Bond Scission in Sulfur Compounds. V.[1] A Kinetic Study of Sulfur–Oxygen and Sulfur–Chlorine Bond Scission in the Methanolysis of *p*-Nitrophenyl Chlorosulfate

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A kinetic study of the reaction of *p*-nitrophenyl chlorosulfate with methoxide ion in methanol has been carried out over the temperature range 5–35°. The results are discussed in terms of two bond scission processes, S—O and S—Cl scission. A stereo-electronic factor is considered dominant in discussion of activation entropies.

L'étude cinétique de la réaction du chlorosulfate de *p*-nitrophényle avec l'ion méthylate en milieu méthanolique entre 5 et 35°, a permis de mettre en évidence la coupure des liaisons S—O et S—Cl. Les paramètres d'activation ont été mesurés pour chaque mode de coupure. Les entropies d'activation sont examinées en fonction d'un facteur stéréo-electronique.

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Reaction of phenyl chlorosulfate with methoxide ion in methanol yields products resulting from S—O bond scission and from S—Cl bond scission (1). Nucleophilic substitution at sulfur in $C_6H_5OSO_2Cl$ hence is associated with leaving group tendencies of phenoxy and chlorine which are approximately equal, in contrast to the situation for substitution at aliphatic carbon (2). To substantiate this unusual order of leaving group tendencies (3), study has been extended to *p*-nitrophenyl chlorosulfate, in which system it was anticipated that the reaction proceeding with S—O bond scission would become relatively more important. Further, with this substrate it appeared possible that yet another process might occur, namely nucleophilic substitution at aromatic carbon (4–7) with OSO_2Cl as the leaving group. The results of the investigation are now reported.

Experimental

p-Nitrophenyl chlorosulfate was prepared from *p*-nitrophenol and sulfuryl chloride in anhydrous ether in presence of pyridine and purified by treatment with boron trichloride according to the method of Gerrard (8). The product obtained on final distillation, b.p. 137–138°/5 mm, slowly crystallized when kept in the refrigerator. The solid material was recrystallized twice from methanol – petroleum ether to yield pale yellow crystals, m.p. 28°; λ_{max} 254 nm (ε 10150) in methanol.

Anal. Calcd. for $C_6H_4O_5ClNS$: C, 30.33; H, 1.70; Cl, 14.92; N, 5.90; S, 13.50. Found: C, 30.84; H, 1.76; Cl, 15.02; N, 5.69; S, 13.27.

Methyl *p*-nitrophenyl sulfate was prepared from *p*-nitrophenyl diazonium fluoroborate and dimethyl sulfate by the method of Whiting and co-workers (9). The product was recrystallized from CCl_4, m.p. 45°; λ_{max} 258 nm (ε 9350) in ether.

Anal. Calcd. for $C_7H_7O_6NS$: C, 36.07; H, 3.03; N, 6.01; S, 13.76. Found C, 35.86; H, 2.59; N, 6.05; S, 13.70.

p-Nitrophenyl sulfate was obtained as the potassium salt from Sigma Chemicals. It was analyzed spectrophotometrically after complete acid hydrolysis to *p*-nitrophenol, which was obtained in 98% yield. (The commercial material was first shown to be free of *p*-nitrophenol.)

Preparation of reaction solutions and the details of the kinetic method were as described previously (1).

Results

Reaction of *p*-nitrophenyl chlorosulfate with methoxide ion in methanol as followed spectrophotometrically results in the appearance of an absorption at 390 nm due to the liberation of *p*-nitrophenoxide ion. However, the 390 nm absorption does not reach the maximum value corresponding to 100% formation of *p*-nitrophenoxide ion based on the initial stoichiometric concentration of substrate. At a given temperature the yield of *p*-nitrophenoxide ion remains constant as the methoxide ion concentration is varied but on increasing the temperature this yield increases (Table 1). Plots of log $(A_\infty - A_t)$ *vs.* time, where A_∞ is the experimental absorbance value at 390 nm on completion of reaction, are linear and yield the pseudo first-order rate constants (k_{obs}) at given methoxide ion concentrations (Table 1).

