Leaving Group Ability in Base-promoted Alkene-forming 1,2-Eliminations

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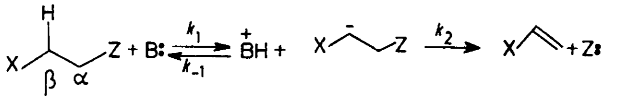
Summary Leaving group ability in 1,2-eliminations has been assigned to a series of 19 groups; it is not predictable from simple molecular parameters but is broadly related to the periodic group to which the linkage atom belongs.

LEAVING group ability in displacement and elimination reactions has been little studied because systems in which a range of leaving groups can be studied are rare.[1] We now report on base-promoted, alkene-forming, 1,2-eliminations in which expulsion of the leaving group, Z, is accelerated by an activating group, X, (Scheme). The results are given in the Table; unless otherwise stated X = $PhSO_2$.

Information on leaving group ability is directly derivable only from reactions with the reversible carbanion $(ElcB)_R$ mechanism[2] in which $k_{-1}\,[\overset{+}{\mathrm{B}}\mathrm{H}] >> k_2$ and $k_{obs} = k_1{\cdot}k_2/k_{-1}\,[\overset{+}{\mathrm{B}}\mathrm{H}]$. The value of the equilibrium constant for carbanion formation, k_1/k_{-1} depends primarily on X. The effect of the leaving group, Z, on the equilibrium constant is relatively small, varying according to the differential in σ^* (z). With X constant, therefore, k_{obs} is a good measure of the leaving group ability of Z. The $(ElcB)_R$ mechanism is assigned to all substrates included in the Table on the basis of the primary kinetic deuterium isotope effect $(k_H/k_D)_\beta = 1 \pm 0{\cdot}05$.



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The results show the following striking features: (a) the range of leaving group ability is very large, at least 10^{16} in k_{rel} expressed in the Table as $\log(k/k_{OPh})$; (b) positively charged groups depart very rapidly irrespective of the type of atom connection; (c) for neutral leaving groups, reactivity shows no correlation with the pK of the acid Z–H, C–Z bond strength, or carbon basicity[3] (as measured by k_{Nu} for Z: +MeI). It shows no simple correlation with group induction (σ_I) but is broadly dependent on the group of the periodic table to which the connecting atom belongs *viz.* VI >> V >> IV, but within a group is rather insensitive to period, *viz.* $PhSO_2$ *ca.* = PhSO·O and AcN(Me) *ca.* = $(EtO)_2P(O)$.

TABLE. Elimination in β-substituted sulphones

Z	k_{obs}/M^{-1} s^{-1}[a]	log(k/k_{OPh})	pK_{Z-H}[b]	log k_{Nu} + 6[c]
$OPO(OEt)_2$	548·8	+3·20	1·4	—
OCSPh[d]	0·20[e]	−0·16	3	—
OSOPh	0·24	−0·24	2	7·6
OPh	0·35[f]	0	10	4·8
OMe	4·3 × 10^{-5}	−3·91	16	5·4
$\overset{+}{S}MePh$	6·2 × 10^{5}[g]	+6·25	−5	4·0[h]
SCOPh	0·22[e]	−0·20	3	—
SO_2Ph	1·05[i]	+0·30	2	7·6[j]
SOPh	0·25	−0·15	5	—
SPh	0·021[k]	−1·22	7	9·0
$\overset{+}{N}Me_2Ph$	5·23 × 10^{4}	+5·17	5	4·7
N(Me)Ts	3·4 × 10^{-5}	−4·03	10	5·3
N(Me)Ac	4·6 × 10^{-6} [l]	−4·88	16	2·3
NMe_2	v. slow	v. neg	*ca.* 30	—
$\overset{+}{P}Ph_3$	8·8 × 10^{3}[m]	+4·40	0	6·1
$P(O)(OEt)_2$	1·2 × 10^{-5}[n]	−4·46	—	—
CN	<10^{-8}[o]	<−7	10	5·8
$C(Me)_2NO_2$	<10^{-10}	<−9	*ca.* 10	—
$CMe(CO_2Et)_2$	<10^{-8}	<−7	17	—

[a] In EtO^-–EtOH 25 °C; [b] values for H_2O (many approximate); [c] values from ref. 3; [d] $(E1cB)_R$ mechanism assigned on basis of proton exchange with medium; [e] estimated from value for $Bu^tO^-K^+$–Bu^tOH reactions; [f] J. Crosby and C. J. M. Stirling, *J. Chem. Soc.*, (*B*), 1970, 671; [g] estimated from Et_3N–EtOH data; [h] value for $(PhCH_2)_2S$; [i] statistically corrected; [j] value for SO_3^{2-}; [k] R. P. Redman and C. J. M. Stirling, *Chem. Comm.*, 1970, 633; [l] value at 40 °C divided by 5; [m] calculated from Et_3N–EtOH rate on $CN[CH_2]_2P^+Ph_3$; [n] value for $PhCO[CH_2]_2P(O)(OEt)_2$ divided by 100, *cf.* footnote f; [o] value for $CN[CH_2]_2CN$, *cf.* footnote f.

The wide range of leaving groups that can be studied in these activated eliminations is in direct contrast to the very restricted range amenable to examination in, for example, nucleophilic displacement at sp^3 carbon. Carbonyl-forming eliminations resemble activated alkene-forming eliminations in possessing a considerable range of leaving groups but quantitative data are difficult to obtain because of mechanistic complexities.

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