Evidence Consistent with a Stepwise Elimination–Addition Process for Hydrolysis and Aminolysis of Aryl Toluene-α-sulphonates

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Summary The hydrolysis and aminolysis of substituted phenyl toluene-α-sulphonates possess a stepwise elimination–addition mechanism (*E1cB*) involving a sulphene intermediate; the *E1cB* pathway for the hydrolysis of 5-nitro-2-hydroxytoluene-α-sulphonic acid sultone is sterically suppressed.

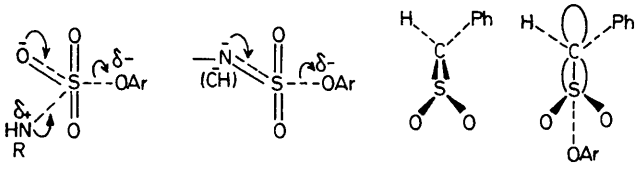
THE following evidence is consistent with a stepwise elimination–addition mechanism (*E1cB*) involving a sulphene intermediate in the hydrolysis and aminolysis of substituted phenyl toluene-α-sulphonates: (1) release of substituted phenol from aryl toluene-α-sulphonates depends

$$PhCH_2SO_2OAr \underset{k_{HB}\cdot HB}{\overset{k_B\cdot B}{\rightleftharpoons}} PhCHSO_2OAr \xrightarrow{k_2} PhCHSO_2$$

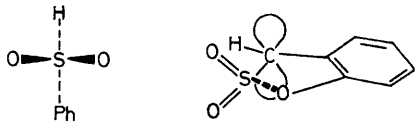
$$PhCHSO_2 + \overline{O}Ar \xrightarrow[\text{fast}]{NH} PhCH_2SO_2N$$

on hydroxide ion concentration; the hydroxide rate parameter possesses a very high selectivity to Hammett's *sigma*-minus (+4·84) and has a high Brønsted $\beta_{1\cdot g}$ (−2·14) consistent with considerable phenolate ion character in the transition-state of the rate-determining step. Alkaline hydrolysis of phenyl benzenesulphonates, a mechanism known to be of the addition-elimination type, has a Hammett selectivity of near +2·5 versus *sigma*.[1] (2) Amine buffers catalyse the release of 4-nitrophenol from the corresponding ester but have no effect on the rate at high buffer concentrations (Figure). The rate constant for 4-nitrophenol release is proportional to hydroxide ion concentration in the buffers at high amine concentration and is independent of amine structure. This is consistent with a two-step mechanism involving a change in rate limiting step (from k_B to k_2) as the amine concentration is increased. Removal of the α-proton concerted with departure of leaving group is not consistent with these results. (3) In the region where change in amine concentration has no effect on the rate of 4-nitrophenol release the product is completely the trapped sulphonamide. Here the rate-limiting step involves formation of sulphene which is rapidly scavenged by amine. The dependence of the rate of 4-nitrophenol release on low values of amine concentration is a result of general base removal of the α-proton by the amine to yield carbanion.

(4) The hydroxide-catalysed rate constant for the 4-nitrophenyl ester is some 1000-fold larger than that for the corresponding benzenesulphonate and methanesulphonate esters which are known to result from an addition–elimination mechanism.



(I) (II) (III) (IV)



(V) (VI)

The absence of a dependence on amine concentration (at high concentration) means that the transition-state for release of the leaving group possesses no N–S bonding; this is similar to the situation for aminosulphonate esters[2] but different for sulphate half esters.[3] In the latter case, an oxyanion (pK_a = *ca.* 1) essentially expels the leaving group whereas in the former cases a carbanion ($pK_a > 10$) and a nitrogen anion (pK_a = *ca.* 9) are involved. It is reasonable that in the oxygen case extra driving force in the form of bonding to the entering nucleophile is needed to assist expulsion of the leaving group (I) whereas in the nitrogen and carbanion cases the internal nucleophile is sufficient (II). These arguments are correct for nitrogen nucleophiles but, by analogy, hydrolysis probably involves bonding to water with the sulphate (analogous to I) but formation of discrete intermediates in the nitrogen and carbon cases (II).

Sulphenes probably have the planar configuration (III) as their most stable form so it is likely that the transition-state for the *E*1 reaction will also be planar or very nearly so for those atoms constituting the sulphene product (IV). This is supported by recent CNDO/2 calculations which show that the planar sulphene CH_2SO_2 is more stable by

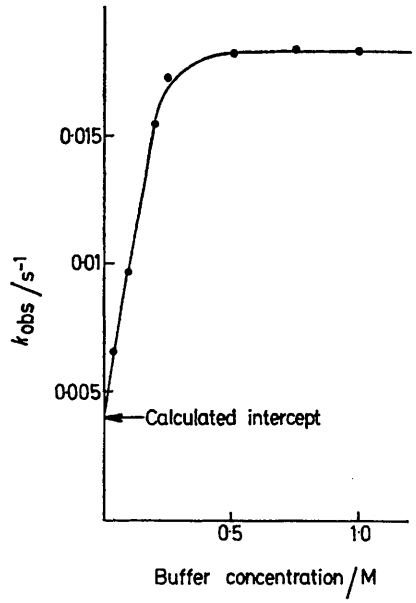


FIGURE. Rate constants for the release of 4-nitrophenol from the toluene-α-sulphonate ester as a function of buffer concentration: buffer, diethylamine; fraction basic component, 0·2; pH, 10·26; ionic strength made up to 1·0 M with sodium chloride; 25°.

some 35 kcal mol^{-1} than the 'perpendicular' form the parent of (V).[4] These considerations provide an answer to the observations, consistent with an addition–elimination mechanism, made by Kaiser and his co-workers for hydrolysis of 5-nitro-2-hydroxytoluene-α-sulphonic acid sultone (VI);[5] although the benzylic proton is labile and the phenolic oxygen is a good leaving atom the sultone does not follow the hydrolysis mechanism of its open-chain analogue but involves nucleophilic attack at the sulphur in the rate-limiting step. Consideration of (VI), essentially the structure of the conjugate base, shows that the transition-state for an *E*1 reaction will resemble the 'perpendicular' sulphene and not the more stable planar form.

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