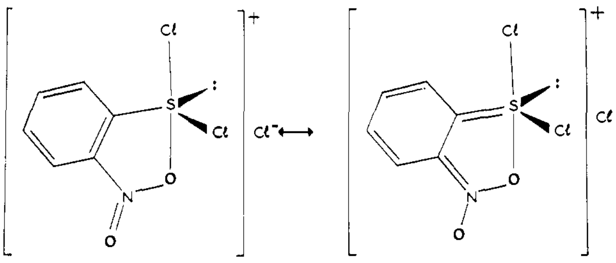


The relative competition between these two paths at particular chlorine concentrations can be expressed by a ratio (R) calculated as in Table IV. The data show that the greater the electron density at sulfur the greater the amount of electrophilic reactivity. Further, a significant shift of the equilibrium toward the sulfur trichloride component may be expected with greater electron density about sulfur; however, this need not be reflected in a change in the transition state or reactivity. This increased reactivity from increased electron density at sulfur ($\rho = -2.4$) was also observed in the 4-substituted benzenesulfenyl chloride series, which, however gave no evidence of reaction *via* path A (see Scheme I). In contrast, the chlorination of *o*-nitro substrate in glacial acetic acid with added acetate ion proceeds only by path A, which is chlorine independent. The question arises as to why the *o*-nitro substituent facilitates the nucleophilic reaction (path A) in preference to the (path B) electrophilic reaction? Moreover, how does the *o*-nitro group alter the reaction mechanism as a function of solvent ionizing power?

The structures of both the sulfenyl chloride and trichloride are pertinent to these questions. An X-ray diffraction study has established the structure of methyl 2-nitrobenzenesulfenate.[25] The O-S-O bond angle is 177° with an apparent strong nonbonded interaction between the sulfur and one nitro oxygen atom. Presumably the sulfenyl chloride will have a similar structure (V) where all of the atoms are coplaner.

A chlorine adduct of a sulfenyl chloride would be expected to have a trigonal-bipyramidal structure where chlorine atoms would occupy the axial positions and the electron pair be situated in an equatorial position.[26] This structure is assigned to analogous sulfur-fluorine compounds, *i.e.*, trifluoromethylsulfur trifluoride[27] and sulfur tetrafluoride.[28] An analogous structure has been proposed for a sulfide-chlorine adduct.[29]

Similar chlorine addition complexes of *o*-nitrobenzenesulfenyl chlorides are questionable because structure V, which has one of its axial positions occupied by a nitro oxygen atom, can accommodate only one chlorine atom entering as a chloronium ion. Straightforward addition of Cl_2 to V would result in 12 electrons around sulfur, for which no analogous sulfur compounds are known.[26] On the other hand, to accommodate the chloride ion, the nitro oxygen atom must be displaced from the axial position. This being unfavorable, an ion pair as in VI is an alternative. Such a structure would have added stability from π–d bond overlap (see VII) and be favored by ionic solvent conditions such as aqueous or methanolic acetic acid.



VI VII

Structure VI seemingly offers an explanation for the role of the *o*-nitro substituent. Specifically, the *o*-nitro group sterically can hinder the formation of the chlorine adduct. The electron-withdrawing effect of the nitro group likewise favors the sulfenyl chloride in the sulfenyl chloride–trichloride equilibrium (Scheme I). Also this group alters the reaction mechanism

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

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

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

(28) W. M. Tolles and W. D. Gwinn, *J. Chem. Phys.*, **36**, 1119 (1962).

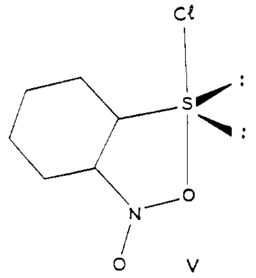
(29) K. Mislow, T. Simmons, J. T. Melillo, and A. L. Ternay, Jr., *J. Am. Chem. Soc.*, **86**, 1452 (1964).

as a function of solvent dielectric as discussed above. Indeed, the nitro group plays a very special role.

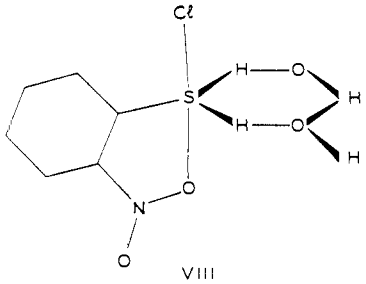
The dependence on water is quite unusual, especially since both the ionic (path B) and SN2 (path A) reactions have fourth-order dependence on water (eq 6). Water is not acting only in a solvation role since the nonionic path A is affected. Any mechanism which attempts to explain the role of water by hydrogen bonding to the nitro group to rotate it out of the axial position and thus make room for chlorine substitution must take into account the enhanced ability of acetic acid solvent to hydrogen bond. Another mechanism which attempts to explain the dependence on water by a pseudo-ring system of diprotonated sulfide VIII in order to account for two reactive water molecules does not explain why methanol will do the same thing, especially in the presence of the stronger acid, acetic acid.

The normal salt effect on path B by added lithium perchlorate and the absence of common ion rate depression conform to the mechanism described for the 4-substituted benzenesulfenyl chloride system, although the magnitudes of the *b* coefficients (eq 8) differ markedly: 24.5 (Table I) *vs.* 180.[1a] The ion equilibria developed earlier needs some alteration here, in that covalent structures are not involved in Scheme II as they appear to be in the earlier case. The absence of covalent chlorine adducts could explain the smaller *b* values for the *o*-nitro series. These ionic species are not as sensitive to very slight changes in solvent dielectric as the covalent trichloride. One might look upon the covalent trichloride as a haven to which the ionic species can retreat under low ionizing conditions; VI has no such shelter.

The normal salt effect requires ion-pair exchange; the absence of a special salt effect demonstrates against external ion-pair return. If external ion does occur, it is followed by exchange or conversion to dissociated ion. The absence of ion return ($IV_{Cl} \rightarrow III_{Cl}$) is in consonance with the absence of common ion rate depression.



V



VIII

The sulfenyl chloride hydrolysis and chlorine-independent chlorination reaction (path A) may have a common first step although the rate-determining processes in the two reactions are clearly not the same. For the hydrolysis reaction the slow step is subsequent to this first step, attack by water on the sulfenyl chloride. The acceleration by lithium perchlorate of the hydrolysis reaction (Table I) suggests that its slow step may be an ionization process. Sulfenium ions have not been formally considered here as intermediates in the chlorine-independent reaction or the hydrolysis reaction because present arguments against the intermediacy of these ions encourage their restricted application in mechanistic pathways.[1a] Strong evidence for their existence seems to be lacking at this time.