Ion-pairing Phenomena involving Sulphonium Cation Intermediates in the Chlorinolysis of Carbon–Sulphur Bonds

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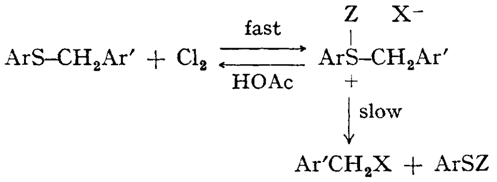
THE normal course of chlorinolysis of carbon–sulphur bonds in arylalkyl sulphides[1,2] is best expressed by the equation:



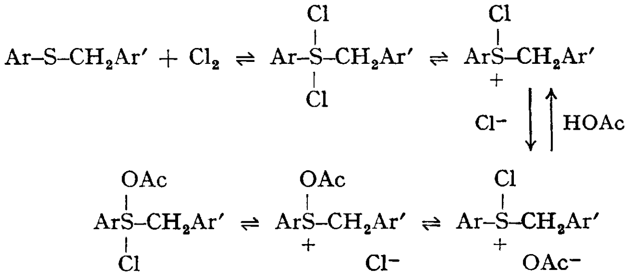
$$\mathrm{ArS{-}CH_2Ar' + Cl_2 \underset{HOAc}{\overset{fast}{\rightleftarrows}} Ar\overset{Z}{\underset{+}{S}}{-}CH_2Ar'\ X^-}$$

$$\Big\downarrow \text{slow}$$

$$\mathrm{Ar'CH_2X + ArSZ}$$

(X^- and Z^- may be Cl^- or AcO^-)

Although it might be presumed by analogy to the work of Hughes and Ingold[3] on the solvolysis of t-alkyldimethylsulphonium derivatives that a classical S_N1 process is involved, a kinetic study of the chlorinolysis of various *para*-substituted benzyl phenyl sulphides discloses a much greater degree of mechanistic complexity. Thus, when such substrates in glacial acetic acid are rapidly mixed with carefully measured quantities of chlorine in the same solvent, a strong u.v. absorbance instantly appears (390 mμ), which is characteristic of neither the separate reactants nor the isolated products. The decay of this absorbance, when pursued with a responsive recording spectrophotometer, follows a good first-order rate law. It has been suggested[4] that the absorbing species is part of a rapidly established equilibrium of covalent (non-absorbing) and ionic (absorbing) components, some of which are more favoured in acetic acid solutions.



$$\mathrm{Ar{-}S{-}CH_2Ar' + Cl_2 \rightleftharpoons Ar{-}\overset{Cl}{\underset{Cl}{S}}{-}CH_2Ar' \rightleftharpoons Ar\overset{Cl}{\underset{+}{S}}{-}CH_2Ar'\quad Cl^-}$$

$$\mathrm{Cl^-}\ \downarrow\uparrow\ \mathrm{HOAc}$$

$$\mathrm{Ar\overset{OAc}{\underset{Cl}{S}}{-}CH_2Ar' \rightleftharpoons Ar\overset{OAc}{\underset{+}{S}}{-}CH_2Ar'\ \ Cl^- \rightleftharpoons Ar{-}\overset{Cl}{\underset{+}{S}}{-}CH_2Ar'\ \ OAc^-}$$

FIGURE 1. *Sulphonium-ion equilibria in aryl benzyl sulphides*
(Positions of equilibrim unspecified)

Examples are known[5] in which the ionization of a covalent bond is a slow step, although both the number and behaviour of the ionic intermediates contribute to the rate of the overall solvolytic process. The criteria for ion-pair formation have been applied in studies of the solvolytic behaviour of the sulphonium ion system outlined by Figure 1. For example, a special salt effect[5] is found in the presence of varying amounts of $LiClO_4$, which might indicate the occurence of more than one sulphonium ion-pair species. The response of rate to added $LiClO_4$ is shown by curve (a) in Figure 2 and provides substantive evidence for both internal and external sulphonium ion-pairs. A clean (pseudo) first-order reaction is also observed in the presence of the common-ion salt lithium chloride, with a small rate increase with increasing LiCl, similar to earlier observations on carbon ion-pairs;[5] [see curve (b), Figure 2]. However, the addition of LiCl to solutions containing $LiClO_4$ depresses the rate considerably from the levels of acceleration obtained in the absence of the added common anion; [see curve (c), Figure 2].

