

ISOTOPE EFFECTS FOR THE BASE-PROMOTED DEHYDROCHLORINATION
OF DDT IN PROTIC SOLVENTS. EVIDENCE FOR E1cB ELIMINATION.

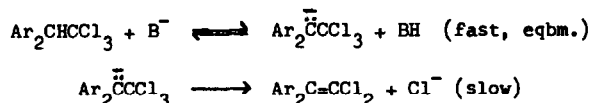
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For a number of years we have been interested in the mechanism of the dehydrochlorination of DDT ($\text{Ar}_2\text{CHCCl}_3$ where $\text{Ar} = p\text{-ClC}_6\text{H}_4$) and its analogues in a variety of base-solvent systems.¹⁻⁴ It has always been 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 mechanism⁵ (E1cB Mechanism I) was rejected on the grounds that general rather than specific base catalysis was observed for reactions in

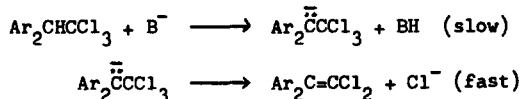
E1cB Mechanism I



ethanolic PhS^-/PhSH buffers, and further, that no isotopic hydrogen exchange between substrate and hydroxylic solvent could be detected.¹

Not so easily dismissed however is a variant of the stepwise carbanionic mechanism (E1cB 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

E1cB Mechanism II



evidence which strongly suggests that the latter mechanism in fact operates in protic solvents.

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 $k_{\text{H}}/k_{\text{D}}$ vs. pK_a (see Figure) is reasonably sharp.⁸

TABLE
Isotope Effects for the Dehydrochlorination
of $\text{Ar}_2\text{CH(D)CCl}_3^{\text{a}}$ in Ethanol.

Base	Temp. ($^{\circ}\text{C}$)	$10^5 k_{\text{H}}^{\text{b}}$	$10^5 k_{\text{D}}^{\text{b}}$	$k_{\text{H}}/k_{\text{D}}$	$\text{pK}_{\text{a}}^{\text{c}}$
PhS^-	45	2.61	0.834	3.1	9.3
$\text{p-NO}_2\text{C}_6\text{H}_4\text{O}^-$	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 $\text{Ar}_2\text{CDCCl}_3$ is (100 \pm 1)% deuterated on C-1. ^bIn $1 \text{ mol}^{-1}\text{s}^{-1}$. ^c pK_{a} of conjugate acid in EtOH, from refs. 1 and 6. ^dIn methanol. ^eIn methanol solvent. Basicity function measurements show that MeO^-/MeOH is less basic than EtO^-/EtOH (ref. 7).

Such an effect is theoretically respectable⁹ 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, $k_{\text{H}}/k_{\text{D}}$ 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 is¹² 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 estimate¹³), use of $\sigma^* = 2.65$ for $-\text{CCl}_3$ and $\sigma^* = 0.490$ for $-\text{H}^{14}$ leads to $\text{pK}_{\text{a}} = 17.1$ for $\text{Ar}_2\text{CHCCl}_3$.

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 ElcB Mechanism I but involving internal rather than external return for carbanion reprotonation¹⁶ 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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