Bond Scission in Sulphur Compounds. Part IV.[1] Sulphur–Oxygen *versus* Sulphur–Chlorine Bond Scission in the Methanolysis of Phenyl Chlorosulphate. Kinetics and Mechanism

By **E. Buncel,*** (Miss) **L. I. Choong**, and **A. Raoult**, Department of Chemistry, Queen's University, Kingston, Ontario, Canada

The reaction of phenyl chlorosulphate with methoxide ion in methanol yields products resulting from S–O and S–Cl bond scission. The yields of phenoxide ion and of methyl phenyl sulphate show a temperature dependence which is consistent with the occurrence of two parallel reactions with different energies of activation. There is an effective compensation in $\Delta H^‡$ and $\Delta S^‡$ in the two reactions. The activation parameters are discussed, in particular the positive $\Delta S^‡$ value for S–O scission. An alternative mechanism, involving a pentaco-ordinate intermediate, cannot be excluded by the results but is considered to be unlikely.

THE presence in chlorosulphates ($RO{\cdot}SO_2Cl$) of more than a single electrophilic reaction centre differentiates this class of acid halide from substrates such as sulphonyl chlorides and acyl chlorides and renders study of their nucleophilic reactions of special interest.[2] We have shown previously[3] that alkyl chlorosulphates react under solvolytic conditions and with some common nucleophiles by attack at carbon ($O{\cdot}SO_2Cl^-$ as the leaving group); attack at sulphur (Cl^- as the leaving group) is only a minor competing process. The latter reaction was observed in the propanolysis of n-propyl chlorosulphate, where formation of di-n-propyl sulphate accounted for *ca.* 5—10% of the total reaction; the major product was di-n-propyl ether which resulted from attack at carbon.[1] The possibility of a fragmentation process ($R \cdots O{\cdot}SO_2 \cdots Cl$) in the hydrolytic reactions of chlorosulphates has been noted.[4]

Phenyl chlorosulphate appeared to be suitable for the study of substitution at sulphur, since substitution at the unactivated aryl carbon atom should be extremely unlikely.[5-8] The results of the reaction of phenyl chlorosulphate with methoxide ion in methanol are now reported.

EXPERIMENTAL

Phenyl chlorosulphate was prepared by the action of sulphuryl chloride on phenol in presence of pyridine in anhydrous ether and was purified by treatment with boron trichloride.[9] Phenyl methyl sulphate was prepared by the method of Whiting *et al.*[10] A solution of sodium methoxide was obtained by dissolving clean sodium metal in dry methanol and was standardized by titration.

The reaction of phenyl chlorosulphate with methoxide ion was followed spectrophotometrically with $[MeO^-] \gg$ [substrate]. Runs were initiated by the addition, with a syringe, of a stock solution of substrate in methanol (0·05 ml) to sodium methoxide in methanol (5 ml) pre-equilibrated in a thermostatted cuvette (20 mm) in the cell compartment of a Unicam SP 800 spectrophotometer. Temperatures were measured by means of a thermocouple. Mixing was effected by means of a glass microstirrer driven by nitrogen gas, the stirring blade being out of the path of the light beam. Reactions with half-lives $\geqslant$*ca.* 2 s could be measured using this technique. The faster reactions were followed by monitoring the increase in absorbance at 288 nm corresponding to the formation of phenoxide ion. The slower reactions (at 5 and 15°) were followed by repeated scanning over the region 225—350 nm. Full spectra were taken at the completion of reaction in all cases.

Pseudo first-order rate constants (k_{obs}) were calculated from the linear plots of log ($A_\infty - A_t$) *vs.* time, where A_t and A_∞ are the absorbances at 288 nm at time t and at the completion of reaction. Second-order rate constants were obtained from the slopes of the linear plots of k_{obs} *vs.* $[CH_3O^-]$ using a least squares program. The error in k_{tot} is thus estimated at 2%.