The probable identity of the second reaction product was considered to be methyl-*p*-nitrophenyl sulfate, resulting from concurrent S—Cl

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[1] For part IV in series, see ref. 1.

TABLE 1. Rate data for reaction of *p*-nitrophenyl chlorosulfate ($5 \times 10^{-5} M$) with sodium methoxide in methanol

Temperature (°C)	[CH_3ONa] ($\times 10^3 M$)	$10^3 k_{obs}$ (s^{-1})	% yield ArO^-	k_{tot}* ($l\ mol^{-1}\ s^{-1}$)	k_{ArO^-}† ($l\ mol^{-1}\ s^{-1}$)	k_{Cl^-}‡ ($l\ mol^{-1}\ s^{-1}$)
5.69	1.30	0.575	67.9	0.443	0.302	0.142
	2.61	1.16	68.1			
	5.22	2.37	68.1			
	7.83	3.48	67.6			
	10.44	4.62	68.8			
			68.1±0.4§			
15.04	1.30	1.54	76.3	1.27	0.963	0.310
	2.61	3.40	75.0			
	5.22	6.90	75.6			
	7.83	9.97	76.2			
	10.44	13.2	75.8			
			75.8±0.4§			
25.00	1.30	5.48	80.6	4.10	3.35	0.750
	2.61	11.2	82.2			
	5.22	20.7	81.7			
	7.83	33.9	81.9			
	10.44	42.2	81.7			
			81.6±0.5§			
34.84	1.30	13.2	85.0	11.16	9.30	1.86
	2.61	28.2	84.3			
	5.22	53.2	82.0			
	7.83	84.7	82.6			
	10.44	115.7	82.8			
			83.3±1.1§			

*Computed slope in plot of k_{obs} *vs.* [CH_3O^-] using a least-squares program.
†$k_{ArO^-} = k_{tot} \times$ % yield *p*-nitrophenoxide ion.
‡$k_{Cl^-} = k_{tot} - k_{ArO^-}$.
§Standard deviation.

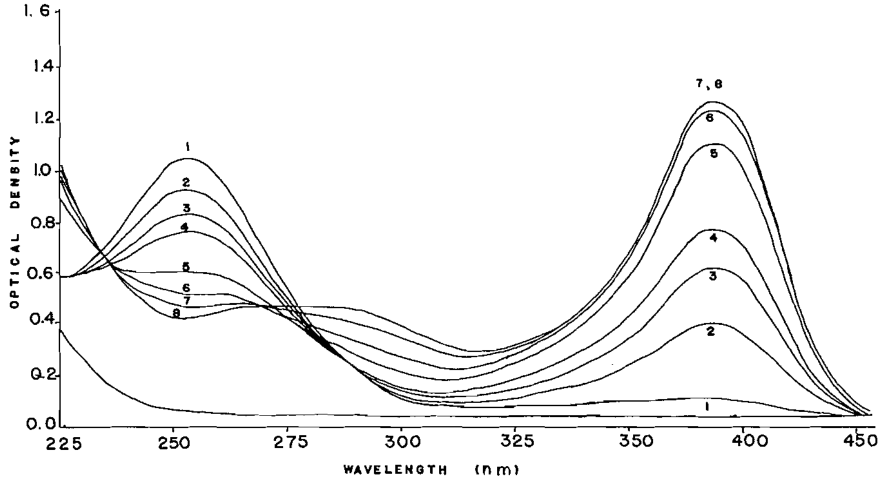


FIG. 1. Spectral scans for reaction of *p*-nitrophenyl chlorosulfate ($5.00 \times 10^{-5} M$) with methanolic sodium methoxide ($1.31 \times 10^{-3} M$) at 5.68°. Spectra taken at various times: no. 1, 1 min; no. 4, 10 min; no. 7, 30 min; no. 8, 1200 min.

