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THE MECHANISM OF THE CHLORIDE ION-PROMOTED DEHYDROCHLORINATION OF DDT AND RING-SUBSTITUTED ANALOGUES IN ACETONE

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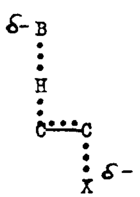
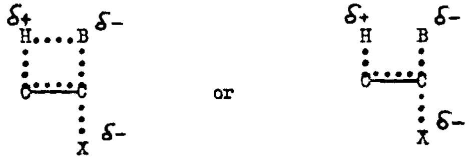
Some controversy has arisen regarding the mechanism of bimolecular elimination reactions promoted by halide ions in dipolar aprotic solvents and by thiolate anions, both of which are weakly basic towards hydrogen (in the thermodynamic sense) but are strong carbon nucleophiles (in the kinetic sense). One view is that such eliminations proceed through the same type of transition state (I) as do normal E2 reactions promoted by conventionally strong bases,[1] while another is that partial covalent attachment of the nucleophile to C_α as well as to the β-hydrogen is important (II).[2]



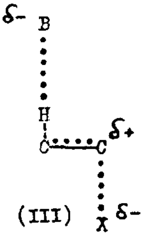
I(E2H)



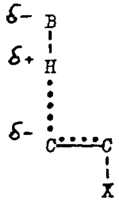
II(E2C)

With one important exception,[1d] evidence that has hitherto been cited in favour of either the E2H or E2C mechanisms appears to be ambiguous to some extent, and is capable of being reasonably explained in terms of the alternative hypothesis. For instance, the fact that the S_N2 reactivities of a series of halide and thiolate ions towards cyclohexyl tosylate parallel their elimination reactivities towards this substrate has been interpreted in terms of the S_N2 and olefin-forming transition states being similar, with the latter necessarily having E2C character.[2c] However, the reactivities of the strong bases OEt^-, OMe^- and OH^- in their undoubted E2H reaction with 2-phenethyl bromide also parallel their S_N2 reactivities (but do not correlate with their hydrogen basicities).[1f]

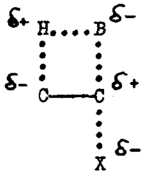
The principal source of the ambiguities is that substrates which readily eliminate with halide ions in dipolar aprotic solvents are secondary and tertiary halides and arenesulfonates, which, when E2H conditions are employed (strong base), pass through a paenecarbonium transition state (III).[1a] Thus a similar pattern of results would be expected for either II or III as the



(III)



(IV)



(V)

transition state, namely Saytzeff orientation,[2a] little sensitivity to acidifying β-substituents,[2e] low Hammett ρ constant,[3] low deuterium isotope effect[4] and solvent effects exemplifying "loose" transition states with much negative charge residing on B and X.[2g] A good case can be made for the transition states of halide-promoted eliminations of substrates so far studied being E2H and having somewhat more paenecarbonium character than the corresponding ones formed under undisputed E2H conditions. This would account for several notable differences in behaviour and is intelligible in view of the relative strengths of Hal....H and RO....H bonds.[1a]

DDT (VI; R = Cl) is dehydrochlorinated under E2H conditions (OEt^-/EtOH) clearly via a paenecarbanion transition state (IV).[5,6] Exploratory work has shown that dehydrochlorination occurs when n-Bu_4NCl in acetone containing 2,6-lutidine is used as the reagent, and that the kinetics are second-order.[7] Thus it is the only substrate known so far that undergoes E2H elimination through a paenecarbanion transition state and also undergoes halide-promoted elimination.

We have obtained the Hammett ρ constant for the reaction series:

$$\underset{\text{VI}}{(p\text{-}RC_6H_4)_2CHCCl_3} \xrightarrow{n\text{-}Bu_4NCl} (p\text{-}RC_6H_4)_2C{=}CCl_2 \quad + \quad HCl$$

and kinetic results are shown in the Table. A plot of log k_2 *vs.* 2σ is linear (correlation coefficient = 0.992; standard deviation = 0.13) and the ρ constant is 1.23. We contend that this value is too high to allow for the operation of an E2C mechanism, and argues in favour of an E2H transition state.