RESULTS

The reaction of phenyl chlorosulphate with methanolic sodium methoxide is characterized by the appearance of absorption at 288 nm due to phenoxide ion, with shoulders at 264 and 272 nm due to phenyl methyl sulphate. At 25° the yields of the two products are 39 and 61%, respectively. The yield of phenoxide ion is calculated from the observed extinction at 288 nm; the yield of methyl phenyl sulphate is taken as the difference between the initial stoicheiometric concentration of phenyl chlorosulphate and the measured yield of phenoxide ion. The theoretical molar extinction coefficient of phenoxide ion in methanol at 288 nm is 2680. Methyl phenyl sulphate has absorptions in methanolic sodium methoxide at 272 (ε 223), 264 (338), and 257 nm (321) and has negligible absorption at 288 nm, the $\lambda_{max.}$ for phenoxide ion. Spectra of 'mock infinity' solutions of phenol and of methyl phenyl sulphate in methanolic sodium methoxide corresponded within experimental error to the experimentally observed spectra resulting from phenyl chlorosulphate on completion of reaction. Methyl phenyl sulphate was shown to be stable under the reaction conditions.

The relative yields of phenoxide ion and of methyl

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phenyl sulphate are independent of the initial concentrations of methoxide ion but are dependent on the reaction temperature. With increasing temperature the yield of phenoxide ion increases and that of methyl phenyl sulphate correspondingly decreases. The relevant experimental data are given in the Table.

Rate data for reaction of phenyl chlorosulphate (2 × 10^{-4}M) with methoxide ion in methanol

Temp. (°C)	[MeONa]/ mol l^{-1}	10^2k_{obs}/ s^{-1}	Yield PhO$^-$ (%)	k_{tot} [a]/ l mol^{-1} s^{-1}	k_{PhO^-} [b]/ l mol^{-1} s^{-1}	k_{Cl^-} [c]/ l mol^{-1} s^{-1}
5·58	0·0326	0·0402	20·6	0·0122	0·00272	0·00945
	0·0652	0·0805	22·6			
	0·104$_4$	0·130	23·6			
	0·130$_5$	0·157	22·6			
			22·3 ± 1·1 [d]			
15·00	0·0326	0·114	29·5	0·0353	0·0109	0·0244
	0·0652	0·228	30·9			
	0·1044	0·371	31·6			
	0·130$_5$	0·458	31·6			
			30·9 ± 0·9 [d]			
25·00	0·0326	0·295	37·0	0·0932	0·0360	0·0572
	0·0652	0·600	38·9			
	0·1044	0·920	39·5			
	0·130$_5$	1·24	39·3			
			38·7 ± 1·0 [d]			
35·00	0·0326	0·825	44·7	0·268	0·125	0·143
	0·0652	1·68	46·5			
	0·1044	2·73	47·9			
	0·130$_5$	3·52	47·7			
			46·7 ± 1·3 [d]			

[a] Computed slope of plot of k_{obs} *vs.* [MeO$^-$] using a least-squares program. [b] $k_{PhO^-} = k_{tot} \times$ % yield phenoxide ion. [c] $k_{Cl^-} = k_{tot} - k_{PhO^-}$. [d] Standard deviation.

The formation of two reaction products whose relative yield remains constant as the methoxide ion concentration is varied is indicative of two parallel reactions first order in methoxide ion.[11] The observed rate constant is hence a total second-order rate coefficient multiplied by [OMe$^-$]. Thus if k_{PhO^-} and k_{Cl^-} are the rate constants for the two processes with phenoxide ion and chloride ion as the leaving group then the relationship (1) follows; k_{tot} is

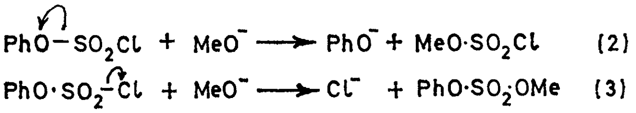
$$k_{obs} = (k_{PhO^-} + k_{Cl^-})[MeO^-] = k_{tot}[MeO^-] \qquad (1)$$

obtained from the slope of k_{obs} *vs.* [MeO$^-$], and k_{PhO^-} and k_{Cl^-} are given by the fractional yields of phenoxide ion of methyl phenyl sulphate respectively. The separated rate constants so obtained are also listed in the Table.

