Tetrahedron Letters No.32, pp. 3601-3604, 1968. Pergamon Press. Printed in Great Britain.

E1cB MECHANISMS

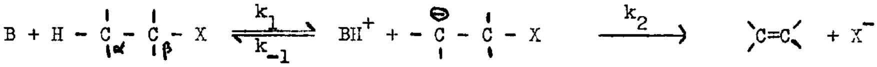
Zvi Rappoport

Department of Organic Chemistry, The Hebrew University,

Jerusalem , Israel

(Received in UK 15 April 1968; accepted for publication 14 May 1968)

A recent review (1) on the E1cB mechanism in base (B)-catalyzed eliminations from (IH) (eqn. 1) discusses its kinetics according to eqn. 2, derived by assuming steady-



$$B + H-\underset{\alpha}{\overset{|}{C}}-\underset{\beta}{\overset{|}{C}}-X \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} BH^+ + -\overset{\ominus}{C}-\overset{|}{C}-X \xrightarrow{k_2} \rangle C{=}C\langle + X^- \quad (1)$$

(IH) (I)

state formation of the intermediate (I). The limiting cases are: (i) The "irreversible" case, $k_2 \gg k_{-1}[BH^+]$, carbanion formation is rate determining, second order reaction, $k_{obs}=k_1$. (ii) The "pre-equilibrium" case, $k_{-1}[BH^+] \gg k_2$, unimolecular elimination from (I) is rate determining, $k_{obs}=k_1k_2/k_{-1}[BH^+]= Kk_2/[BH^+]$ where $K=k_1/k_{-1}$. Second order kinetics for excess $[BH^+]$, and decreasing rate coefficients if $[BH^+]$ is not in excess, and a rapid hydrogen exchange compared to the elimination rate are expected. Both (i) and (ii) show first order dependency on [IH].

Although this is the most studied case of E1cB reactions, it is only a limiting one in a series of E1cB mechanisms. We would discuss the other limiting, hitherto unrecognized E1cB mechanism, and comment on intermediate situations.

The kinetics of an E1cB elimination is affected by the acidity of IH and the basicity of B (reflected in K values), by the nature of X^- (connected with k_2) and by the acidity of HX. Some of these factors are interconnected. In the up to now studied cases, the combination of IH and B systems was such that K value was low, leading to a small steady state concentration of I. In most systems X^- was a good leaving group, e.g., halide ion, being therefore responsible for the "irreversible" case. HX was invariably stronger than IH, the base concentration decreased during the reaction. We would call this mechanism "Type-I E1cB".

In the other limiting case, K becomes very high by using IH with very acidic α-hydrogen and a relatively strong B, while X^- leaves slower than halide ion. In one variant HX is still stronger than IH. When $[B]\geqslant[IH]$, fast, almost complete neutralization takes place and $[IH]\simeq[I]$ before the elimination starts. The elimination rate$=k_2[I]$ becomes first order in IH and zero order in B. A stronger base would change K, but not the elimination rate, since the concentration of I remains nearly constant.

If $[B]<[IH]$, then $[I]\simeq[B]$ and within a run the reaction is zero order in B and first order in IH, if $[HX]$ at the end of the reaction is taken equal to $[B]$. For different initial concentrations, the reaction is first order in $[B]$ at constant $[IH]$ and zero order in $[IH]$ at constant $[B]$.

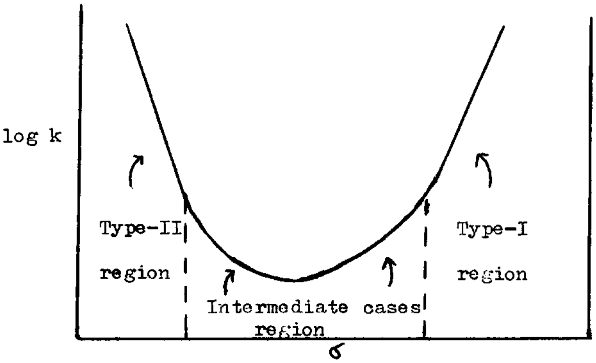
When HX is weaker (e.g., by two pK units) than IH, competition between IH and HX for B favours the former. With $[B]>[IH]$ the behaviour is similar to that discussed. However, as far as $[B]<[IH]$ the reaction is of zero order in both B and IH within a run, and when the concentrations become equal the reaction is first order in the remaining IH. The base is thus a "catalyst", causing elimination of higher concentrations of HX than its own. At constant $[B]$ a zero order dependency on the initial concentration of IH is expected, while keeping $[IH]$ constant and changing $[B]$ results in first-order dependency at low base concentration and zero order dependency when $[B]>[IH]$. We would call this limiting case "Type-II E1cB".

