The Carbanion Mechanism of Olefin-forming Elimination. Part VII.[1] The Isotope Effect Maximum in the Dehydrochlorination of 2,2,2-Trichloro-1,1-bis-(*p*-chlorophenyl)ethane by Various Bases in Alcholic Solvents

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When the *E*1cB dehydrochlorination reactions of $Ar_2CH\cdot CCl_3$ and $Ar_2CD\cdot CCl_3$ ($Ar = p\text{-}ClC_6H_4$) are induced by a series of bases in ethanol ranging in strength from PhS^- to OEt^-, a maximum in k_H/k_D is observed for phenoxide as base. The kinetics of the phenoxide-induced reactions are re-examined using conditions under which buffering of the reaction solutions is ensured. The maximum is found to be real. An Arrhenius equation study of the reactions, and the reactions of PhS^-, OMe^- (in MeOH), and OEt^- with these substrates fails to reveal a significant contribution from proton tunnelling to k_H/k_D values. It is proposed that the maximum is caused by variations in transition state symmetry.

In Parts IV[2] and V[3] of this series we have presented evidence which strongly suggests that the mechanism of dehydrochlorination of 1,1-diaryl-2,2,2-trichloroethanes by anionic bases in alcoholic solvents is *E*lcB with the initial proton transfer being irreversible and rate-determining [equation (1)]. One item of evidence

$$Ar_2CH\cdot CCl_3 + B^- \longrightarrow Ar_2\overset{-}{\ddot{C}}\cdot CCl_3 + BH \quad \text{slow}$$

$$Ar_2\overset{-}{\ddot{C}}\cdot CCl_3 \longrightarrow Ar_2C{:}CCl_2 + Cl^- \quad \text{fast} \qquad (1)$$

presented[2] was that the hydrogen–deuterium isotope effect passed through a maximum[4] as the strength of the base was increased. The maximum was thought to correspond to a ΔpK value close to zero † [$\Delta pK = pK_a(Ar_2CH\cdot CCl_3) - pK_a(BH)$] as shown in Table 1, and as could be expected for a reaction in which direct proton transfer is rate determining.[5] We now reinvestigate in more detail two aspects of this work.

First, the reality or otherwise of the maximum in k_H/k_D rests largely on its value when phenoxide is the base. In these reactions, the position of equilibrium (2) and the relative reactivities of PhO^- and OEt^- are such

$$PhO^- + EtOH \rightleftharpoons PhOH + OEt^- \qquad (2)$$

that rate constants obtained under second-order conditions ($[PhO^-]_0$ and $[substrate]_0$ comparable) must be measured in the presence of an excess of phenol. A plot of k_2(obs) against $[PhOH]^{-1}$ should give the true second-order rate constant for phenoxide attack, k_{PhO}, as the intercept.[6] Under such conditions however, [PhOH] will increase during the course of the reaction as PhO^- is consumed, and uncertainty is thus attached to the derived value of k_{PhO}.

Secondly, we consider the origin of the isotope effect maximum. One theory is that such a maximum is to be expected when the proton in the transition state is held equally strongly by the donor and acceptor species.[4] The condition, $\Delta pK = 0$, is thought to be a reasonable criterion for such a transition state.[5] A conflicting theory[7] is that the influence of proton tunnelling (which has the effect of increasing isotope effects) is at a maximum at $\Delta pK = 0$.

RESULTS

The reactions of $Ar_2CH\cdot CCl_3$ and $Ar_2CD\cdot CCl_3$, *ca.* 10^{-4}M, with PhO^- (0.02—0.12M) were studied at various temperatures in buffers of varying phenol content. Since $[PhO^-]_0 \gg [substrate]_0$, the solutions are truly buffered and the observed kinetics are first-order, with rate constants k_ψ. Under these conditions, equation (3) is applicable. Here, k_{OEt} is the

$$k_\psi/[PhO^-] = k_{PhO} + K_b k_{OEt}/[PhOH] \qquad (3)$$

second-order rate constant for concomitant ethoxide attack and K_b is the basicity constant of phenoxide in ethanol. The values of $[PhO^-]$ and [PhOH] employed are calculated

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† See Part VIII for a reassessment of this statement. The value of ΔpK at the maximum is not however relevant to the present study.

