The Carbanion Mechanism of Olefin-forming Elimination. Part VI.[1] Mechanism of the Dehydrochlorination of 1,1-Diaryl-2,2-dichloroethanes

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Rate constants for dehydrochlorination of the title compounds induced by NaOMe in MeOH and Bu^{t}OK in Bu^{t}OH are reported. Primary deuterium isotope effects for the reaction of 1,1-dichloro-2,2-bis-(*p*-chlorophenyl)ethane (DDD) with NaOMe in MeOH have been measured and these, together with the activation parameters, point to the importance of proton tunnelling. The rate of dehydrochlorination is faster than the rate calculated to pertain to carbanion formation from the latter compound. The Hammett ρ value (1·93) for the $Ar_2CH{\cdot}CHCl_2$ series with NaOMe in MeOH is significantly less than that for the $Ar_2CH{\cdot}CCl_3$ series, which has been shown to eliminate *via* carbanion intermediates. The sensitivity of DDD dehydrochlorination rates to [NaOMe] is less than that for $Ph_2CH{\cdot}CCl_3$. These three items of evidence suggest that compounds in the $Ar_2CH{\cdot}CHCl_2$ series undergo predominantly concerted *E*2 elimination, but the reaction may involve a *ca.* 20% contribution from an *E*1cB pathway.

IN the preceding two Parts,[1,2] it has been shown that the dehydrochlorination of DDT-type compounds ($Ar_2CH{\cdot}CCl_3$) by anionic bases in alcoholic solution proceeds *via* a carbanionic (*E*1cB) mechanism [3] in which the initial proton transfer is irreversible and rate determining.

We now turn our attention to compounds having one less α-chlorine atom, namely the DDD series ($Ar_2CH{\cdot}CHCl_2$), and enquire into the mechanism of the reaction in equation (1). Investigations of these reactions have been reported previously.[4,5] However

$$Ar_2CH{\cdot}CHCl_2 + B^- \longrightarrow Ar_2C{:}CHCl + Cl^- + BH \quad (1)$$

in both cases the medium was ethoxide in ethanol (dry ethanol in one case [4] and azeotropic ethanol in the other).[5] In order to facilitate comparison of the DDD system with the DDT reactions we have used sodium methoxide in methanol and potassium t-butoxide in t-butyl alcohol as the base–solvent systems.

DDD and DDT themselves (Ar = *p*-ClC_6H_4) differ in two ways as far as they are concerned as potential substrates for elimination. The pK_a of DDD, as calculated by the linear free energy relationship (l.f.e.r.) method previously outlined,[1,2] and referred to a standard state in dilute aqueous solution, is 23·9, whilst the pK_a of the more acidic DDT is 20·3. Secondly, the reacting chlorine in DDD is in a better environment for departure than is that in DDT [4,6] and so it should be a better leaving group from the former compound. A consequence of these facts is that DDD may possibly eschew the *E*1cB mechanism for dehydrochlorination and instead eliminate primarily *via* the concerted *E*2 route. Our evidence suggests that this is indeed the case.

RESULTS AND DISCUSSION

Isotope Effects and Rate of Carbanion Formation.—Rate constants and associated parameters for the reactions of DDD and its deuteriated analogue ($(p\text{-}ClC_6H_4)_2CD{\cdot}CHCl_2$) ([^{2}H]DDD) with 0·24M-NaOMe in MeOH at 30 and 45° are shown in Table 1. The expressed uncertainties in rate constants are standard or mean deviations derived

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[1] Part V, D. J. McLennan and R. J. Wong, *J.C.S. Perkin II*, preceding paper.

[2] D. J. McLennan and R. J. Wong, *J.C.S. Perkin II*, 1974, 526.

[3] D. J. McLennan, *Quart. Rev.*, 1967, **21**, 490.

[4] D. J. McLennan, *Austral. J. Chem.*, 1969, **22**, 1905.

[5] S. J. Cristol, N. L. Hause, A. J. Quant, H. W. Miller, K. R. Eiler, and J. S. Meek, *J. Amer. Chem. Soc.*, 1952, **74**, 3333.

[6] D. J. McLennan and R. J. Wont, *Tetrahedron Letters*, 1970, 881.

from the results from repeated runs. The derived activation parameters are not particularly accurate in an absolute sense, being based on rate constants measured at two temperatures 15° apart, but as will be seen later, they are sufficiently precise for our purposes.