If IH have a moderate acidity and the base strength decrease gradually, intermediate cases, where $[I]$ concentration is smaller than $[B]$ but not as small as in type-I reactions would be observed. A complete removal of the proton is possible with higher concentrations of a weaker B , and the kinetics would be dependent on the concentration and the nature of B. Decreasing gap between the pK's of IH and HX, or increasing the leaving ability of X^- will move the mechanism in the direction of type-I reactions.

In addition to the kinetics the following is predicted for type-II reactions : A faster α-hydrogen exchange compared to the elimination would always be observed, while it characterize only the pre-equilibrium type-I reactions. The hydrogen isotope effect is predicted to be 1 for both types, although such a value was not found yet for type-I reactions. No isotope effect is expected for type-II even in non-protonic media.

Hammett's ρ value is predicted (1) to be highly positive for type-I reactions, but since electron-donating substituents will facilitate the bond-breaking of X^-, ρ will be negative for type-II reactions, provided that only this mechanism operates along the series. Since the substituent change may decrease the acidity of IH, intermediate cases as well as type-I reaction in the limit could be obtained, and a curved log k - σ relationship as shown schematically in Figure 1 may be sometimes expected.

Figure 1. Log k - σ Relationship for ElcB Eliminations



A Brönsted slope of near unity is predicted for the pre-equilibrium type-I reactions. The slope is expected to be near zero for type-II reactions as already discussed. This is shown schematically in Figure 2.

The characteristic features of the ElcB reactions are summarized in Table 1. In some kinetic aspects and in the ρ values, type-II are similar to El reactions. This is expected since the rate determining step in both is similar, starting either from a

Figure 2. Brönsted Relationship for ElcB Eliminations

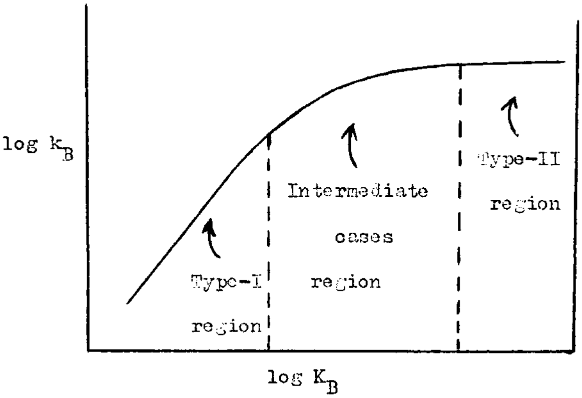


Table 1. Summary of the two E1cB Reactions

	Type-I	Type-II
Kinetics	First order in both $[B]$ and $[IH]$	$[B] > [IH]$, Zero order in $[B]$, first order in $[IH]$ $[B] < [IH]$ (i) Zero order in both $[B]$ and $[IH]$ [a] (ii) Zero order in $[IH]$, first order in $[B]$ [b]
ρ Value	Positive	Negative
Brönsted slope	1	0
Isotope exchange	Only in the pre-equilibrium case	Always
k_H/k_D	1	1

[a] In the same run. [b] On comparing runs with different initial concentrations.

negatively charged or a neutral species. However, the two eliminations differ in the nature of the activating substituents, and in the hydrogen exchange phenomena. Structural and enviromental changes would cause the E1 to move toward the E2 and the type-II E1cB toward the type-I reactions.

The type-II behaviour requires very strong electron-attracting groups on the α-carbon, and if possible also on the β-carbon. At present, the most promising systems are derived from 1,1,2,2-tetracyanoethane, since the dicyanomethyl hydrogen is highly acidic (2), the leaving CN^- is a poor leaving group, and its conjugate acid, HCN, is weaker than the cyanocarbon acids. Elimination of HCN from 2,6-dimethyl-4-(1,1,2,2-tetracyanoethyl)aniline indeed show the kinetics, the dependence on base and the isotope effects expected for type-II reactions with a suitable base (3). Investigations on this and related systems are now in progress.

REFERENCES

(1) D. J. McLennan , Quart. Revs. , 21 , 490 (1967) .
(2) R. H. Boyd , J. Phys. Chem. , 65 , 1834 (1961).
(3) Z. Rappoport and E. Shohamy , Paper submitted for publication .