The data listed in the Table demonstrate that added neutral salts have a profound effect on product composition, as well as on solvolysis rate, a result for which there is no precedent in the classical S_N1 solvolysis mechanism.[3] Nor does the classical picture predict the antagonistic roles of LiCl and $LiClO_4$ in determining rate and product composition. Thus, as little as 0·06M-$LiClO_4$ induces a more than 13-fold increase in the acetate component; but, whereas 0·08M-LiCl exerts essentially no effect on the product composition by itself, this same amount is able to negate the influence of 0·06M-$LiClO_4$, which is normally acting to enhance both the rate of reaction and the formation of the acetate product. On the other hand, in the presence of a massive amount (0·25M) of the basic acetate anion, the acetate product is increased by less than a factor of two. As $LiClO_4$ is normally presumed[5] to act by preventing return to internal ion-pair, the steep ascent in the proportion of acetate component, induced by its presence in the medium, is readily comprehensible if this product arises principally from external ion-pairs and/or completely separated ions.

TABLE

Product composition in the chlorinolysis of benzyl phenyl sulphide

Moles/l. added salt			Product mole ratio $= \frac{[PhCH_2Cl]}{[PhCH_2OAc]}$
NaOAc	$LiClO_4$	LiCl	
0	0	0	1·9
0	0·06	0	0·14
0	0·06	0·08	1·75
0	0	0·08	2·1
0·25	0	0	1·1

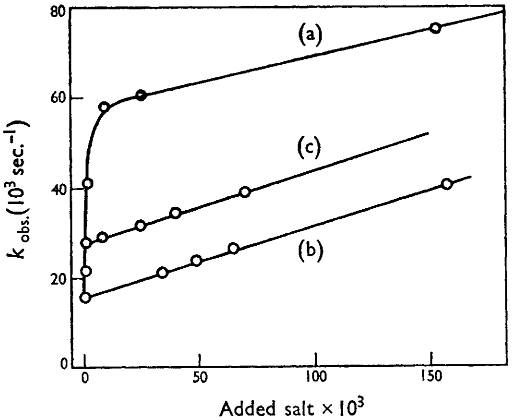


FIGURE 2. *Effect of rate on solvolysis of added salt*: (a) $LiClO_4$, (b) LiCl; (c) 0·25M-LiCl, $LiClO_4$.

In interpreting these results, it must be recalled that the properties which have been termed the "special salt effect" have never been identified previously in reactions involving other than carbonium ion-pairs. Moreover, the benzyl cation is known not to be sufficiently stable to manifest these identifying features.[5] That added neutral salt has biassed both rate and product composition is unusual. These results must be correlated with the ion-pairing properties of the sulphonium cations which control the destiny of the carbonium ion-pairs formed during and after the breaking of the $-\overset{|}{\underset{|}{C}}-S-$ bond. It could be that the sulphonium ion is capable of existing in more than one ion-pair relationship. The solvent structure around each cation is distinctive and characteristic of the ion-pair relationship. Whilst the carbon–sulphur bond is rupturing, the solvent structure along with the anion (if there is one) is transferred more or less intact to the developing carbonium ion centre simultaneously with the loss of charge on the sulphur. Essentially, then, the transferred solvent structure is capable of sustaining the developing carbonium ion-pair long enough to impart the characteristics of the precursor sulphonium ion-pair type. The leaving group, by virtue of the nature of its charge distribution and the solvent structure with which it surrounds itself, creates the environment in which the carbonium ion will be born and then consumed in product formation.

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[3] E. D. Hughes and C. K. Ingold, *et al.*, *J. Chem. Soc.*, 1948, 2038. However, for discussion of these and related references, see C. K. Ingold, "Structure and Mechanism in Organic Chemistry", Cornell University Press, Ithaca, New York, 1953, ch. 7, p. 346, *et seq.*; and M. Cocivera and S. Winstein, *J. Amer. Chem. Soc.*, 1963, **85**, 1702.

[4] (a) K. Fries and W. Vogt, *Annalen*, 1911, **381**, 337; (b) F. Feher and H. Munzer, *Chem. Ber.*, 1963, **96**, 1131; (c) I. B. Douglass, *et al.*, *J. Amer. Chem. Soc.*, 1951, **73**, 5787; 1952, **74**, 5770; 1953, **75**, 4582.

[5] See, for example, S. Winstein, E. Clippinger, A. H. Fainberg, and G. C. Robinson, *J. Amer. Chem. Soc.*, 1954, **76**, 2597, and *Chem. and Ind.*, 1954, 664.