scission, by analogy with the phenyl chlorosulfate–methoxide reaction (1). An alternative possibility would be *p*-nitroanisole, the product of substitution at aromatic carbon. In fact spectra of "mock infinity" solutions prepared from calculated amounts of *p*-nitrophenol and methyl-*p*-nitrophenyl sulfate in methanolic sodium methoxide correspond within experimental

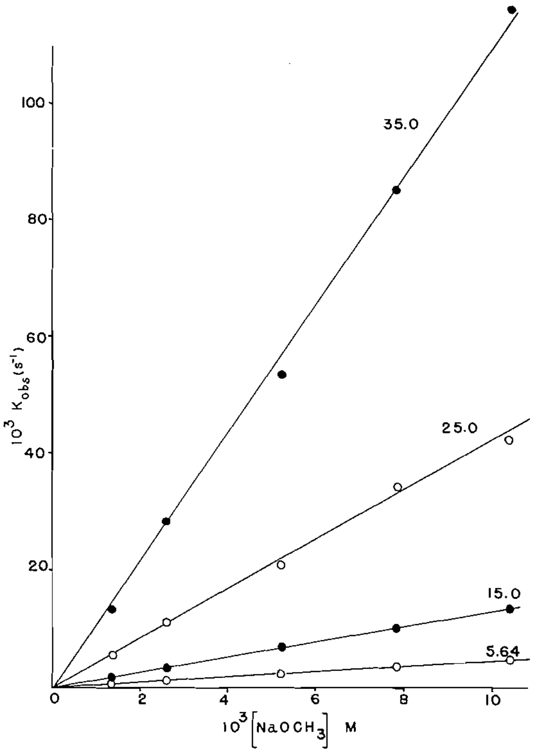


FIG. 2. Plots of k_{obs} *vs.* [CH$_3$O$^-$] at various temperatures for reaction of *p*-nitrophenyl chlorosulfate with methoxide ion.

error with spectra of solutions resulting on completion of reaction between *p*-nitrophenyl chlorosulfate and methoxide. When *p*-nitroanisole was substituted for methyl-*p*-nitrophenyl sulfate (20% *p*-nitroanisole/80% *p*-nitrophenoxide), the spectrum was significantly different in the 300 nm region from that of the experimental infinity solution (in methanolic sodium methoxide *p*-nitroanisole has λ_{max} at 305 nm (ε 12 000) whereas methyl-*p*-nitrophenyl sulfate has λ_{max} at 260 nm (ε 9400) and only small absorption at 305 nm (ε 930)).

Further evidence indicating that the second reaction product was methyl-*p*-nitrophenyl sulfate was found in the consecutive solvolysis of the latter yielding *p*-nitrophenyl sulfate. This secondary reaction was detected spectrally in the *p*-nitrophenyl chlorosulfate – MeO$^-$ reaction as a continuing increase in absorption in the 275–325 nm region once the absorption at 390 nm had reached *ca.* 90% of its maximum value. *p*-Nitrophenyl sulfate absorbs at 283 nm (ε 9200), it has negligible absorption at 390 nm, and is stable in the methanolic methoxide solutions (*cf.* refs. 10, 11). The increase in absorption was also seen in the "mock infinity" solution spectra prepared from *p*-nitrophenol and methyl-*p*-nitrophenyl sulfate. In contrast, the solutions containing *p*-nitrophenoxide and *p*-nitroanisole showed no spectral change, as expected.

Selected spectra obtained in a kinetic run with *p*-nitrophenyl chlorosulfate and methoxide ion are shown in Fig. 1 to illustrate the various spectral changes. It is seen that the reasonably good isosbestic behavior, which is maintained during most of the primary reaction, becomes progressively more poorly defined as the secondary solvolysis reaction takes over.

