Solvent and Micellar Effects on the Hydrogen Exchange of Sulphonium Salts

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Summary The relative rates of H–D exchange for the α-protons in methyl and allyl sulphonium salts is strongly dependent on both solvent and micellar effects.

THE rate of base catalysed hydrogen exchange for a carbon acid is commonly used as a measure of carbanion stability. It has also been shown that the stereochemical preference for the exchange of α-hydrogen atoms in sulphoxides[1] and sulphonium salts[2,3] is strongly dependent on the solvent–base system. We present another example of such a dependency in the base-catalysed H–D exchange of alkylallylmethylsulphonium salts (see Table and Figure).

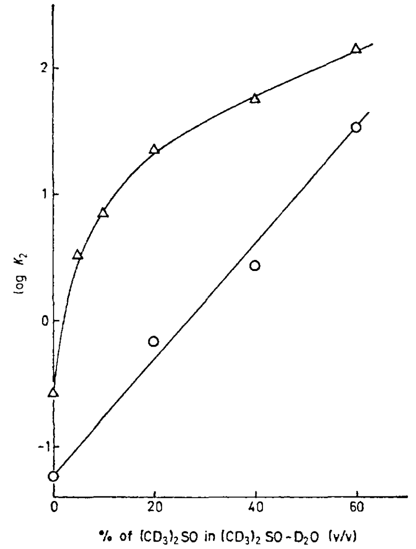

FIGURE. Solvent effect on the second-order rate constants (k_2) of the base-catalysed H–D exchange of allyl-n-butylmethylsulphonium chloride in $(CD_3)_2SO–D_2O$ solvent mixtures under the conditions given in the Table: △ exchange of the allyl α-proton; ○ exchange of methyl proton.

Previously, we have shown that the methyl group of micelle-forming lauryldimethylsulphonium salts is much more reactive than that of the corresponding non-micelle-forming salts in base-catalysed H–D exchange[4] and oxiran-forming[5] reactions. Such a micellar effect can be accounted for by the combined effects of enhanced reactivity of the OD^- ion and the microenvironmental solvent effect on a relatively non-polar micellar surface.[4] The Table indicates that the reactivity of the methyl groups is essentially the same when one of them is replaced by an allyl group. However, the micellar allylmethylene group is 520 fold more reactive in the micelle-forming salt than in the corresponding non-micellar salt, a much larger micellar effect than for the CH_3 group (73 fold). The results in the Figure may possibly account for this micellar effect. As the proportion of $(CD_3)_2SO$ increases in $(CD_3)_2SO–D_2O$ solvent mixtures, the reactivity of the non-micellar CH_3 group increases exponentially, while the reactivity of the allyl group increases in a more complex manner. [k(allyl)/$k(CH_3)$ = 4·5, 33·5, 20·9, and 4·2 in solvents containing, respectively, 0, 20, 40, and 60% of $(CD_3)_2SO$].

TABLE. Relative rates for the base-catalysed H–D exchange for the α-hydrogen atoms of sulphonium chlorides in D_2O at 42 °C ([salt = 0·1 M; [NaOD] = 1·34—40·2 × 10^{-3} M).

$C_4H_9\overset{+}{S}(CH_3)_2$	1[a]	$C_{12}H_{25}\overset{+}{S}(CH_3)_2$	64
$C_4H_9\overset{+}{S}\langle\begin{smallmatrix}CH_3\\CH_2{\cdot}CH:CH_2\end{smallmatrix}$	0·91 (CH$_3$) 3·81	$C_{12}H_{25}\overset{+}{S}\langle\begin{smallmatrix}CH_3\\CH_2{\cdot}CH:CH_2\end{smallmatrix}$	66 1990

[a] k_2 = 6·76 × 10^{-2} l mol^{-1} min^{-1}, determined by the n.m.r. method (ref. 4).

These results show that one must be careful in correlating relative kinetic acidities with certain structural changes.

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