Elimination–Addition Mechanisms of Acyl Group Transfer: Evidence for Rate-limiting Breakdown of a Sulphene-2,4-dinitrophenoxide Ion Encounter Complex in the Base-catalysed Hydrolysis of 2,4-Dinitrophenyl Arylmethanesulphonate Esters

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Summary The base-catalysed hydrolysis of 2,4-dinitrophenyl arylmethanesulphonate esters *via* an $E1cB_{\text{I}}$ mechanism undergoes a change in rate limiting step in pyridine buffers of high concentration from proton transfer to breakdown of a sulphene-2,4-dinitrophenoxide ion encounter complex.

IT was shown that substituted phenyl phenylmethanesulphonate esters hydrolyse in base *via* an *ElcB* mechanism;[1,2] substrates with phenol leaving groups more acidic than 4-nitrophenol have a mechanism with proton transfer rate limiting ($ElcB_1$).[2]

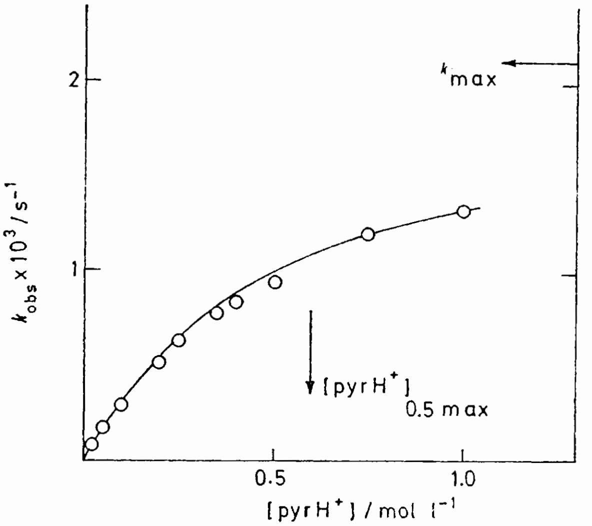

FIGURE. Variation in rate constant with buffer concentration for the hydrolysis of 2,4-dinitrophenyl phenylmethanesulphonate: pyridine buffers, 4% ethanol–water, 25 °C, ionic strength maintained at 1 mol l^{-1} with KCl, pH 5·55, fraction of base = 0·5.

We observe that the rate constant for hydrolysis in pyridine buffers of the 2,4-dinitrophenyl arylmethanesulphonate esters is non-linear in buffer concentration (Figure) consistent with a change in rate-limiting step.† Added solutes at constant ionic strength (pyrimidine, potassium iodide, *N*-methylpyridinium iodide, and indole) have minor specific effects on the hydrolysis rate for the 2,4-dinitrophenyl phenylmethanesulphonate ester and these are negligible compared with the observed effects of changing buffer concentrations. The non-linear buffer plots may be analysed *via* a standard hyperbolic function according to the simple equation (1) (pyr = pyridine). The

$$\mathrm{SH} \underset{k_{pyrH}[pyrH]}{\overset{k_{pyr}[pyr]}{\rightleftharpoons}} \mathrm{S}^- \xrightarrow{k'_2} \text{products} \qquad (1)$$

observed rate constant reaches a maximum value (k_{max}) and this is proportional to hydroxide ion concentration yielding the second order rate constant k_{OH}^{max}. The value of K_{SH} may be obtained from k_{pyr} (footnote for the Table) and from k_{max} and k'_2 (footnote e of the Table); the value of k'_2 is obtained from analysis of the data according to equation (1) from the relationship $k'_2 = k_{pyrH}[pyrH]_{0\cdot5max}$. These methods for K_{SH} are independent and both assume that protonation of the carbanion with the conjugate acid of pyridine is effectively diffusion controlled. The good agreement between the values from the independent methods indicates that the analysis is internally self consistent. We are therefore confident that buffer curvature is the result of a change in rate-limiting step despite its occurring at a relatively high buffer molarity[3] and is not due to an effect specific to the pyridine buffers.

