Elimination–Addition Mechanisms of Sulphonyl Group Transfer: Evidence for a Dicarbanionic Intermediate in the Alkaline Hydrolysis of Aryl Methylsulphonylmethanesulphonate Esters

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Summary Kinetic evidence has been obtained from the hydrolysis of the title compounds that is consistent with a dissociative mechanism; ionization of the substrate is followed by the slow unimolecular breakdown of the conjugate base to phenoxide ion and sulphene, but at high pH values a further ionization occurs to give a dicarbanion which undergoes $E1$-elimination of phenolate ion to yield a sulphene anion in the rate determining step.
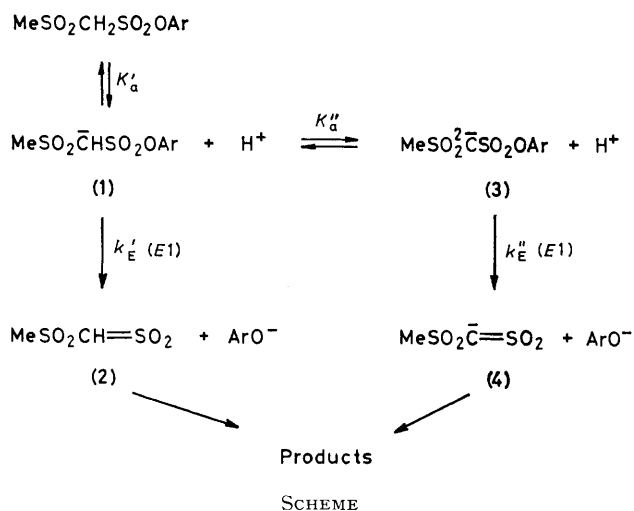
In continuation of previous research on the occurrence of elimination–addition (EA) mechanisms in the hydrolysis of aryl sulphonate esters possessing labile α-protons,[1,2] we report here that aryl methylsulphonylmethanesulphonate (mesylmethanesulphonate) esters hydrolyse in aqueous buffered solution with quantitative release of substituted phenol, and the reaction rates are independent of the nature and concentration of the buffers employed. The pseudo-first order rate-constants in ester vary with pH according to equation (1). The parameters K'_a represent kinetic acidity constants, as they are identical (within experimental error) with the thermodynamic values measured spectrophoto-

$$k_{obs} = (k_a + k_b[OH])/(1 + a_H/K'_a) \tag{1}$$

metrically for the same esters (under similar experimental conditions). Values of K'_a follow a Hammett relationship (ρ +1·29). Both parameters k_a and k_b possess high Brønsted selectivities (β_a −1·71; β_b −1·53) and Hammett

sigma minus selectivities (ρ_a +4·2; ρ_b +3·8). The observed dependence of rate on pH could arise from S_N2 attack of hydroxide ion on both neutral ($k'_{OH} = k_a K'_a/K_w$) and ionised ($k''_{OH} = k_b$) substrate but then the corresponding Hammett selectivities would be 5·49 and 3·8 respectively. The alkaline hydrolysis of aryl benzenesulphonate esters, a *bona fide* S_N2 process, possesses a much lower Hammett coefficient (+2·5).[3]

MeSO₂CH₂SO₂OAr

$$\updownarrow K'_a$$

MeSO₂C̄HSO₂OAr + H⁺ $\overset{K''_a}{\rightleftharpoons}$ MeSO₂²C̄SO₂OAr + H⁺

(1)   (3)

$\downarrow k'_E$ (*E1*) $\downarrow k''_E$ (*E1*)

MeSO₂CH=SO₂ + ArO⁻   MeSO₂C̄=SO₂ + ArO⁻

(2)   (4)

Products

SCHEME

The high selectivity to leaving group and Hammett sigma minus relationship are diagnostic for an *E1cB* process, and the mechanism depicted in the Scheme is suggested for the reaction. According to the Scheme, the pH-independent rate constant k_a ($=k'_E$) arises from the unimolecular elimination of phenolate ion from the conjugate base (1) (monocarbanion) of the ester to yield (2). The parameter k_b ($=K''_a k''_E/K_w$) represents the ionization of (1) to give its conjugate base [presumably the 1,1-dianion (3)] which eliminates a phenolate ion to give (4) in an *E1* step. Fast addition of a water molecule to the unsaturated intermediates (2) or (4) finally leads to the mesylmethanesulphonic acid product. The effect on reactivity of substituting a methyl group for an α-hydrogen atom in the 4-nitrophenyl ester (*vide infra*) and the lack of deuterium incorporation into the methyl group of the same ester under alkaline conditions are not consistent with the formation of the dianion (C̄H₂SO₂C̄H–SO₂–OAr).

