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RATE-ACIDITY CORRELATION FOR THE BASE-PROMOTED DEHYDROCHLORINATION OF DDT IN METHANOL.

EVIDENCE FOR E1cB ELIMINATION.

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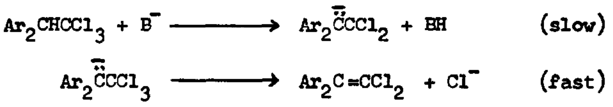
Streitwieser and co-workers[1] have recently shown that a Brönsted-type correlation exists between log k_2^T, the rate constants for second-order detritiation of tritiated indene and fluorene-type hydrocarbons in $MeO^-/MeOH$ at 45°C, and the hydrocarbon pK_a values relative to caesium cyclohexylamide in cyclohexylamine (CsCHA/CHA). The rate-determining step was identified as simple proton transfer to form the carbanion, from consideration of the magnitude of the Brönsted β parameter (0.369) and the hydrogen isotope effects. Internal return was found to be unimportant.

It follows that if the dehydrochlorination of DDT (Ar_2CHCCl_3, where Ar = p-ClC_6H_4) proceeds via the "irreversible" carbanion or E1cB mechanism[2] as previously proposed,[3] the point pertaining to the rate constant for elimination from tritiated DDT in $MeO^-/MeOH$ at



$$Ar_2CHCCl_3 + B^- \longrightarrow Ar_2\overset{-}{\ddot{C}}CCl_2 + BH \qquad \text{(slow)}$$

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

45° and the pK_a of DDT relative to CsCHA/CHA should lie on the Streitwieser Brönsted plot, as the rate-determining step is carbanion formation. Neither of these quantities has been measured but they can be estimated with reasonable precision.

The primary deuterium isotope effect for DDT dehydrochlorination by $MeO^-/MeOH$ at -0.1°C is 7.5 ($k_H = 3.24 \times 10^{-4}$ l mol^{-1} s^{-1}; $k_D = 4.31 \times 10^{-5}$ l mol^{-1} s^{-1}). From the 30°C rate constants quoted,[3] the k_H/k_D value at 45°C can be calculated as 4.7. The tritium isotope effect k_H/k_D can be obtained from this latter figure using the Swain-Schaad equation[4] (Eq. 1), and is found to be 9.3 at 45°C. The rate constant for dehydrochlorination of Ar_2CHCCl_3 by $MeO^-/MeOH$ at 45°C is[5]

$$\log(k_H/k_T) = 1.44 \log(k_H/k_D) \qquad \ldots\ldots\ldots\ldots\ldots\ldots(1)$$

5.14×10^{-2} l mol^{-1} s^{-1} and so k_T, the rate constant for detritiochlorination of Ar_2CTCCl_3 at this temperature is 5.53×10^{-3} l mol^{-1} s^{-1}.

The pK_a of DDT relative to CsCHA/CHA can be calculated as before.[3] The pK_a of Ph_2CH_2 relative to CsCHA/CHA is[6] 33.45. The reasonable assumption[7] of a Hammett ρ value of 5 leads to $pK_a = 31.15$ for Ar_2CH_2. If a Taft ρ^* value of 5 is then assumed[7] and σ^* values of 2.65 ($-CCl_3$) and 0.490 ($-H$) employed, the relevant pK_a of DDT is calculated to be 20.35.

The log k_T vs. pK_a point for DDT is shown, together with Streitwieser's hydrocarbon data,[1] in the Figure. It is clear that the DDT point lies on the line, as the deviation of 0.14 log units (rate) is well within the standard deviation of fit (0.200).[1] From the Brönsted equation pertaining to Streitwieser's least-squares plot[1] we may calculate $k_T = 4.0 \times 10^{-3}$ l mol^{-1} s^{-1}; a result which compares most favourably with the value calculated independently above. This is of course not direct evidence for the rate-determining step in DDT dehydrochlorination being irreversible deprotonation, but it is strongly suggestive, especially in view of the fact that the previous approach to the question yields the same conclusion.[3] Only arguments invoking coincidence could justify retention of our earlier assumption of a concerted E2 elimination in protic solvents.[4,8]

However, our previous conclusions based on the E2 mechanism require little modification, as it has always been recognised that the transition state has considerable carbanionic character at C_β and a poorly broken C_α-Cl bond. High $RO^-:RS^-$ rate ratios,[4] high Hammett ρ values (2.11 for $PhS^-/EtOH$;[8(a)] 2.37 for $MeO^-/MeOH$;[8(b)] 2.64 for $EtO^-/EtOH$,[9] the similarity indicating mechanistic similarity) and somewhat anomalous solvent effects pertaining to alkaline $MeOH/H_2O$ mixtures[8(c)] can be explained equally well if not better by an E1cB mechanism as by a paenecarbanion E2 process. However one apparent anomaly remains. Our isotope effects[3] suggest that the proton is about half-transferred, in force constant terms[10] rather than geometrically, in the transition state when phenoxide ion in ethanol is the base. On the other hand, the Brönsted β value for the DDT/p-$RC_6H_4O^-$ reaction series in ethanol (0.88) implies an almost completely transferred proton. Such discrepancies between k_H/k_D and β have been noted previously for disparate systems,[11] and in all cases it has been concluded that β is the less reliable criterion of transition state structure.

Bordwell has suggested that all β-eliminations from activated substrates should involve the intermediacy of carbanions,[12] and the present conclusions agree with his view. Whether a mechanistic extrapolation can be made to non-activated substrates such as simple alkyl halides and arenesulphonates is another matter however. Indirect evidence as presented here, and more direct evidence of the type adduced by Bordell and his co-workers for nitro- and sulphonyl-activated substrates[13] is lacking for simpler systems. In fact it seems clear that the chloride ion induced dehydrochlorination of DDT in acetone and DMF is a single-step E2 process, since the Hammett ρ values (1.31 for acetone and 0.99 for DMF)[14] are very much lower than those expected for carbanion formation.

The approaches to the identification of E1cB dehydrochlorination in this and the preceding paper are somewhat similar to one employed by Hine and Ramsey.[15]

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