TABLE. Parameters for the hydrolysis of 2,4-dinitrophenyl-substituted phenylmethanesulphonates.[a]

Ester[b]	k_2'[c] $\times 10^{-10}$	$pyrH^+_{0\cdot5max}$ /mol l^{-1}[d]	pK_{SH}[e]	pK_{SH}[f]	k_{pyr}/ /l mol^{-1} s^{-1}[g]	$k_{OH} \times 10^{-4}$ /l mol^{-1} s^{-1}[h]	$k_{max} \times 10^{-6}$ /l mol^{-1} s^{-1}[i]	pK_a^{ArOH}[j]
4-Cl	2·0	1·0	18·0	18·0	$6{\cdot}11 \times 10^{-3}$	0·81	1·75	9·38
3-Cl	2·0	1·1	17·7	17·7	$1{\cdot}25 \times 10^{-2}$	1·34	4·01	9·02
3-NO_2	1·2	0·5	17·0	17·0	$5{\cdot}81 \times 10^{-2}$	3·49	12·6	8·35
4-CN	1·6	0·8	16·4	16·4	$2{\cdot}12 \times 10^{-1}$	5·66	58·1	7·95
4-NO_2	2·0	1·0	15·1	16·0	$7{\cdot}08 \times 10^{-1}$	7·60	246	7·14
2-NO_2-4-Cl	0·72	0·37	15·7	16·0	$6{\cdot}82 \times 10^{-1}$	9·00	83·2	6·46
3,5-$(NO_2)_2$	1·4	0·7	15·4	15·7	1·31	28·7	309	6·68
2-Cl-4-NO_2	0·60	0·34	14·8	15·1	5·4	28·6	479	5·45
H	1·2	0·60	18·3	18·4	$2{\cdot}3 \times 10^{-3}$	0·42	0·618	9·95
4-Me				18·7	$1{\cdot}17 \times 10^{-3}$	0·23		10·19
3-Me				18·4	$2{\cdot}8 \times 10^{-3}$	0·35		10·08
2-Cl	1·1	0·55	17·4	17·5	$2{\cdot}08 \times 10^{-2}$		4·19	8·48
2-NO_2				16·4	$2{\cdot}65 \times 10^{-1}$	4·65		7·23

[a] 25 °C, 1 mol l^{-1} ionic strength maintained with KCl, 4% EtOH, reactions followed spectroscopically at 400 nm.

[b] The esters, synthesised in the usual way (ref. 2b), had good analyses; structures were confirmed by n.m.r. spectroscopy.

[c] Calculated from $k'_2 = k_{pyrH^+}[pyrH^+]_{0\cdot5max}$ assuming k_{pyrH^+}, the rate constant for protonation of the carbanion by the conjugate acid of pyridine, is a diffusion controlled parameter; the value for the latter is obtained from E. F. Caldin, 'Fast Reactions in Solution, Oxford University Press, 1964 for the collision of an anion and cation and is *ca.* 2×10^{10} l mol^{-1} s^{-1} at 25 °C.

[d] This is the value of the concentration of the conjugate acid of pyridine at $k_{obs} = 0{\cdot}5\, k_{max}$.

[e] $pK_{SH} = \log k_2' - \log k_{max} + pH$.

[f] $pK_{SH} = -\log k_{pyr} + pK_a^{pyrH^+} + \log k_{pyrH^+}$.

[g] $k_{pyr} = dk_{obs}/d[pyr]$ in the limit at $[pyr] = 0$.

[h] The hydroxide rate constant at zero buffer concentration is $k_{OH} = k_{zero\ buffer}/[OH^-]$.

[i] The hydroxide ion concentration is calculated from $pK_w = 13{\cdot}97$ measured for the present system; $k_{OH}^{max} = k_{max}/[OH^-]$.

[j] Values of pK_a^{ArOH} obtained from W. P. Jencks and J. Regenstein in 'Handbook of Biochemistry,' 2nd edn., ed. H. A. Sober, Chemical Rubber Co., Cleveland, Ohio, 1970, section J-187.