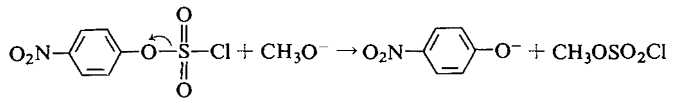
The evidence presented above is fully consistent with the occurrence of two parallel processes in the reaction of *p*-nitrophenyl chlorosulfate with methoxide ion: S—O scission yielding *p*-nitrophenoxide ion and S—Cl scission yielding methyl-*p*-nitrophenyl sulfate.

The dissected rate constants for the two parallel processes are obtained by standard methods (12, 13). The total second-order rate constant, $k_{tot} = k_{ArO^-} + k_{Cl^-}$, is obtained from the linear plot of k_{obs} *vs.* [CH$_3$O$^-$], Fig. 2. The constituent rate constants, k_{ArO^-} and k_{Cl^-}, are then obtained from the fractional yields of the products. The resulting data at various temperatures are given in Table 1, while Table 2 contains the derived activation parameters. The Arrhenius plots for the two processes are presented in Fig. 3.

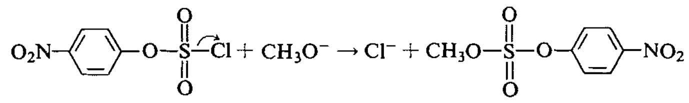
Discussion

The parallel reactions representing S—O bond scission and S—Cl bond scission are given by reactions 1 and 2. Nucleophilic displacement

[1]



[2]



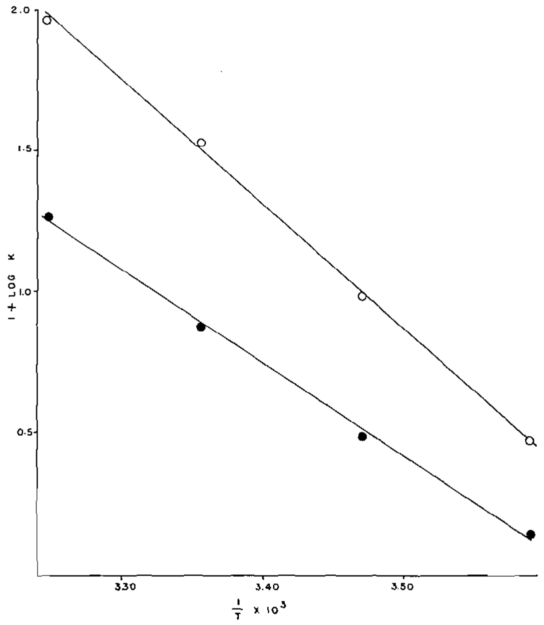


FIG. 3. Arrhenius plots for the two bond scission processes in the methanolysis of *p*-nitrophenyl chlorosulfate: *p*-nitrophenoxide ion leaving (open circles) and chloride ion leaving (full circles).

at aromatic carbon has not been detected. Reactions 1 and 2 are both followed by secondary processes. The methyl chlorosulfate formed in reaction 1 will undergo rapid solvolysis yielding dimethyl ether (14) (OSO_2Cl^- leaving group). The methyl-*p*-nitrophenyl sulfate produced in reaction 2 undergoes relatively slow solvolysis as described above (*p*-nitrophenyl sulfate leaving group).

Comparison with the phenyl chlorosulfate–methoxide system shows that S—O scission is relatively more important in the nitro-substituted case. For instance the 82% yield of *p*-nitrophenoxide ion at 25° (Table 1) compares with only 39% yield of phenoxide ion at this temperature (1). This observation is in accord with *p*-nitrophenoxide being the better leaving group compared to phenoxide. It is interesting that for S—O scission the rate constant ratio $(k'/k)_{\mathrm{S—O}}$ at 25° for the two systems is 93, whereas for S—Cl scission the $(k'/k)_{\mathrm{S—Cl}}$ ratio is 13, where k' and k are the constituent rate constants at 25° in reaction of *p*-nitrophenyl chlorosulfate and of phenyl chlorosulfate respectively. At the other temperatures the rate ratios take on somewhat different values, though the orders of magnitude remain unchanged. In energy terms S—O scission is favored for *p*-nitrophenyl chlorosulfate over the unsubstituted compound by a $\Delta\Delta F^{\ddagger}$ value of 2.8 kcal/mol, whereas the S—Cl scission process is favored in the same direction by a $\Delta\Delta F^{\ddagger}$ value of only 1.5 kcal/mol.

