Reaction of Phenyl Chlorosulphate with Anions. A Possible Displacement at Chlorine

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Summary Kinetic data are reported for formation of phenol in reaction of phenyl chlorosulphate with anions and a possible mechanism involving initial nucleophilic attack at chlorine is proposed.

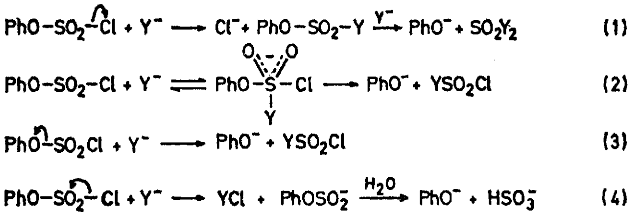
IN studies of nucleophilic reactivity at sulphur, its oxidation states are of particular interest. Previous studies[1a,b] with $ROSO_2Cl$[1c] were concerned principally with carbon as the electrophilic centre. Nucleophilic substitution at sulphur has been detected hitherto only as a minor competing process.[1b]

Reaction of phenyl chlorosulphate with various anions was studied spectrophotometrically in 1% aqueous ethanol in an acetate buffer (pH 5·0—5·5) at 25° under first-order conditions, with the anion in large excess. As an example, in the reaction of I^- with phenyl chlorosulphate one observes the appearance of a spectral absorption characteristic of phenol which is produced quantitatively. The rate of reaction was measured by following the increase in absorbance at 270 nm and the pseudo-first-order rate constant, k_{obs}, was obtained from the linear plot of log $(A_\infty - A_t)$ *vs.* time. Rates measured over a range of anion concentration yield the second-order rate constant, k_N (Table). Kinetic data obtained with other nucleophiles are also recorded in the Table. In the case of Na_2SO_3 the reactive species was shown to be SO_3^{2-}, rather than HSO_3^-, by the usual techniques.[2] In addition to the results in the Table, the rate of reaction of the thiosulphate anion was too large to be measurable, and Br^-, Cl^-, and F^-, had a very small effect on the rate of formation of phenol in the acetate buffers. Thus the observed order of nucleophile reactivity toward phenyl chlorosulphate is $S_2O_3^{2-} > CN^- > I^- > SO_3^{2-} > SCN^- >> Br^-,\ Cl^-,\ F^-,\ AcO^-$. The overall reaction is:

$$PhOSO_2Cl + 2H_2O \xrightarrow{Y^-} PhOH + H_2SO_4 + HCl.$$

Possible mechanistic pathways are indicated in reactions (1)—(4).

The pathway in reaction (1) is unlikely, since, if $PhOSO_2Y$ were first formed it would presumably have to react further with Y^- (or solvent) by attack at sulphur and a leaving-group order $PhO^- > Y^-$ would be required. (For $Y^- = I^-$ the leaving group order would be $PhO^- < Cl^-$ in the first stage and $PhO^- > I^-$ in the second stage, which is quite improbable). Concerning (2), there is at present no positive evidence for formation of a five-co-ordinate intermediate in reactions at sulphonyl centres[3] and there is no requirement for such a postulate in the present case.



The direct displacement pathway (3) would correspond to the leaving group order $PhO^- > Cl^-$, which is apparently unprecedented for four-co-ordinate sulphur or carbon.[4] Further, the high reactivity of polarizable nucleophiles presently observed suggests a soft electrophilic site. In aryl disulphones,[3b] the sulphonyl centre has been termed hard on the basis of high reactivity of non-polarizable nucleophiles such as F^-. Similarly, in reaction of benzenesulphonyl chloride with nucleophiles,[5] where it was concluded that a normal displacement at sulphur occurs with chloride leaving, the polarizable I^- and SCN^- ions were found to be unreactive.

TABLE

Rate constants, k_N, for reaction of phenyl chlorosulphate with nucleophiles in 1% aqueous ethanol at 25°[a]

Anion[b]	pH[c]	k_N ($l\ M^{-1}\ s^{-1}$)
SCN^-	5·06	0·353
SO_3^{2-}	5·45	2·55
I^-	5·06	15·9
CN^-	5·50	4300

[a] Reactions were followed in a thermostatted cell, with a concentration of phenyl chlorosulphate of $2·5—5 \times 10^{-5}$ M. [b] The anions were present as sodium salts, in the concentration range $1 \times 10^{-3}—5 \times 10^{-2}$M depending on nucleophile reactivity. With SO_3^{2-} and CN^- correction was made for the fraction of reagent present as the free base at a given pH on the basis of their pK_a values. [c] Acetate buffers with [NaOAc] = 0·05M except for CN^- runs where a better pH control was obtained with [NaOAc] = 0·097M.

As indicated previously, nucleophilic displacement at chlorine [pathway (4)] results in initial formation of phenyl sulphite ion, which will be hydrolysed rapidly to phenol and HSO_3^-. The latter is expected to be oxidized by the pseudo-halogen formed in the first stage of the reaction, yielding HSO_4^- and Cl^- and regenerating the anionic nucleophiles.

Nucleophilic displacement at halogen centres has been investigated in a few instances only[6] and there are no reports of quantitative data for displacement at chlorine. However, in those cases where displacement at univalent halogen has been observed (or proposed), relatively polarizable nucleophiles have been involved. Thus, while alkoxides and amines react with sulphonyl halides by attack at sulphur, the 'softer' mercaptide and carbanion reagents give products suggestive of attack at chlorine.[7] Nucleophilic displacement at aromatic halogen by the dimsyl anion[6b] and several aryl anions [6c] has also been observed. A nucleophilicity order $I^- > Br^- > Cl^- > Sn^{2+}$ has been observed for attack at bromine in the debromination of dibromostilbene.[6d]

Thus, univalent halogen appears to be a 'soft' electrophilic site. On this basis, it is reasonable to conclude that the reactivity order which we have observed in the phenyl chlorosulphate–anion system is consistent with nucleophilic displacement at chlorine.

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