TABLE 1

Rate constants, isotope effects, and activation parameters for the reactions of DDD and [^{2}H]DDD with NaOMe in MeOH

	$(p\text{-}ClC_6H_4)_2CH\cdot CHCl_2$	$(p\text{-}ClC_6H_4)_2CD\cdot CHCl_2$
10^3k_2/l mol^{-1} s^{-1} (30°)	4·58 ± 0·03	0·423 ± 0·001
10^3k_2/l mol^{-1} s^{-1} (45°)	17·4 ± 0·2	2·43 ± 0·01
k_H/k_D (30°)	10·8 ± 0·1	
k_H/k_D (45°)	7·2 ± 0·1	
E_a/kcal mol^{-1} [a]	17·1 ± 0·6	22·4 ± 0·6
log A [a]	9·97 ± 0·44	12·79 ± 0·43
$\Delta H^‡$/kcal mol^{-1} [b]	16·5 ± 0·6	21·0 ± 0·6
$\Delta S^‡$/cal K^{-1} mol^{-1} [b]	−17·0 ± 2·0	−4·1 ± 0·5

[a] From Arrhenius equation. [b] From Eyring equation.

The isotope effects at both temperatures are abnormally high. If the zero-point energy difference for C–H against C–D bond stretching is taken as 1·15 kcal mol^{-1},[7,8] and if a symmetrical C · · · H · · · B arrangement is assumed for the transition state,[8] the maximum values of k_H/k_D are 6·74 (30°) and 6·17 (45°). Effects due to bending mode changes are probably not important in linear proton transfers [9] and we now examine the possibility that proton tunnelling [10,11] is responsible for the high isotope effects.

Three further kinds of evidence, apart from high isotope effects, for proton tunnelling have been discussed by Caldin.[11] Non-linear Arrhenius behaviour is irrelevant to the present case. However, the value of $(E_a)_D - (E_a)_H$ (5·3 ± 1·2 kcal mol^{-1}) is significantly greater than the aforementioned 1·15 kcal mol^{-1} zero-point energy difference, and this type of behaviour is regarded as a criterion of tunnelling. The value of log A_D/A_H is 2·8 ± 1·4, and this is significantly greater than the 'classical' value of this quantity (*ca.* 0).[10,11] The case for proton tunnelling being of importance seems to be clearly proved by these results.

Tunnelling is also clearly implicated in the dehydrobromination of 1-bromo-2-phenylpropane by NaOEt in EtOH, although in this case the isotope effects are close to 'normal'.[12] However other relevant cases do involve high isotope effects,[13] including a further elimination example.[14]

The aim in evaluating the deuterium isotope effects was to calculate the hydrogen–tritium isotope effect using the Swain–Schaad equation [15] [equation (2)] and

$$\log k_H/k_T = 1{\cdot}44 \log k_H/k_D \qquad (2)$$

thence the rate constant for detritiochlorination of [^{3}H]DDD (k_T) by NaOMe in MeOH. If we then assume that the mechanism of detritiochlorination is 'irreversible' *E*1cB, with triton transfer to form the carbanion $Ar_2\bar{\ddot{C}}\cdot CHCl_2$ as the rate-determining step, then k_T is the second-order rate constant for this step. The rate constant for carbanion formation may also be estimated from the pK_a of DDD (23·9) and the Brønsted equation pertaining to protodetritiation of indene and fluorene-type hydrocarbons by NaOMe in MeOH at 45° [equation (3)].[16] From the experimental k_H/k_D value and equation

$$\log k_T = 5{\cdot}1085 - 0{\cdot}369\ \mathrm{p}K_a \qquad (3)$$

(2), log k_T is calculated to be −2·99 ± 0·01. From equation (3), log k_T for carbanion formation is −3·7 ± 0·2. The discrepency of 0·7 log units in rate is outside experimental uncertainty. We now consider various reasons why DDD should eliminate faster than it is estimated to form carbanions.

Proton tunnelling could be the cause of the deviation from the Brønsted plot. This phenomenon is known to give rise to serious deviations from the Swain–Schaad equation,[11] although this is not always the case.[9,12,13] It is calculated that a coefficient of 2·28 in equation (2) is needed to bring the experimental and theoretical values of k_T into agreement. However, we are not aware of a coefficient of such magnitude applying to any reaction, whether or not proton tunnelling is important. This possibility is thus most unlikely.

It could be that the l.f.e.r. pK_a of 23·9 is in error, and in fact a pK_a value of 21·9 for DDD would bring the DDD point down to lie on the hydrocarbon–carbanion Brønsted plot. The discrepancy of 2 pK units is not outside the bounds of possibility. However, no discrepancies of this magnitude were found when k_T values for 'irreversible' *E*1cB detritiochlorinations in the DDT series were compared with those from equation (3).

