A VERY SLOW E1cB ELIMINATION UNDER EXTREME E1cB CONDITIONS
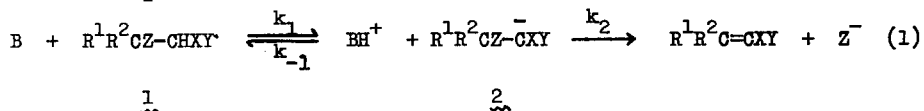
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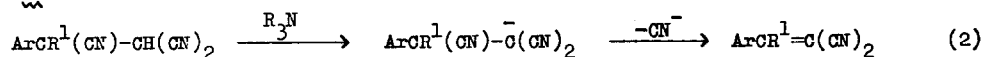[†]Department of Chemistry, Bar-Ilan University, Ramat-Gan, Israel
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Most work dealing with E1cB eliminations (equation 1, B = base, X and/or Y = electron attracting groups, Z = leaving group)[1] was under conditions where $k_2 > k_{-1}[BH^+]$ ("irreversible case") or $k_2 < k_{-1}[BH^+]$ ("pre-equilibrium case") where the carbanions 2 are formed in steady-state concentrations.[1b] Another variant, designated "E1cB of the second type"[2] or "irreversible first order carbanionic elimination",[3] where 2 is formed in an appreciable concentration and k_2 is rate determining was recently recognized.[2-7] The predictions that

$$B \ + \ R^1R^2CZ-CHXY \ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \ BH^+ \ + \ R^1R^2CZ-\overset{-}{C}XY \ \overset{k_2}{\longrightarrow} \ R^1R^2C=CXY \ + \ Z^- \quad (1)$$

$$1 \qquad\qquad\qquad\qquad\qquad 2$$

this variant will show certain kinetic behaviour depending on the $[1]/[B]$ ratio, and that negligible deuterium isotope effects and negative Hammett's ρ values for R^2=Ar should be observed were fulfilled in the amine-catalyzed elimination of cyanide ion from compounds 3 and 4 in chloroform and acetonitrile (equation 2).[4,5]
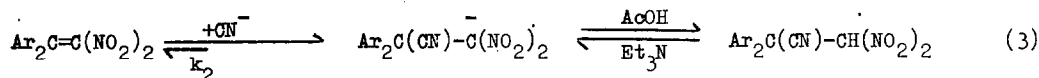
$$ArCR^1(CN)-CH(CN)_2 \ \overset{R_3N}{\longrightarrow} \ ArCR^1(CN)-\overset{-}{C}(CN)_2 \ \overset{-CN^-}{\longrightarrow} \ ArCR^1=C(CN)_2 \quad (2)$$

3: R^1=CN ; Ar=3,5-Me$_2$-4-H$_2$NC$_6$H$_2$

4: R^1=Me ; (a)Ar=p-MeOC$_6$H$_4$. (b)Ar=Ph

When k_1 is rate determining, increase in the electron-attracting ability of X and Y would increase the elimination rate. Following Breslow[8,9] we predict that such structural change for the 2nd-type E1cB would lower the elimination rate,[10] since delocalization of the negative charge by X and Y reduces the charge and the nucleophilicity of the α-carbon and hence lowers its tendency to "push" out the leaving group. However, a different view

that "the effect of the activating group on the magnitude of k_2 is slight" was suggested[11c]

following a study of a pre-equilibrium E1cB in compounds 1a ($\underline{1}$, $R^1=R^2=Y=H$, $Z=OPh$).[11] We

studied therefore an extreme situation where X and Y are nitro groups.

Addition of KCN to the dinitroethylenes 5 and 6 gave immediately the spectra of the

carbanions 7 (λ_{max}(MeCN):372 nm (ε 8,700)) and 8 (λ_{max}(MeCN): 373 nm (ε 8,300)).

β,β-Dinitro-α,α-diphenylpropionitrile 9 and its bis(p-methoxyphenyl) analog 10 were

isolated by addition of AcOH (equation 3). On addition of one or five molar equivalents of

$$Ar_2C=C(NO_2)_2 \underset{k_2}{\overset{+CN^-}{\rightleftharpoons}} \quad Ar_2\overset{-}{C}(CN)-\overset{\cdot}{C}(NO_2)_2 \underset{Et_3N}{\overset{AcOH}{\rightleftharpoons}} \quad Ar_2C(CN)-CH(NO_2)_2 \qquad (3)$$

$\underline{5}$: Ar=Ph $\underline{7}$: Ar=Ph $\underline{9}$: Ar = Ph

$\underline{6}$: Ar=p-MeOC$_6$H$_4$ $\underline{8}$: Ar=p-MeOC$_6$H$_4$ $\underline{10}$: Ar = p-MeOC$_6$H$_4$

Et$_3$N to 9 and 10 in acetonitrile the spectra of 7 and 8 appeared immediately. However, no

further spectral change corresponding to the formation of 5 and 6 was observed during 17

hrs at 40°, and 9 and 10 were recovered unchanged on acidification. No elimination was

observed when 9 was in excess over the Et$_3$N, although a possible re-addition of the CN$^-$ to

the formed 5 should be inhibited by protonation of the CN$^-$ by the unreacted acid 9.[4b]

