Ionisation Rates of Sulphones in Calibration of Leaving Group Abilities and Assignment of Mechanism in Eliminations

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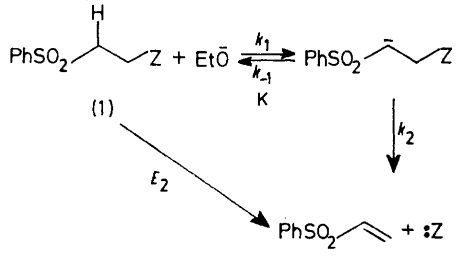
Summary A Taft plot for the ionisation of sulphones has been applied to the calibration of leaving group ability in sulphonyl-activated 1,2-eliminations and to the assignment of mechanism.

WE recently reported[1] on leaving group ability in the system in the Scheme. Assignment of leaving group ability can be made only when expulsion of the leaving group from the carbanion (k_2) is rate determining. For this case, the observed rate constant is the product of the rate constant for expulsion of the leaving group from the carbanion and the equilibrium constant, K, for its formation. The leaving group, Z, affects, by induction, the magnitude of this equilibrium constant and for quantitative comparison between leaving groups, their differential effects on K should be known. Equilibrium constants for ionisation of sulphones in ethanolic sodium ethoxide are not available but we have measured ionisation rates of a series of sulphones (**1**) using detritiation rates and n.m.r. spectroscopy. The Taft plot (Figure) allows interpolation of ionisaton rates for systems in which σ^* (CH_2Z) values are available or calculable. Equilibrium constants for simple sulphones in ethanolic sodium ethoxide are very small and reprotonation of even relatively weakly basic sulphonyl-stabilised carbanions is very fast.[2] The effect of Z is likely to be much greater on k_1 than on k_{-1} and the k_{obs} values (Table 1), on substraction of interpolated k_1 values, give the leaving group order defined as ($\log k_{obs} - \log k_1)_Z - (\log k_{obs} - \log k_1)_{OPh}$. The leaving group order that emerges is that of the periodic group to which the connecting atom belongs, *viz.* Group 6 > Group 5 > Group 4, with the exception of positively charged groups. This order is that of the k_{obs} values but within periodic groups correction for ionisation lowers the rank of $PhSO_2$ which is a highly inductive but only moderately reactive group. By contrast, PhO is notable in being at the top of the order of neutral leaving groups.



SCHEME

TABLE 1. Elimination in sulphones, $PhSO_2CH_2CH_2Z$[a]

Leaving group Z	k_{obs}/ l mol^{-1} s^{-1}	Leaving group rank[b] $\log k_{elimination}$- $\log k_{ionisation}$
Me_2S^+	$6{\cdot}2 \times 10^5$	0·87
$Ph\overset{+}{N}Me_2$	$5{\cdot}2 \times 10^4$	0·26
PhO	0·35	0·00
PhS	0·021	−0·27
$PhSO_2$	1·05	−0·36
PhSO	0·25	−1·90
MeO	$4{\cdot}3 \times 10^{-5}$	−2·96
TsNMe	$3{\cdot}4 \times 10^{-5}$	−3·51
AcNMe	$4{\cdot}6 \times 10^{-6}$	−3·88
CN	$<10^{-8}$	−9

[a] EtO^-–EtOH, 25 °C, $k_H/k_D(\beta) = 1 \pm 0{\cdot}05$. [b] Rank for OPh defined as 0·0.

The ionisation plot may also be employed in assignment of mechanism in carbanionic eliminations. Table 2 gives values of k_{obs} for sulphones in which primary deuterium

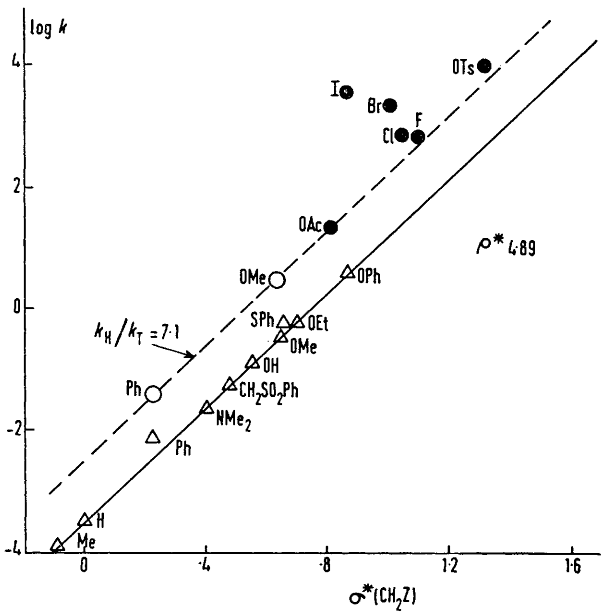


FIGURE. △, detritiation of sulphones $PhSO_2CH_2CH_2Z$ in EtO^-–EtOH; ○, values calculated from deprotonation in EtO^-–EtOD, corrected for solvent deuterium isotope effect for detritiation in EtO^-–EtOD; ●, elimination in sulphones $PhSO_2CH_2CH_2Z$ in EtO^-–EtOH. All reactions at 25 °C.

isotope effects show that β-CH fission is involved in the rate determining step. Distinction between concerted elimination and rate-determining ionisation is made by reference to the Figure, using appropriate σ^* (CH_2Z) values. The results show that when Z = F, Cl, OTs, and OAc, but not Br and I, a satisfactory match between k_{obs} and $k_{ionisation}$ is observed, and the $(E1cB)_I$ (k_1 rate-determining) and not the E_2 mechanism is assigned. These results contra-indicate a mechanistic discontinuity at the $E_2/E1cB$ borderline[3] and complement earlier quantitative studies of elimination in β-halogeno-sulphones.[4]

TABLE 2. Comparison of elimination and interpolated ionisation rates[a] for sulphones $PhSO_2CH_2CH_2Z$

Z	$k_{elimination}$	k_H/k_D	$k_{ionisation}$ (predicted)
F[b]	800	2·0[c]	710
Cl	798	3·6	399
Br	2600	5·0	224
I	2900	5·6	44
OTs	6700	2·0	14,000
OAc	21·2	1·9	22

[a] EtO^-–EtOH at 25 °C. Units l mol^{-1} s^{-1}. [b] k_e from ref. 4, corrected for change from MeO^-–MeOH to EtO^-–EtOH. [c] For MeO^-–MeOH, ref. 4.

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[1] D. R. Marshall, P. J. Thomas, and C. J. M. Stirling, *J.C.S. Chem. Comm.*, 1975, 940.
[2] J. Hine, J. C. Philips, and J. I. Maxwell, *J. Org. Chem.*, 1970, **35**, 3943.
[3] R. A. More O'Ferrall and P. J. Warren, *J.C.S. Chem. Comm.*, 1975, 483.
[4] V. Fiandese, G. Marchese, and F. Naso, *J.C.S. Perkin II*, 1973, 1538.