Evidence Consistent with an Elimination Mechanism in the Hydrolysis of Aryl *N*-Methylamino-sulphonates

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Summary pH-independent rate constants for hydrolysis of the title esters obey a Brønsted relationship with β — 1·85; participation of an elimination mechanism involving $MeN{=}SO_2$ intermediate is consistent with the above data (indicating considerable SO bond cleavage in the transition state) with the absence of a glycine buffer effect, and with a 10^8 fold greater reactivity of the 4-nitrophenyl ester compared with the dimethylamino-ester to reaction with hydroxide ion.

WE report here the first clear-cut evidence for the participation of an elimination mechanism in the hydrolysis of aryl *N*-alkylaminosulphonates. The pH-dependence of the pseudo-first-order rate constants for hydrolysis of 4-nitrophenyl *N*-methylaminosulphonate fits equation (2). The

$$k = k(H_2O) + k'/\{1 + K_w/([OH]K_a)\} \qquad (2)$$

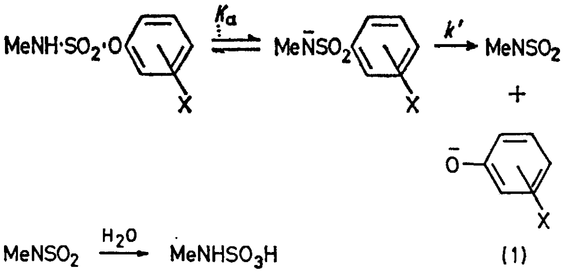
rate constant k' varies with leaving group according to a Hammett equation; the σ^- parameters (ρ 4·04, r 0·9998) indicate significant S–O cleavage in the transition state of the rate-determining step. Oxygen-18 studies indicate exclusive S–O cleavage rather than aryl-O cleavage. A plot of $\log_{10}k'$ *vs.* pK_a of the leaving phenol has a slope of $-1·8$ implying that the rate-determining step has considerable phenolate ion character in its transition state.

The Brønsted relationship for alkaline hydrolysis of phenyl sulphonates has a small slope and the Hammett relationship correlates[1] with σ rather than with σ^-; these esters hydrolyse *via* an S_N2 process. The rate constant k' could derive from an S_N2 attack of hydroxide ion on neutral substrate [k(OH)] which is inhibited as the substrate ionises. Thus k' could be composite [$K_wk(OH)/K_a$]. The ρ values for K_a and k' are known (+2·54 and +4·04 respectively) and yield a calculated ρ value of 6·58 for k(OH) which is larger by about 4 units than the expected value (2·75).[1]

Nitrogen nucleophiles are known to attack sulphonyl derivatives[2] but glycine buffers do not accelerate the rate of release of 4-nitrophenol from the corresponding ester in accord with an elimination mechanism.[3,4]

The ratio of the 'second-order' rate constant for hydroxide attack on the neutral 4-nitrophenyl ester (k' K_a/K_w) to water attack [$k(H_2O)$] is 2500. It is reasonable that the water term reflects a simple S_N2 mechanism; if the hydroxide term arises from a similar mechanism, this ratio should be reflected in those sulphonyl cases where both water and hydroxide terms are from an S_N2 process; this ratio is only 14 for the *NN*-dimethylaminosulphonyl chloride case.[5]

It is unlikely that attack of water on the conjugate base (S_N2) could be the mechanism for k' as this is > 1000 times the rate constant for attack of water on the *neutral* species [$k(H_2O)$].



(1)

The second-order rate constant for reaction of hydroxide ion with 4-nitrophenyl *NN*-dimethylaminosulphonate ($2·36 \times 10^{-6} M^{-1} s^{-1}$) is some 10^8 fold smaller than the term $k'K_a/K_w$ for the monosubstituted ester providing excellent confirmation of the elimination mechanism.

Although we have not isolated the intermediate, recent reports[6] describe the isolation of species identified as $RNSO_2$ which are exceedingly reactive to nitrogen nucleophiles and are probably too reactive to be observed even transiently in aqueous solution.

(*Received, 8th February* 1973; *Com.* 170.)

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