The following evidence is also consistent with the proposed mechanism. i, Substituting a methyl group for an α-proton in the 4-nitrophenyl ester increases k_a by ca. 500-fold (and K'_a decreases 150 times, hence k'_{OH} is more than tripled), in accord with an *E1cB* rather than an associative mechanism. The k_b term vanishes owing to suppression of the second ionization. ii, Substituting methyl groups for both the α-hydrogen atoms in the 4-nitrophenyl ester causes the
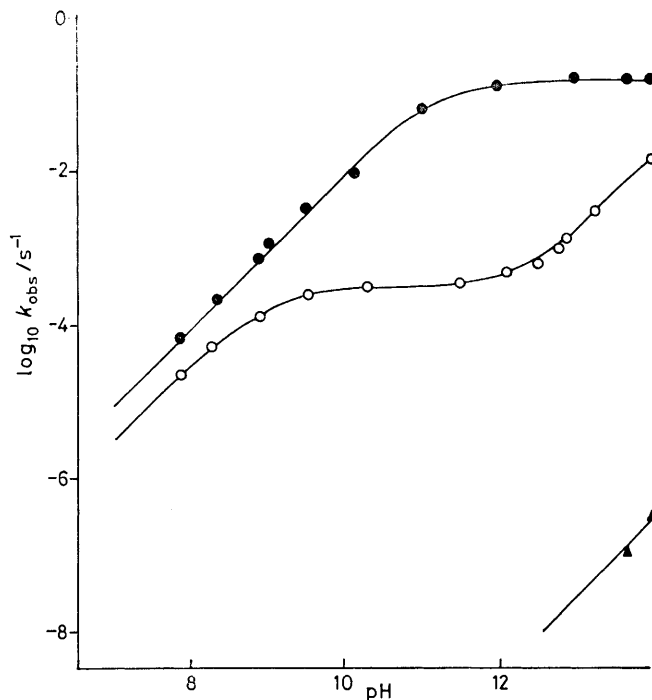

FIGURE. Dependence on pH of the hydrolysis of 4-nitrophenyl methylsulphonylmethanesulphonate (open circles) and its α-methyl- (closed circles) and αα-dimethyl- (closed triangles) substituted analogues in water at 25 °C.

apparent hydroxide rate constant to decrease by some 10⁸-fold with respect to the unsubstituted ester (Figure). The large decrease is very much more than would be expected on steric grounds.[2-4] iii, The αα-dimethyl-substituted 4-nitrophenyl ester hydrolyses in alkali with exclusive S–O bond cleavage rather than aryl–O bond cleavage, as shown by ¹⁸O-studies and, *a fortiori*, the same type of cleavage is expected to take place for the other esters as well. This result allows us to discard the $S_N Ar$ mechanism as the one giving rise to the large observed β_a and ρ_a values. iv, Although the presence of benzylamine has no accelerative effect on the reaction, yields of ca. 70 and 100% of benzylamide are obtained at pH 10 (where $k_{obs} = k_a$) and pH 13 (where $k_{obs} = k_b$ [OH]) respectively from the hydrolysis of the unsubstituted 4-nitrophenyl ester in the presence of 1 M benzylamine. This result is consistent with the existence of an intermediate (sulphene) following the rate-determining step.[2,5]

Several papers concerning preparation and synthetic usefulness of 1,1-dicarbanions have been published in the last decade.[6] To our knowledge this paper discusses the first example of a 1,1-dicarbanion present in aqueous solution and its elimination to anionic sulphene.

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