Structural Effects on Elimination from Carbanions

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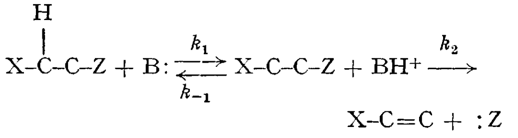
Summary Buffer saturation plots show, for β-eliminations from carbanions, that the balance between rate-determining ionisation and elimination steps is delicately held by the leaving group, that steric effects are important in deciding ionisation rates, and that the competition between elimination from carbanions and their reprotonation is insensitive to structure.

For 1,2-eliminations *via* carbanion intermediates, the following general scheme applies:


$$\text{X--}\overset{\text{H}}{\overset{|}{\text{C}}}\text{--C--Z} + \text{B:} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{X--C--C--Z} + \text{BH}^+ \xrightarrow{k_2} \text{X--C=C} + \text{:Z} \qquad (1)$$

Steady-state treatment of the intermediate carbanion gives the expression

$$k_{\text{obs.}} = k_1k_2[\text{B}]/(k_{-1}[\text{BH}^+] + k_2)$$

Two extreme cases exist: k_{-1} [BH$^+$] $<<$ k_2, when $k_{\text{obs.}} = k_1$ (irreversible E_1cB), and k_{-1} [BH$^+$] $>>$ k_2, when $k_{\text{obs.}} = Kk_2/[\text{BH}^+]$, where K is the dissociation constant for ionisation of the substrate in the medium (reversible E_1cB).

For reactions in buffered media, and with appropriate balance between the magnitudes of k_2 and k_{-1}, a change in mechanism from rate-determining ionisation ($k_{\text{obs.}} = k_1[\text{B}]$) to pre-equilibration ($k_{\text{obs.}} = Kk_2[\text{B}]/[\text{BH}^+]$) may be accomplished by increase in [B] at constant buffer ratio. As [B] is increased, $k_{\text{obs.}}$ increases to a limiting value, this being the phenomenon of buffer saturation.[1] Earlier examples for single systems have been described.[2]

The values of k_1 and of k_2/k_{-1} are derived from double reciprocal plots of $1/k_{\text{obs.}}$ *vs.* $1/[\text{B}]$ in which the slope is equal to $1/k_1$, and the intercept to $k_{-1}[\text{BH}^+]/k_1k_2[\text{B}]$.

We now report on the structural factors which determine the operative mechanism by controlling the rates of the processes involved. The substrates examined are given in the Table.

Table

Structural effects on rate constants[a] *for base-promoted eliminations*

		$\frac{10^2k_1}{\text{M}^{-1}\,\text{s}^{-1}}$	$\frac{10^4k_2/k_{-1}}{\text{M}}$
(1)	$\text{PhSO}_2\text{CH}_2\underset{\text{Ph}}{\underset{\vert}{\text{CH}}}\cdot\text{OAc}$	4·6	—
(2)	$\text{PhSO}_2\text{CH}_2\underset{\text{Ph}}{\underset{\vert}{\text{CH}}}\overset{+}{\text{N}}\text{Me}_3$	850	6·7
(3)	$\text{PhSO}_2\text{CH}_2\text{CH}_2\overset{+}{\text{N}}\text{Me}_3$	86	—
(4)	$\text{PhSO}_2\underset{\text{Ph}}{\underset{\vert}{\text{CH}}}\text{--CH}_2\overset{+}{\text{N}}\text{Me}_3$	24	10
(5)	$\text{PhSO}_2\underset{\text{Ph}}{\underset{\vert}{\text{CH}}}\text{--CH}_2\overset{+}{\text{N}}\text{MeEt}_2$ ..	6·8	19
(6)	$\text{PhSO}_2\text{CH}_2\text{CH}_2\overset{+}{\text{N}}\text{Et}_2\text{Me}$	53	—
(7)	$\text{PhSO}_2\text{CH}_2\text{CH}_2\overset{+}{\text{N}}\text{Me}_2\text{Ph}$	160	18

[a] Triethylamine buffers, in EtOH at 25°, $\mu = 0{\cdot}05$

Values of k_1 and of the elimination-reprotonation ratio, k_2/k_{-1}, show the following features:

(i) *Control of mechanism by the leaving group.* For the acetate (**1**), expulsion of the leaving group is easy and ionisation is rate determining. Change of the leaving group to Me_3N^+ has two effects: ionisation rate is increased by the powerful inductive effect of the 'onium group, and this (probably) poorer leaving group causes a decrease in the k_2/k_{-1} ratio, allowing the pre-equilibrium mechanism to manifest itself as the buffer concentration is raised. Such buffer saturation is not observed for the acetate. Comparison of substrates (**2**) and (**3**) shows that an α-phenyl group accelerates ionisation.

(ii) *Ionisation rate is very susceptible to steric retardation.* Transfer of the phenyl group to C_β results in a thirty-fivefold *lowering* of ionisation rate despite the fact that *acceleration* of ionisation would be expected to the extent that k_1 follows pK_a. This is attributed to steric retardation in stage 1, and when the leaving group is increased in size, further reduction of k_1 results [*cf.* also substrates (**3**) and (**6**)]. These results confirm earlier ideas[3] that the meagre accelerative effect of a β-phenyl group when associated with a bulky activating group such as phenylsulphonyl is steric in origin.

(iii) *Elimination–reprotonation ratios for carbanions are insensitive to structural change.* Values of k_2/k_{-1} for substrates (**2**), (**4**), (**5**), and (**7**) are almost constant. Thus, relative to reprotonation, elimination from the carbanion is little affected by α- or β-phenyl substitution or by change of leaving group, suggesting that there is little development of double-bond character in the transition state. These results again confirm earlier work[3] in which interpretation was limited to the comparison of overall rate constants.

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