A case of carbanionic elimination proceeding faster than the predicted rate of carbanion formation has been discussed.[17] This was rationalized in terms of the latter reaction involving an important internal return component. However in the present model reaction series, internal return was shown to be negligible.[16]

We are thus left with the strong possibility that DDD eliminates predominantly *via* an *E*2 mechanism, at a

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[7] R. P. Bell, 'The Proton in Chemistry,' Cornell University Press, Ithaca, 1959, p. 203.

[8] F. H. Westheimer, *Chem. Rev.*, 1961, **61**, 265.

[9] R. A. More O'Ferrall and J. Kouba, *J. Chem. Soc.* (*B*), 1967, 985.

[10] Ref. 7, ch. 11.

[11] E. F. Caldin, *Chem. Rev.*, 1969, **69**, 135.

[12] V. J. Shiner and M. L. Smith, *J. Amer. Chem. Soc.*, 1961, **83**, 593; V. J. Shiner and B. Martin, *Pure Appl. Chem.*, 1964, **8**, 371.

[13] E. S. Lewis and L. H. Funderburk, *J. Amer. Chem. Soc.*, 1967, **89**, 2322; E. S. Lewis and J. K. Robinson, *ibid.*, 1968, **90**, 4337.

[14] L. F. Blackwell, P. D. Buckley, K. W. Jolly, and A. K. H. MacGibbon, *J.C.S. Perkin II*, 1973, 169.

[15] C. G. Swain, E. C. Stivers, J. F. Reuwer, and L. J. Schaad, *J. Amer. Chem. Soc.*, 1958, **80**, 5885.

[16] A. Streitwieser, W. B. Hollyhead, A. H. Pudjaatmaka, P. H. Owens, T. L. Kruger, P. A. Rubenstein, R. A. MacQuarrie, M. L. Brokaw, W. K. C. Chu, and H. M. Niemeyer, *J. Amer. Chem. Soc.*, 1971, **93**, 5088.

[17] F. G. Bordwell, J. Weinstock, and T. F. Sullivan, *J. Amer. Chem. Soc.*, 1971, **93**, 4728.

rate faster than that for carbanion formation. On the basis of the 0·71 log rate discrepancy, it may be estimated that an 'irreversible' *E*1c*B* mechanism contributes no more than 30% to the overall process. Is co-existence of these two mechanisms permitted in the present system?

More O'Ferrall has shown that *E*2 and *E*1cB mechanisms may function co-operatively if reprotonation of the carbanion occurs at a rate lower than that for diffusion control.[18] It can easily be shown that this applies to the DDD system. From the pK_a values of DDD and MeOH[2] we calculate $\Delta G^0 = 9{\cdot}6$ kcal mol^{-1} for the equilibrium in equation (4), and since equation (3) predicts $\Delta G_f^\ddagger = 19{\cdot}4$ kcal mol^{-1}, then $\Delta G_r^\ddagger = 9{\cdot}8$ kcal mol^{-1}, which is far from the diffusion limit. Simultaneous operation of *E*2 and *E*1cB mechanisms is thus permitted.

$$(p\text{-ClC}_6\text{H}_4)_2\text{CH}{\cdot}\text{CHCl}_2 + \text{OMe}^- \rightleftharpoons (p\text{-ClC}_6\text{H}_4)_2\text{C}{\cdot}\text{CHCl}_2 + \text{MeOH} \qquad (4)$$

We have previously remarked that the use of hydrogen isotope effects as a guide to *E*2 transition-state character may be fraught with errors.[1] In the DDD system we have the added complications of proton tunnelling and a dual reaction pathway. The measured isotope effects thus cannot be used to assign the *E*2 transition state to an area on the *E*2 spectrum.[19] Intuitive reasoning however would place it in the paenecarbanion region, where extensive proton transfer is associated with little C_α–Cl bond breaking.

The isotope effect has also been measured for Bu^{t}OK–Bu^{t}OH as the base–solvent system. It is a characteristic of *E*2 reactions that k_H/k_D for the latter base acting on a given substrate is greater than that for OMe$^-$–MeOH.[1,2] A simple explanation would be that tunnelling is more important when the bulkier base is employed, thus giving the higher isotope effect, but a limited number of probes for tunnelling have failed to reveal conclusive evidence for it.[20]