The energies of activation for the two processes are obtained from plots of log k_{PhO^-} *vs.* $1/T$ and log k_{Cl^-} *vs.* $1/T$. Enthalpies and entropies of activation were computed using standard expressions. For S–O scission [reaction (2)], $\Delta H^\ddagger = 90{\cdot}0 \pm 1{\cdot}3$ kJ mol^{-1}, $\Delta S^\ddagger = 29{\cdot}3 \pm 1{\cdot}7$ J K^{-1} mol^{-1}, and $\Delta F^\ddagger = 82{\cdot}0$ kJ mol^{-1}. For S–Cl scission [reaction (3)] $\Delta H^\ddagger = 63{\cdot}2 \pm 0{\cdot}8$ kJ mol^{-1}, $\Delta S^\ddagger = -57{\cdot}8 \pm 2{\cdot}5$ J K^{-1} mol^{-1}, and $\Delta F^\ddagger = 80{\cdot}4$ kJ mol^{-1}.

DISCUSSION

The formation of two products, phenoxide ion and methyl phenyl sulphate, in the reaction of phenyl chlorosulphate with methanolic sodium methoxide is consistent with the occurrence of the two parallel reactions (2) and (3). Both reactions involve nucleophilic displacement at sulphur but in reaction (2) the leaving group is phenoxide ion while in reaction (3) chloride ion is the leaving group. The methyl chlorosulphate formed in reaction (2) will be unstable in methanolic sodium methoxide and undergo solvolysis at the carbon atom with formation of dimethyl ether as the main decomposition reaction (*cf.* ref. 1).



$$PhO{-}SO_2Cl + MeO^- \longrightarrow PhO^- + MeO{\cdot}SO_2Cl \qquad (2)$$

$$PhO{\cdot}SO_2{-}Cl + MeO^- \longrightarrow Cl^- + PhO{\cdot}SO_2OMe \qquad (3)$$

The widely different activation parameters for the parallel reactions (2) and (3) have significance for the characteristics of the two bond scission processes. $\Delta H^\ddagger$ is considerably higher for reaction (2) but $\Delta S^\ddagger$ is more positive by *ca.* 86 J K^{-1} mol^{-1}, with the result that $\Delta F^\ddagger$ is only slightly greater for the phenoxide ion reaction. Thus there is an effective compensation in enthalpies and in entropies of activation.[12]

The activation process for reactions (2) and (3) involves in each case partial bond formation at the sulphur atom by methoxide ion. If bond formation in the two transition states occurs to the same extent, then the requisite desolvation of methoxide ion will be the same in both processes. On that basis the relative values of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ would be ascribed principally to the different nature of the bond rupture processes. The larger $\Delta H^\ddagger$ value for reaction (2) is in accord with the greater bond energy of the S–O bond (301 kJ mol^{-1}) compared with that of the S–Cl bond (251 kJ mol^{-1}). Concerning $\Delta S^\ddagger$, the incipient chloride ion in the transition state of reaction (3) will have a greater solvation requirement compared with the phenoxide ion in reaction (2), which will result in a more negative $\Delta S^\ddagger$ value in the former case, as observed. Hydrolysis of sulphonyl chlorides is associated with negative $\Delta S^\ddagger$ values.[13-15]

In addition to the solvation factor discussed above, the entropies of activation may also be determined in part by a stereoelectronic factor. Thus in the ground-state conformation of phenyl chlorosulphate in benzene,[16] as indicated (structure A) in the Newman projection viewed along the S–O bond, the chlorine is situated approximately above the plane of the benzene ring (Cl–S–O–C dihedral angle 0—60°). In this conformation there is considerable interaction between the chlorine atom and the phenyl group and a partial

