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ISOTOPE EFFECTS FOR THE BASE-PROMOTED DEHYDROCHLORINATION OF DDT IN PROTIC SOLVENTS. EVIDENCE FOR ElcB ELIMINATION.

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For a number of years we have been interested in the mechanism of the dehydrochlorination of DDT (Ar_2CHCCl_3 where Ar = p-ClC_6H_4) and its analogues in a variety of base-solvent systems.[1-4] It has always been assumed that the mechanism is the normal concerted E2 process, in which proton transfer from C_β and chloride loss from C_α occur simultaneously. The pre-equilibrium carbanionic mechanism[5] (ElcB Mechanism I) was rejected on the grounds that general rather than specific base catalysis was observed for reactions in ethanolic $PhS^-/PhSH$ buffers, and further, that no isotopic hydrogen exchange between substrate and hydroxylic solvent could be detected.[1]

ElcB Mechanism I

$$\mathrm{Ar_2CHCCl_3 + B^- \rightleftharpoons Ar_2\overset{-}{\ddot{C}}CCl_3 + BH} \quad \text{(fast, eqbm.)}$$

$$\mathrm{Ar_2\overset{-}{\ddot{C}}CCl_3 \longrightarrow Ar_2C{=}CCl_2 + Cl^-} \quad \text{(slow)}$$

Not so easily dismissed however is a variant of the stepwise carbanionic mechanism (ElcB Mechanism II) in which carbanion formation is irreversible and rate-determining, since general base catalysis and no hydrogen exchange are predicted for this process.[5] We now present evidence which strongly suggests that the latter mechanism in fact operates in protic solvents.

ElcB Mechanism II

$$\mathrm{Ar_2CHCCl_3 + B^- \longrightarrow Ar_2\overset{-}{\ddot{C}}CCl_3 + BH} \quad \text{(slow)}$$

$$\mathrm{Ar_2\overset{-}{\ddot{C}}CCl_3 \longrightarrow Ar_2C{=}CCl_2 + Cl^-} \quad \text{(fast)}$$

Primary deuterium isotope effects have been measured for the dehydrochlorination of DDT by a variety of anionic bases in ethanol (and by methoxide ion in methanol). Some of the results have been reported previously,[1] and are collected with more recent data in the Table. The isotope effect clearly rises to a maximum and then decreases as the base strength is increased. The maximum in a plot of k_H/k_D vs. pK_a (see Figure) is reasonably sharp.[8]

TABLE

Isotope Effects for the Dehydrochlorination of $Ar_2CH(D)CCl_3$[a] in Ethanol.

Base	Temp.(°C)	10^5k_H[b]	10^5k_D[b]	k_H/k_D	pK_a[c]
PhS^-	45	2.61	0.834	3.1	9.3
p-$NO_2C_6H_4O^-$	45	0.145	0.030	4.8	13.3
PhO^-	45	17.4	2.77	6.3	15.8
MeO^- [d]	30	1130	210	5.4	18.1[e]
EtO^-	45	36100	10600	3.4	20.3

[a] Ar_2CDCCl_3 is (100±1)% deuterated on C-1. [b] In 1 $mol^{-1}s^{-1}$. [c] pK_a of conjugate acid in EtOH, from refs. 1 and 6. [d] In methanol. [e] In methanol solvent. Basicity function measurements show that MeO^-/MeOH is less basic than EtO^-/EtOH (ref. 7).

Such an effect is theoretically respectable[9] but has only rarely been observed, and only a single report pertaining to elimination reactions exists, albeit for slightly different circumstances.[10] It is generally agreed that for reactions in which proton transfer is rate-determining, k_H/k_D should reach a maximum when the pK_a of the substrate is equal to the pK_a of the conjugate acid of the base producing the maximum isotope effect.[11] If DDT dehydrochlorination in fact proceeds by E1cB Mechanism II, the pK_a of DDT would thus be approximately 16. An uncertainty of one pK unit would appear to be reasonable (Figure).

The pK_a of DDT can be independently estimated. The pK_a of Ph_2CH_2 in methanol is[12] 30.2. If the reasonable[5,13] assumption of a Hammett ρ value of 5.0 for diphenylmethane ionization is made, the pK_a of Ar_2CH_2 can be calculated to be 27.9. If the Taft ρ^* value is assumed to be 5.0 for diarylmethane ionization (again a reasonable estimate[13]), use of $\sigma^* = 2.65$ for $-CCl_3$ and $\sigma^* = 0.490$ for -H[14] leads to $pK_a = 17.1$ for Ar_2CHCCl_3.

The agreement between the "kinetic" and L.F.E.R. estimates for the pK_a of DDT is remarkably good.[15] It is not direct proof for the rate-determining step in DDT dehydrochlorination being carbanion formation, but it is strongly suggestive.

A third variant of the carbanionic mechanism, similar to E1cB Mechanism I but involving internal rather than external return for carbanion reprotonation[16] can be easily rejected. Internal return invariably results in the observation of small (and even inverse) primary hydrogen isotope effects[12,16(a-d)] and there is no suggestion of these in the present system. These results, together with those in the accompanying communication,[17] point to simple deprotonation of DDT being rate-determining. Discussion of the nature of the transition states in our reactions, and of isotope effects for other ring-substituted DDT-type compounds in further base-solvent systems, is deferred to the full paper.

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