With Bu^{t}OK–Bu^{t}OH, k_H/k_D for DDD as substrate at 30° is $4{\cdot}93 \pm 0{\cdot}07$ ($k_H = 1{\cdot}07 \times 10^{-2}$, $k_D = 2{\cdot}17 \times 10^{-3}$ l mol^{-1} s^{-1}). This is less than the methoxide value, and is also lower than the theoretical maximum expected in the absence of tunnelling. If it is accepted that the *E*2 mechanism prevails in both base–solvent systems, it follows that the anomalous ordering of the isotope effects is a consequence of the importance of tunnelling in the OMe$^-$–MeOH medium, and its relative lack of importance when Bu^{t}OK–Bu^{r}OH is used. This is seemingly at variance with the general rule that severe steric crowding in transition states often leads to manifestations of the tunnel effect.[11,13] However, we are reminded that in the base-catalysed formation of enolate ions from ethyl 2-oxocyclopentanecarboxylate in water, tunnelling is more marked for F$^-$ as base than when ClCH$_2$CO$_2^-$ is the base.[21] It would thus appear that the size of the solvated base must be taken into account. Since MeOH is a more polar solvent than Bu^{t}OH, it is not unlikely that OMe$^-$ solvated by MeOH is a larger species than Bu^{t}O$^-$ solvated by Bu^{t}OH, and that tunnelling is thus more important with the former base. In these terms, the ordering of the isotope effects is not necessarily indicative of a non-*E*2 mechanism for DDD dehydrochlorination. Confirmation of this view awaits our intended studies of leaving group effects (chlorine isotope effects and element effects) for eliminations from the DDD systems with both bases.

The activation parameters for the reaction of DDD with OEt$^-$ in EtOH do not reveal the presence of an important tunnelling contribution.[4] Interpolation of rate constants[4] gives $k_H/k_D = 4{\cdot}56 \pm 0{\cdot}23$ at 30° in this system, which is lower than the Bu^{t}OK–Bu^{t}OH value of $4{\cdot}93 \pm 0{\cdot}07$ at the same temperature. The ordering of isotope effects is thus in line with the previously established *E*2 pattern for cases where tunnelling complications are absent.[2]

Basicity Function Correlation.—As with Ph$_2$CH·CCl$_3$ in the DDT system,[1] we have evaluated the sensitivity of the DDD rate constants in NaOMe–MeOH to the base concentration. Measured first-order rate constants, k_ψ obtained with $[\text{NaOMe}]_0 \gg [\text{DDD}]_0$, and the second-order rate constants k_2 derived from equation (5) are shown in Table 2. It is seen that k_2 is almost completely

$$k_2 = k_\psi/[\text{NaOMe}] \qquad (5)$$

insensitive to base concentration. This situation is very different from that met with when the *E*1cB substrate, Ph$_2$CH·CCl$_3$, was examined.[1] A plot for the DDD system of log k_ψ against the H_M function pertaining to NaOMe in MeOH (and derived from ionization measurements with a hydrocarbon acid)[22] is linear (r 0·998, s 0·03) with slope 0·58. The corresponding slope for processes in which the rate-determining step is proton transfer leading to carbanion formation is in the range 0·847—0·853.[1,22] These results imply, but do not demand, that the rate-determining step in DDD dehydrochlorination is not carbanion formation. A slope of around unity is expected for *E*1cB processes in which internal return is an important component.[1] Thus we

TABLE 2

Rate constants for the reactions of $(p\text{-ClC}_6\text{H}_4)_2\text{CH}{\cdot}\text{CHCl}_2$, in MeOH, with varying concentrations of NaOMe, at 30°

[NaOMe]/M	10^3k_ψ/s^{-1}	10^3k_2/l mol^{-1} s^{-1}
0·236	1·08	4·58
0·473	1·96	4·14
0·709	3·19	4·50
0·945	4·19	4·43
1·96	9·23	4·71

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[18] R. A. More O'Ferrall, *J. Chem. Soc.* (*B*), 1970, 268.

[19] J. F. Bunnett, *Angew. Chem. Internat. Edn.*, 1962, **1**, 225; *idem.*, in 'Survey of Progress in Chemistry,' ed. A. E. Scott, Academic Press, New York, 1969, vol. 5, p. 53.

[20] A. F. Cockerill, S. Rottschaefer, and W. H. Saunders, *J. Amer. Chem. Soc.*, 1967, **89**, 901; A. F. Cockerill and W. J. Kendall, *J.C.S. Perkin II*, 1973, 1352.

[21] R. P. Bell, J. A. Fendley, and J. R. Hulett, *Proc. Roy. Soc.*, 1956, *A*, **235**, 53.

[22] A. Streitwieser, C. J. Chang, and A. T. Young, *J. Amer. Chem. Soc.*, 1972, **94**, 4888.

are again left with the *E*2 mechanism as the most plausible possibility for elimination from DDD.