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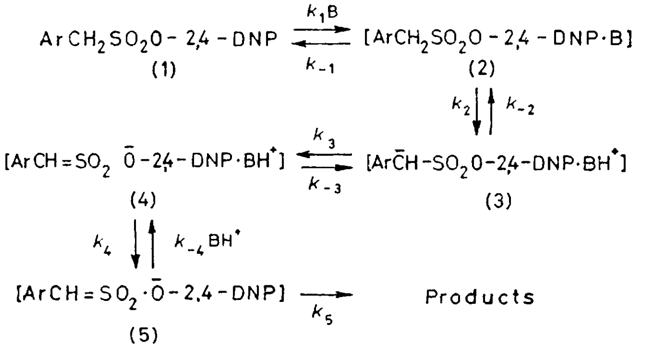
† In the previous study (ref. 2) the non-linear buffer concentration relationship was missed owing to the low buffer concentrations employed.

The maximal, buffer independent, rate constant for hydrolysis of 2,4-dinitrophenyl phenylmethanesulphonate ($k_{OH}^{max} = 618\,000$ l mol^{-1} s^{-1}) is several orders of magnitude less than that calculated from previous work[2b] for the $ElcB_r$ mechanism [k_{OH} ($ElcB_r$) = $2{\cdot}7 \times 10^9$ l mol^{-1} s^{-1}]‡ indicating that the rate-limiting step is not decomposition of the carbanion in the buffers of high pyridine concentration. Further evidence against the $ElcB_r$ mechanism at high buffer concentration is the absence of deuterium incorporation (measured kinetically and on a preparative scale) in the unreacted ester in D_2O solvent at concentrations of pyrD$^+$ ion where the change in rate-limiting step is essentially complete; the absence of incorporation is due to the very unfavourable equilibrium of step (**3**) $\rightleftharpoons$ (**4**) in the Scheme which is proposed to account for the present results.



SCHEME

The Scheme may be analysed by the steady state method to yield the rate law [equation (**2**)]§ which may be simplified to equation (3) at high levels of concentration of the conjugate acid of the base (HB). At low levels of acid concentration (HB) the law reduces to equation (4).¶ Thus at high

$$k_{obs} = k_1k_2k_3k_4k_5[B]/k_{-1}\{k_5(k_4k_3 + k_{-3}k_{-2}) + k_{-4}k_{-3}k_{-2}[HB]\} \tag{2}$$

$$k_{obs} = k_1k_2k_3k_4k_5[B]/k_{-1}k_{-2}k_{-3}k_{-4}[BH] \tag{3}$$

$$k_{obs} = k_1k_2[B]/k_{-1} \tag{4}$$

buffer concentration k_5, the breakdown of the sulphene–aryloxide association complex, is the rate-limiting step and at low concentrations it is the proton transfer step k_2.

The present Scheme involves a 'pre-association' or 'spectator'[4] mechanism with the acid (HB) not participating in the elimination step (stage **3** in the Scheme). The meaning of k_{OH}^{max} is apparent from equation (3) on substituting for the ratio [B]/[HB].

These results confirm and extend the mechanism advanced by us for the alkaline hydrolysis of aryl arylmethanesulphonate esters.[2]

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‡ For aryl phenylmethanesulphonate hydrolysis in alkali the following relationship is used (ref. 2b): $\log k_{OH}^{(ElcB_r)} = 19{\cdot}3 - 2{\cdot}4\,pK_a^{ArOH}$

§ The assumptions $k_2 < k_{-1}$ and $k_3 > k_{-2}$ are used in deriving this rate law and are reasonable since k_3 is already known to be limited by the S–O bond vibration time and k_{-1} is a diffusion rate constant.

¶ The assumption $k_{-3}k_{-2} < k_4k_3$ is made in deriving this simplification and is reasonable since k_4 and k_3 are known to be exceedingly large.

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[3] For discussions of similar problems, see: E. S. Hand and W. P. Jencks, *J. Amer. Chem. Soc.*, 1975, **97**, 6221; J. L. Hogg and W. P. Jencks, *ibid.*, 1976, **98**, 5643; A. Williams and W. P. Jencks, *J.C.S. Perkin II*, 1974, 1760.

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