TABLE: The $(p\text{-}RC_6H_4)_2CHCCl_3$/$n$-$Bu_4NCl$ Reaction[a] in Acetone Containing 2,4,6-Collidine[b] at 65°.[c]

R =	Me	H	Cl	Br	NO_2
10^5k_2 (litre $mole^{-1}$ $sec.^{-1}$)[d]	7.62	15.0	83.8	113	1430

[a] The requisite olefinic product has been isolated in good yield for R = Cl. [b] [Coll.] has no effect on k_2. [c] Analysis by acid-base titration using a Radiometer automatic titrator. Potentiometric titration for Cl^- gave concordant results. [d] [DDT] ~ 0.02M; [n-Bu_4NCl] ~ 0.01M; [Coll] ~ 0.03M. Mean of two or more runs.

An E2C transition state resembles an S_N2 transition state except that in the former a little C_β— H bond loosening has occurred, although little β-carbanionic character is visualised.[2e] The ρ value for the S_N2 series $ArCH_2CH_2Cl/I^-$ in acetone[8] is 0.59, and those for the $ArCH_2CH_2OTs/OEt^-$ S_N2 series are 0.67 (EtOH) and 0.53 (t-BuOH).[9] One would expect ρ for E2C reactions of β-arylethyl compounds to be somewhat higher than this, but hardly around twice as great.

Our ρ value is significantly smaller than that found for the DDT E2H dehydrochlorination using OEt^-/EtOH[5] (2.46 at 40.2°, extrapolating to approximately 2.27 at 65°) but this is to be expected in view of the difference in basic strengths of the hydrogen nucleophiles. The transition state for the chloride-promoted dehydrochlorination of DDT thus appears to be E2H, and closer to "central" than is that for the OEt^-/EtOH reaction. C_β— H and C_α— Cl bond-breaking will have made roughly equal progress[1a] but there must still be a significant negative charge density at C_β. In fact, ρ is larger than that observed for the clearly E2H reaction of $ArCH_2CMe_2Cl$ with $OMe^-/MeOH$.[10] S_N2-like interaction between the nucleophile and C_α of DDT will be energetically discouraged by the other halogens on C_α[11] and even the extremely strong carbon nucleophile, PhS^-, does not undergo S_N2 reaction with DDT.[6]

A second important piece of evidence in favour of the E2H mechanism is that $(p\text{-}ClC_6H_4)_2CHCHCl_2$ (DDD) is not visibly dehydrochlorinated using $n\text{-}Bu_4NCl$ in acetone under conditions where DDT is at least 50% decomposed. This is intelligible in terms of an E2H process, in which α-halogens accelerate,[1e, 5] but not in terms of an E2C mechanism involving important S_N2-like interactions, since α-halogens retard S_N2 reactions.[11]

Although these conclusions cannot be directly extended to other reactions for which the E2C mechanism has been postulated, we believe that if halide ions in dipolar aprotic solvents are sufficiently strong hydrogen nucleophiles to promote an E2H reaction in which C_β— H bond-breaking is a significant cost factor, then there is no compelling need to discard the E2H mechanism when C_β— H bond-breaking is not an important activating process, as in III. In cases where paenecarbonium transition states are favourable, nucleophiles such as RS^- and halide ions in dipolar aprotic solvents often promote more facile elimination than do conventionally strong bases in protic solvents. The low desolvation energies in these systems appear to be an important factor, while thermodynamic basicity must be largely irrelevant because of the small degree of B....H bond formation. Using a different approach to ours, Eck and Bunnett have provided evidence against the E2C mechanism in cases where paenecarbonium transition states are likely to be involved.[1d]

It has been stated that E2C transition states have a well-developed double bond.[2e] Naively visualising the bonding situation at C_α in such a transition state as involving sp^2 hybridization with 4 electrons in a p-type orbital for the B....C....X moiety, it is difficult to see how overlap between this incipient p-type orbital and the incipient p-orbital at C_β containing the best part of 2 electrons, to form a partial π-bond could occur.[12] A charge-separated transition state such as V would overcome this difficulty, but all the available evidence, including that presented here, indicates that negative charge density on C_β is low relative to that found under E2H conditions, whereas this cannot be the case in V.

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