Hammett Equation Study.—Second-order rate constants for the dehydrochlorination of several $(p\text{-}RC_6H_4)_2CH\cdot CHCl_2$ compounds, induced by 0·24M-NaOMe in MeOH at 30° are shown in Table 3. The usual plot[1] of log k_2 against $2\sigma_I + (1 + \alpha)\sigma_R$ yields for α 0·63, ρ 1·93 (r 0·999, s 0·04). This ρ value may be contrasted with that for the *E*lcB $(p\text{-}RC_6H_4)_2CH\cdot CCl_3$ series (2·54 ± 0·07 with NaOMe–MeOH at 30°).[1] The conclusion is that the DDD transition states are less carbanionic than are those in the DDT series. This is in accordance with a predominantly *E*2 mechanism for DDD dehydrochlorination.

TABLE 3

Rate constants for the reactions of $(p\text{-}RC_6H_4)_2CH\cdot CHCl_2$ with *ca*. 0·24M,NaOMe in MeOH at 30°

R	MeO	Me	H	Cl	Br
10^3k_2/l mol^{-1} s^{-1}	0·095	0·103	0·395	4·58	4·66

The present ρ value cannot be used to assign *E*2 transition state character with certainty for the reason that no strictly relevant *E*2 ρ values that can serve as points of reference are available. It may be noted that ρ is not greatly diminished on going from the DDT to the DDD series, and this is consistent with a paenecarbanion *E*2 transition state for DDD. The acidifying β-phenyl groups and non-reacting α-chlorine atom will assist proton transfer,[18,19] whilst the leaving chlorine should not be particularly well severed from the α-carbon atom in the transition state because of the presence of an electron-withdrawing species on that carbon. A more direct approach to the problem of transition state structure will have to await the aforementioned studies of leaving group effects.

General.—In previous papers we have mentioned the DDT–DDD rate ratio for reactions in alkaline alcoholic solution as a possible mechanistic criterion.[4,6,23] It is now clear that such a comparison has little validity because of the mechanistic difference. However, the difference should be subtle in that the DDT transition state has intact C_α–Cl bonds whilst the DDD transition state may have a weakened C_α–Cl bond and a poorly-formed double bond. In this regard it is to be noted that although DDD is calculated to be more acidic than one of our *E*lcB substrates, $(p\text{-}MeO_6H_4)_2CH\cdot CCl_3$, it nonetheless avoids the *E*lcB mechanism almost completely. No anomaly exists, since the reactivity of the latter is governed entirely by the kinetic acidity of the β-proton, whilst the reactivity of DDD is determined both by acidity and leaving group ability.

Bordwell has recently questioned the very existence of the concerted *E*2 mechanism, and has favoured stepwise processes for elimination, that for acidic substrates being of course the *E*lcB pathway.[24] Our results run counter to this claim, and if the *E*2 mechanism is available to a substrate as acidic as DDD, it should also be the most important route used by non-activated substrates such as alkyl halides. An alternative stepwise process for second-order elimination, the Sneen–Robbins carbonium ion-pair mechanism[25] may be dismissed for the DDD case, for reasons connected with the reasonably high ρ value.[26] We are thus left with the *E*2 mechanism, which may be viewed as a hybrid between stepwise routes involving $[Ar_2CH\cdot\overset{+}{C}HCl]Cl^-$ and $Ar_2\overset{\overline{\cdot\cdot}}{C}\cdot CHCl_2$ intermediates, as providing the best rationalization of our results.

EXPERIMENTAL

Preparations and properties of materials employed have been described earlier.[2,4,22] [^{2}H]DDD was found to be 97·5% isotopically pure by mass spectrometry, and observed rate constants for reactions of this compound were adjusted accordingly.

Reactions were carried out in the thermostatted cell compartment of a Unicam SP 3000 spectrophotometer. The choice of fixed wavelength, in the 260—280 nm range, was governed by the expected 'infinity' absorbance. Slower reactions were run with the solutions contained in sealed ampoules. After cooling and volumetrically acid-quenching samples at various times, spectrophotometric measurements were made. Hydrogen–deuterium exchange accompanying the reactions of [^{2}H]DDD was not observed.

2-Chloro-1,1-bis-(p-chlorophenyl)ethylene,[23] the DDD reaction product, did not react with NaOMe–MeOH or Bu^{t}OK–Bu^{t}OH under the conditions employed for dehydrochlorination.

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[23] D. J. McLennan and R. J. Wong, *J.C.S. Perkin II*, 1972, 279.

[24] F. G. Bordwell, *Accounts Chem. Res.*, 1972, **5**, 374.

[25] R. A. Sneen and H. M. Robbins, *J. Amer. Chem. Soc.*, 1969, **91**, 3100.

[26] D. J. McLennan, *J.C.S. Perkin II*, 1972, 1577.