In order to exclude more rigorously a hidden elimination as part of a rapid elimination-

addition sequence of the cyanide ion (e.g., $7 \rightarrow 5 \rightarrow 7$), the reactions of (a)0.048 mole/1

of ^{14}C-cyanide labelled 9 , 0.053 mole/1 Et$_3$N and 0.143 mole/1 KCN for 20 hrs at 40° in MeCN

and (b)0.027 mole/1 of 10 , 0.02 mole/1 Et$_3$N and 0.01 mole/1 of K[14]CN for 5 hrs at 40° in

MeCN were investigated. In reaction (a) where the experimental error is rather high ($\pm$7%)

the recovered 9 showed a loss of 7% of its radioactivity, while in reaction (b) the

incorporation of the inorganic - [14]CN in the recovered 10 was at most 0.32%. Since 10 would

react faster than 9 in a 2nd-type E1cB as predicted and found $(k_2(4a) > k_2(4b)$)[5] the latter

value (which was obtained by a more accurate technique) is the upper limit for the exchange

for both 7 and 8. If it is assumed that the exchange and the C-CN cleavage rates are

identical, then k_2 for 8 is 6.10^{-7} sec^{-1} at 40°.

The very slow elimination from 8 demonstrates that k_2 is indeed dependent on the

activating group. Expulsion of the cyanide ion from 8 with two activating nitro groups is

at least [12] 500-times slower than from 4a ($k_2^{40°}$ $= 3.4 \cdot 10^{-4}$ sec^{-1} in MeCN) where X,Y=CN.

We found no other data suitable for comparison, since although k_2 changes by 21 orders of

magnitude in ElcB eliminations[4-7b,13,14] this is mainly due to a change in the leaving group.

Our results fit the explanation given for the better correlation of ElcB rates from conpounds 1a *with the rates of ionization rather than with the equilibrium constants for* conpounds MeX.[11b,15] *It also suggests that in nucleophilic vinylic substitution of the* addition-elimination type[16] (equation 4) some of the highly activated systems may be less

$$R^1CZ=CXY + Nu^- \rightleftharpoons R^1C(Nu)(Z)-\overset{-}{C}XY \xrightarrow{k_2} R^1C(Nu)=CXY \qquad (4)$$
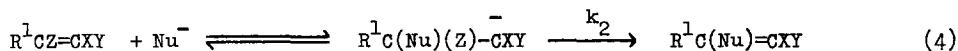
reactive than expected if the second step (which is analogous to k_2) becomes rate determining.

Protonation of the $\overset{-}{C}H(CN)_2$ carbanion is much faster than that of $\overset{-}{C}H(NO_2)_2$[18] and hence the two carbanion-consuming processes k_{-1} and k_2 respond similarly to a change in X and Y. However, this should not be generalized since the "deviant Bronsted relations"[19] when X= NO_2 were interpreted as due to increase in k_{-1} when Y and R^1 become more electron-attracting,[19a,b] and it was suggested that similar behaviour may be observed with other carbon acids.[19a,c] *If k_{-1} and k_2 are governed by the same factors*[20] *the higher k_2 for 3* compared with *4a and 4b*[4b,5] *may be the first example for such behaviour for cyanocarbon* acids.[21] Such analogies have interesting implications regarding both Breslow's suggestion that ElcB elimination from a carbanion may be slower than that from a partially formed carbanion, and Bordwell's suggestion[3] *that it is energetically more economic to form olefin* from an activated system in a two-step (ElcB) rather than in a concerted (E2) process. Experiments are now in progress to clarify this problem.

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9. However, in our system the ground state of 2 may be lower than that of 1.

10. This fits the suggested analogy between the El and the 2nd-type ElcB routes.[4b]

11. J. Crosby and C.J.M. Stirling , (a)<u>J.Amer.Chem.Soc.</u>, <u>90</u> , 6869 (1968); (b)<u>J.Chem.Soc.(B)</u>, 671 (1970) ; (c)<u>ibid.</u>, 679 (1970).

12. Both electronic and steric factors which were shown to be important for system 4 [5] should make 8 more reactive than the conjugate base of $4a$, while k_2 for 8 represents an upper limit.

13. While elimination of MeO^- from 2-phenyl-<u>trans</u>-2-methoxy-1-nitrocyclopentane ($k_2^{30°}$ values $\sim 10^{-5}$ sec^{-1} in MeOH)[6] is slower than that from 4-methoxy-2-butanone (estimated $k_2^{30°}$ values = 1.3-0.0003 sec^{-1} in water[14a] the different solvents and systems make the comparison unreliable.

14. (a)L.R. Fedor , <u>J.Amer.Chem.Soc.</u>, <u>91</u> , 908 (1969); (b)T.I. Crowell, R.T. Kemp, R.E.Lutz and A.A. Wall , <u>ibid.</u>, <u>90</u> , 4638 (1968); (c)W.K.Kwok, W.G. Lee and S.I. Miller, <u>ibid.</u>, <u>91</u> , 468 (1969).

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20. In this case reaction 4 may be used for investigating the "deviant Bronsted relations". The "structural reorganization" suggested in one explanation[19a,b] occurs here at the β-carbon (an $sp^2 \longrightarrow sp^3$ change) rather than at the α-carbanionic center. The "inter-molecular effect" of another explanation[19c] is replaced in reaction 4 by interactions of Nu^- and the substituents both in the transition state and in the product carbanion.

21. For another explanation see ref. 5.