An $E2$ Mechanism for the Alkaline Hydrolysis of Toluene-α-sulphonate Esters of Acidic Phenols

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Summary Only a concerted ($E2$) mechanism is possible for the formation of phenyl sulphene in alkali from toluene-α-sulphonate esters of phenols with $\mathrm{p}K_a < 6$ because the corresponding anions are estimated to have half-lives less than the vibration time of an S–OAr bond and hence do not exist as identifiable species.

There is considerable evidence for the formation of a sulphene *via* a concerted $E2$ mechanism in the action of a tertiary amine on an alkanesulphonyl halide.[1] This contrasts with recent reports favouring an $E1cB$ pathway for the alkaline hydrolysis of aryl esters of toluene-α-sulphonic acid.[2]

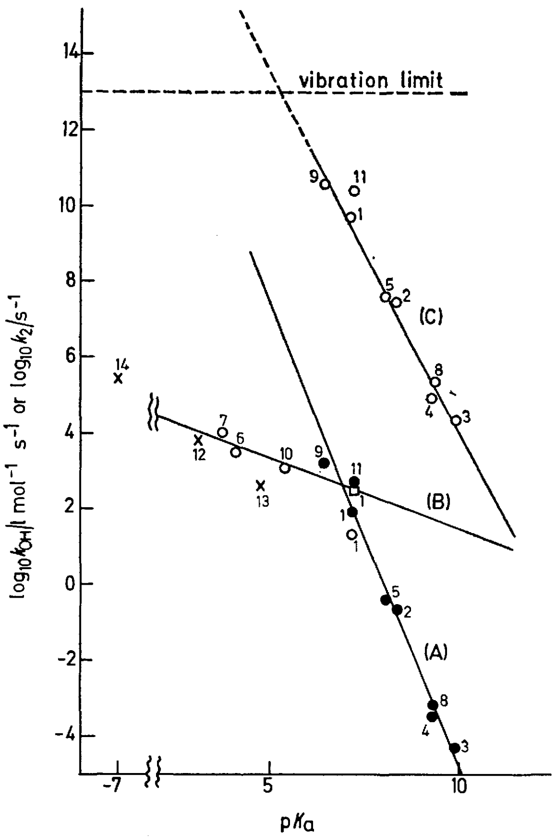

Figure. Plot of $\log_{10}k_{OH}$ and $\log_{10}k_2$ (aqueous solution, 25°, ionic strength made up to 1M with NaCl) for the hydrolysis of toluene-α-sulphonate derivatives *versus* the pK_a of the conjugate acid of the leaving group. Filled circles for line (A) represent buffer-independent values and open circles for line (B) are values for zero buffer concentration. The open square is the hydroxide dependent exchange rate for the protio-ester in water (obtained by correction of the value for D_2O). Ionisation constants are from: R. P. Bell, 'The Proton in Chemistry' 2nd edn., Chapman and Hall, London, 1973; W. P. Jencks and J. Regenstein, 'Handbook of Biochemistry,' 2nd edn., ed. H. A. Sobers, The Chemical Rubber Co., Cleveland, 1970, section J-187; G. B. Barlin and D. D. Perrin, *Quart. Rev.*, 1966, **20**, 820. The points represent the following toluene-α-sulphonates; (**1**) 4-nitrophenyl; (**2**) 3-nitrophenyl; (**3**) phenyl; (**4**) 3-fluorophenyl; (**5**) 4-acetophenyl; (**6**) 2,4-dinitrophenyl; (**7**) 2,6-dinitrophenyl; (**8**) 4-chlorophenyl; (**9**) 4-chloro-2-nitrophenyl; (**10**) 2-chloro-4-nitrophenyl; (**11**) 2-nitrophenyl; (**12**) fluoride; (**13**) azide; (**14**) chloride.

We find that the plot of $\log_{10}k_{OH}$ *versus* the pK_a of the leaving phenol in the hydrolysis of aryl toluene-α-sulphonates possesses two distinct limbs (Figure). The limb with high slope (A) involves buffer-independent hydrolyses with no primary deuterium isotope effect ($PhCD_2SO_2OAr$). The limb of low slope (B) is for hydrolyses which are buffer-dependent and have a high primary deuterium isotope effect. These facts supplement the evidence already available[2] for the *E*1c*B* mechanism (1) ('reversible' for **A** and 'irreversible' for B).

$$\mathrm{PhCH_2SO_2X} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{Ph\bar{C}HSO_2X} \xrightarrow{k_2(-\mathrm{X}^-)} \mathrm{PhCH{=}SO_2} \xrightarrow{\mathrm{H_2O}} \text{product} \qquad (1)$$

The ionisation constant of the carbon acid may be determined from the rate constant for proton transfer to hydroxide ion because the acid is so weak that protonation of the conjugate base by water is normally diffusion-controlled.[3a] The proton transfer rate constant in water is identical with the hydroxide ion-catalysed hydrolysis in the case of esters (**6**), (**7**), and (**10**) since for these k_1 is the rate-limiting step. The proton transfer step (k_1) is not rate-determining for the 4-nitrophenyl ester (**1**) but may be measured (for D_2O solvent) by observing exchange of protio-ester in a hydrolysis experiment where the primary isotope effect effectively monitors the exchange. This rate constant may be corrected for solvent using the ratio of the rate of hydrolysis of the 2,6-dinitrophenyl ester (k_1 is rate limiting) in H_2O and D_2O. The free energy relationship (B) generated from the proton transfer rate constants may be used to estimate pK_{SH} for the esters corresponding to line (A) using equation (2).[3b] Values from these calculations vary from 21 to 23 and are of the order expected from results (measured by other methods) for similar compounds.[4]

Values for k_2 may now be estimated for those esters where k_2 is rate-limiting using K_{SH}, k_{OH} (line A), and the equation: $k_{OH} = K_{SH} \times k_2/K_W$. The resultant free- energy relationship (line C) has a $\beta_{l.g.} = -1{\cdot}9$ indicating that the transition-state is 'loose,' similar to those for the analogous reactions involving nucleophilic attack on heterocumulenes[5] and the *E*1 decomposition of the aryl methylaminosulphonate anion.[6]

Extrapolation of line (C) indicates that k_2 is greater than 10^{13} s^{-1} for leaving phenols of $pK_a < ca$ 6. Thus, carbanions from these esters have a lifetime less than the vibration time of an S–OAr bond (*ca.* 10^{-13}s) and therefore do not exist as identifiable species. Only a concerted *E*2 mechanism is possible for these esters and the transition-state has 'carbanion-like' character[7] in agreement with that proposed for alkanesulphonyl chloride hydrolyses.[1]

(*Received*, 6*th March* 1975; *Com.* 282.)

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