[1] Part VI, A. B. N. Gray and D. J. McLennan, *J.C.S. Perkin II*, 1974, 1377.

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

[3] D. J. McLennan and R. J. Wong, *J.C.S. Perkin II*, 1974, 1373.

[4] (*a*) F. H. Westheimer, *Chem. Rev.*, 1961, **61**, 265; (*b*) J. Bigeleisen, *Pure Appl. Chem.*, 1964, 8, 217; (*c*) R. A. More O'Ferrall and J. Kouba, *J. Chem. Soc.* (*B*), 1967, 985; (*d*) A. O. Cohen and R. A. Marcus, *J. Phys. Chem.*, 1968, **72**, 4249.

[5] R. P. Bell and D. M. Goodall, *Proc. Roy. Soc.*, 1966, *A*,**294**, 273; R. P. Bell and D. J. Barnes, *ibid.*, 1970, *A*,**318**, 421.

[6] J. W. Baker and A. J. Neale, *J. Chem. Soc.*, 1952, 3225.

[7] R. P. Bell, W. H. Sachs, and R. L. Tranter, *Trans. Faraday Soc.*, 1971, **67**, 1995.

assuming that on dissolution of excess of phenol in ethanolic sodium ethoxide, $[PhO^-] = [OEt^-]_{st}$, and $[PhOH] = [PhOH]_{st} - [OEt^-]_{st}$, where $[PhOH]_{st}$ corresponds to the quantity of phenol used and $[OEt^-]_{st}$ is the alkali concentration. This will not be exactly so according to equilibrium (2), and Bunnett and Rettallick[8] have devised a more correct iterative computational procedure. In selected cases it was found that values of k_{PhO} calculated from equation (3) and by the iterative method differed by <2%. The former method was employed in the majority of cases since it is less tedious.

TABLE 1

Hydrogen–deuterium isotope effects for reactions of $Ar_2CH{\cdot}CCl_3$ ($Ar = p\text{-}ClC_6H_4$) with various bases at 45°

Base	Solvent	k_H/k_D	ΔpK [a]
PhS^-	EtOH	3.13	7.8
$p\text{-}NO_2C_6H_4O^-$	EtOH	4.83	3.8
PhO^-	EtOH	6.2	1.3
OMe^-	MeOH	4.71	−1.2
OEt^-	EtOH	3.40	−3.2

[a] Based on pK_a ($Ar_2CH{\cdot}CCl_3$) = 17.1.[2]

TABLE 2

Reaction of NaOPh (0.121M) with $Ar_2CH{\cdot}CCl_3$ in ethanol at 35.0°

$[PhOH]/M$	0.331	0.250	0.177	0.128	0.102
$10^5k_\psi(obs)/s^{-1}$	3.68	4.95	6.58	8.91	10.9
$10^5k_\psi(calc)/s^{-1}$	3.69	4.93	6.57	8.85	11.0

[a] Calculated from equation (3) using $10^5k_{PhO} = 5.04$ l mol^{-1} s^{-1}, $k_{OEt} = 0.135$ l mol^{-1} s^{-1}, and $K_b = 6.46 \times 10^{-4}$.

TABLE 3

Reactions of NaOPh with $Ar_2CH{\cdot}CCl_3$ and $Ar_2CD{\cdot}CCl_3$ in ethanol

	$Ar_2CH{\cdot}CCl_3$		$Ar_2CD{\cdot}CCl_3$		
$T/°C$	10^5k_{PhO} [a]	pK_b [b]	10^5k_{PhO} [a]	pK_b [b]	k_H/k_D
35.0	5.04	3.19			
45.0	17.8	3.15	3.17	3.21	5.6 ± 0.4
54.9	48.4	3.12	9.29	3.10	5.2 ± 0.5
60.4	81.8	3.20	17.9	3.08	4.6 ± 0.4
65.2	147	3.07	28.5	3.03	5.1 ± 0.4
75.5			78.9	3.08	

[a] In 1 mol^{-1} s^{-1}. [b] Uncorrected for activity coefficient effects.