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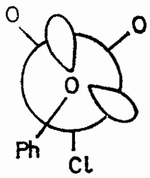
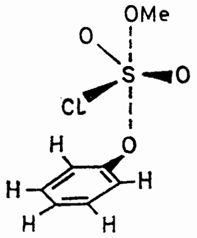
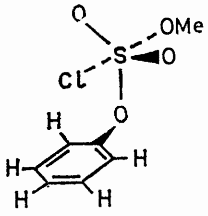
restriction in rotation about the S–O bond, as well as a severe restriction in rotation about the C–O bond. Thus phenyl chlorosulphate can be considered as a molecule with internal strain, whose internal rotational and vibrational degrees of freedom are restricted. On the assumption that phenyl chlorosulphate in methanol reacts in this conformation (A) and that displacement occurs by back-side attack at the sulphur atom, one obtains the transition states B and C for the cases of phenoxide and chloride ion displacement, respectively. The important difference in these transition states is that in B a considerable relief in internal strain results upon partial rupture of the S–O bond, while no such effect accompanies S–Cl rupture in C. It is suggested that the positive $\Delta S^\ddagger$ value in phenoxide ion displacement arises in large measure from the relief in the transition state of internal interactions present in the ground state, with a concomitant gain of vibrational and rotational degrees of freedom. This effect could be further enhanced if the phenoxy-oxygen–sulphur bond possessed in the ground state any partial double bond character, as this would also be relieved in the transition state. Electron donation to sulphur has been considered to contribute to the ground-state properties of *N*-sulphenylsulphonamides,[17] aryl sulphanilides,[18] and dialkylsulphamoyl chlorides.[19]



A

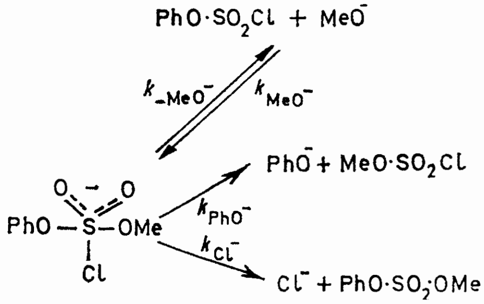


B



C

Finally, one should consider also an alternative explanation of the formation of two products in the reaction of phenyl chlorosulphate with methoxide ion. In accord with postulates for pentaco-ordinate intermediates in substitution at a sulphur atom,[20-23] it is conceivable that in the present system the reaction pathway involves formation of a metastable intermediate, present in steady-state concentration, which then decomposes along two routes as shown in equation (4). The case that decomposition of the intermediate is rate-determining, *i.e.* that $k_{-\text{MeO}^-} > k_{\text{PhO}^-} + k_{\text{Cl}^-}$, is highly unlikely since methoxide ion should be a much poorer leaving group than phenoxide or chloride ion. However, the alternative possibility, that formation of intermediate is rate-determining, *i.e.* that $k_{-\text{MeO}^-} < k_{\text{PhO}^-} + k_{\text{Cl}^-}$, may not be excluded. The observed comparable leaving group facility of chloride and phenoxide ion might well be indicative of this pathway. However it would seem most unlikely that the bond rupture processes in the decompositions of the intermediate, both being essentially fast reactions, should be associated with so widely different enthalpies and entropies of activation.* This consideration, as well as the lack of definitive evidence for pentaco-ordinate intermediates in substitution at sulphonyl centres, leads us to prefer the simultaneous reactions (2) and (3).



(4)

The balance of bond scission processes in the reactions of chlorosulphates will be investigated in related systems.

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* For the mechanism of equation (4), a plot of log (% yield PhO^-)/(% yield $PhO{\cdot}SO_2{\cdot}OMe$) *versus* $1/T$ gives the difference in the activation energies for the partitioning paths of the intermediate in S–O rupture and S–Cl rupture. One thus obtains $\Delta\Delta H^\ddagger = 26{\cdot}8$ kJ mol^{-1} and $\Delta\Delta S^\ddagger = 85{\cdot}8$ J K^{-1} mol^{-1}.

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