Clearly the sulfur center is more positively charged in *p*-nitrophenyl chlorosulfate than in the unsubstituted isomer, which should lead to a greater extent of bond formation between methoxide ion and sulfur in the transition state for the *p*-nitrophenyl chlorosulfate reaction. The resulting gain in bond energy is expected to make $\Delta H^{\ddagger}$ smaller in the case of *p*-nitrophenyl chlorosulfate for both S—O and S—Cl scissions, as observed experimentally (Table 2). Similarly, the concomitant greater desolvation of MeO^- in the *p*-nitrophenyl chlorosulfate case will result in a more positive $\Delta S^{\ddagger}$ value in that system compared with the phenyl chlorosulfate case, as observed.

It will be noted (Table 2) that a striking dissimilarity exists between the $\Delta S^{\ddagger}$ values for the S—O and the S—Cl pathways, the former being associated with a rather large positive entropy of activation. In the case of S—Cl scission, the entropy of activation is negative, as reported for the hydrolysis of sulfonyl chlorides (15–17). Though the greater solvation of the incipient chloride ion, compared with the aryloxide ion, in the transition state will tend to lead to a more negative $\Delta S^{\ddagger}$ in the former case, it appears unlikely that such differential solvation would account for a difference in $\Delta S^{\ddagger}$ of about 20 e.u. The positive $\Delta S^{\ddagger}$ for S—O scission is hence ascribed largely to a stereo-electronic effect.

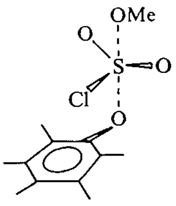
The ground state conformation of aryl chlorosulfates (18), with the chlorine atom above the plane of the benzene ring, is associated with considerable internal strain and restricted rotation about the aryloxy–sulfur bond as well as about the carbon–oxygen bond. In the transition states (**1** and **2**) for nucleophilic attack by CH_3O^- at sulfur (trigonal bipyramidal configurations resulting from backside nucleophilic attack with respect to the departing ligand), S—O cleavage (**1**) will result in a relief of internal strain but S—Cl cleavage (**2**) does not lead to such relief of strain. Further, partial rupture of the S—O bond is accompanied by a

TABLE 2. Activation parameters for reactions of *p*-nitrophenyl chlorosulfate and phenyl chlorosulfate with methoxide ion in methanol*

Parameter	Value			
	S—O scission		S—Cl scission	
	p-$NO_2.C_6H_4.OSO_2Cl$	$C_6H_5OSO_2Cl$	p-$NO_2.C_6H_4.OSO_2Cl$	$C_6H_5OSO_2Cl$
ΔH^* (kcal mol^{-1})	19.5	21.5	14.4	15.1
ΔS^* (cal deg^{-1} mol^{-1})	9.3	7.0	−10.8	−13.8
ΔF^* (kcal mol^{-1}) at 25°	16.8	19.6	17.7	19.2

*Data for phenyl chlorosulfate are taken from ref. 1.

gain in vibrational and rotational degrees of freedom, an effect absent in S—Cl bond weakening. The combined result of these effects will be to yield a considerably more positive $\Delta S^{\ddagger}$ for aryloxide displacement.



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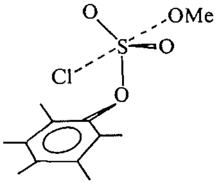

2

The *p*-nitrophenyl chlorosulfate–methoxide ion reaction has been considered only within the framework of the two parallel processes mechanism. An alternative possibility, that a pentacoordinate intermediate (19–22) is formed which then partitions along two paths with *p*-nitrophenoxy and chlorine departing, is considered to be unlikely as has been discussed for the phenyl chlorosulfate–methoxide ion system (1).

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