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CONCERNING CARBANION INTERMEDIATES IN ELIMINATION REACTIONS

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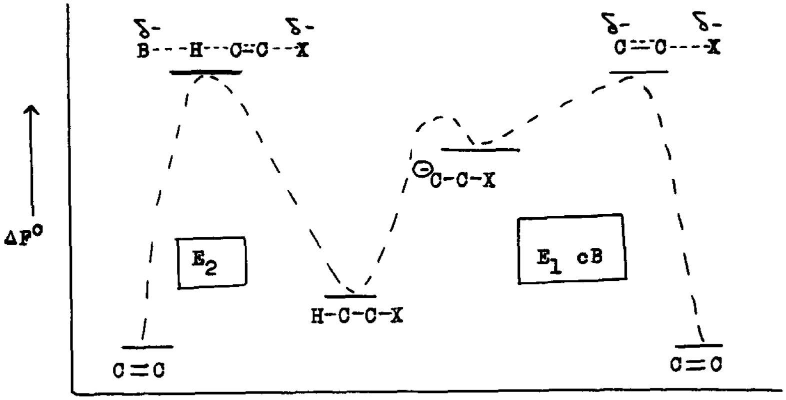
IN formulating general schemes by which elimination reactions might occur Ingold(1) described a two-step base-catalyzed elimination via the carbanion as the E_1 cB mechanism, although he pointed out that there was no definitive evidence for its occurrence in any real case at the time. In most base-catalyzed eliminations it has been found that the E_2 mechanism obtains, albeit with considerable carbanion character to the transition state in some cases.(2,3)

Recently mechanisms involving carbanions have been proposed for a number of elimination reactions. The claim that such mechanisms have been proved is also made in some recent review articles.(3,4) Generally the evidence consists of the finding that base-catalyzed deuterium exchange is faster than elimination, so the reversible carbanion mechanism is at least possible.

Such fast deuterium exchange under basic conditions has been observed during the elimination of HBr from 1,2-dibromoethylene (and in related reactions),(5) the elimination of HF from $CDCl_2CF_3$ and similar compounds,(6) the dehydration of malic acid to fumaric acid,(7) the formation of benzyne from chlorobenzene or fluorobenzene, although not from bromobenzene,(8) and the formation of dihalocarbenes by α-elimination from a variety of trihalomethanes, although not from difluorohalomethanes.(9) Some deuterium exchange also accompanies elimination from β benzene hexachloride.(10)

While it is generally recognized that in principle deuterium exchange accompanying elimination could be an irrelevant side reaction, it is apparently commonly assumed that this is only a formal possibility. The argument has been put forward that departure of the leaving group must certainly be easier from the free carbanion than from an incipient carbanion, so elimination via the carbanion will be the preferred path. Tacit agreement with such an argument seems to be the only explanation for the widespread conclusion that demonstrating reversible carbanion formation under elimination conditions is tantamount to demonstrating a carbanion elimination mechanism. However, this argument is fallacious. The fallacy is a common one, met when relative rates are discussed in terms of the reactivity of intermediates.

The difficulty is illustrated in the energy diagram.



In the competition between two mechanisms, the E_2 and the E_1 cB processes, the starting material(H-C-C-X) will be reversibly equilibrated with the carbanion ($^{-}$C-C-X) if the transition state for anion formation is lower than that for either elimination, but the relative rates of the E_2 and E_1 cB processes depend only on the relative energies of their transition states. The postulated high reactivity of carbanions in elimination reactions chiefly reflects the high energy of these species, but this same high energy results in a low equilibrium concentration of carbanion.

Considering enthalpies alone, it would generally be expected that the E_2 transition state will be the more stable. It has less negative charge on carbon, and so it resembles the stable hydrocarbon rather than its less stable anion. This agrees with the experimental findings for E_2 elimination in β-phenethyl derivatives: the cases with more carbanion character localized on the benzylic position are slower, while the cases with electron-withdrawing substituents on the phenyl ring, which decrease the charge density on the benzylic carbon, are faster.(3) This is expected, since electron-withdrawing groups lower the energy of a partially anionic transition state. However, it would not be expected if the important factor were the ability of the incipient anion to "push" the leaving group off. Entropy considerations will favor the stepwise carbanion process since the E_2 mechanism ties down the base in the transition state.

There are experimental criteria which will distinguish between these mechanisms, such as general vs. specific base catalysis (with the well-recognized ambiguities) or kinetic hydrogen isotope effects (although if proton exchange occurs complications arise(8) which can be explained equally well with either mechanism). In the absence of such evidence, care must be taken to distinguish between demonstrating that a carbanion may be formed and demonstrating that it is a reaction intermediate.

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