Raw rate data obtained at a sample temperature are shown in Table 2. Further data are contained in Supplementary Publication No. SUP 21682 (3 pp.).* Values of k_{PhO} and pK_b were calculated by a least-squares procedure from equation (3), using concentrations which were corrected for temperature differences, and are presented in Table 3. The values of k_{OEt} for each temperature are either known or can be extrapolated.[9] The pK_b values in Table 3 compare well with the reported[10] spectrophotometric values of 3.3 (25°) and 3.0 (45°). None of the plots of k_ψ against $[PhOH]^{-1}$ have correlation coefficients <0.998, and the standard deviations in the intercepts correspond to no more than a 4% uncertainty in k_{PhO}. At each temperature, the same concentration of PhO^- was used for $Ar_2CH{\cdot}CCl_3$ and $Ar_2CD{\cdot}CCl_3$, and the isotope effects for phenoxide attack are also shown in Table 3.

TABLE 4

Reactions of $Ar_2CH{\cdot}CCl_3$ and $Ar_2CD{\cdot}CCl_3$ with various bases in ethanol

		10^5k_2/l mol^{-1} s^{-1}		
Base	$T/°C$	$Ar_2CH{\cdot}CCl_3$	$Ar_2CD{\cdot}CCl_3$	k_H/k_D
PhS^-	45.0	2.61	0.834	3.13
PhS^-	55.0	8.09	2.89 [a]	2.80
PhS^-	65.0	26.4	9.49	2.78
PhS^-	75.0	76.7	30.6 [b]	2.67
PhS^-	84.8	205	79.1	2.59
OMe^- [c]	0.0	32.8	5.12	6.40
OMe^- [c]	21.4		79.6	5.65 [d]
OMe^- [c]	25.0	741		6.02
OMe^- [c]	30.0	1 130	219	5.16
OMe^- [c]	35.0	1 660	386	4.30
OMe^- [c]	45.0	5 180	1 100	4.71
OEt^-	0.0	270	60.3	4.48
OEt^-	21.4	3 460	836	4.13
OEt^-	25.0	4 920	1 280	3.84
OEt^-	35.0	13 800	3 940	3.50
OEt^-	45.0	36 100	10 600	3.40

[a] At 54.9°. [b] At 75.5°. [c] Solvent MeOH. [d] At 21.4°, by interpolation. [e] At 25°, by interpolation.

In Table 4 are shown second-order rate constants and isotope effects for the reactions of $Ar_2CH{\cdot}CCl_3$ and $Ar_2CD{\cdot}CCl$ in the base–solvent systems PhS^-–EtOH, OMe^-–MeOH, and OEt^-–EtOH at various temperatures. Some of these have been taken from earlier work.[2,9]

DISCUSSION

Reactions of Phenoxide.—The adherence of the observed first-order rate constants to equation (3) is impressive. This is not however the case when reactions catalysed by EtS^- in methanolic EtS^-–EtSH buffers are considered, where the iterative calculation must be employed.[8] The reason that the present approximate calculations work as well as the iterative method is that PhO^- in ethanol is *ca.* 10 times less basic with respect to the solvent than is EtS^- in methanol so that the aforementioned assumptions are closer to the truth in the present case. The second-order rate constants at 45° agree reasonably well with those obtained under second-order partially buffered conditions (17.4×10^{-5} and 2.8×10^{-5} l mol^{-1} s^{-1} for $Ar_2CH{\cdot}CCl_3$ and $Ar_2CD{\cdot}CCl_3$ respectively [2]). The value of k_H/k_D at 45° is a little lower than that reported earlier,[2] but even when the larger than usual uncertainty of *ca.* 8% is considered, the phenoxide isotope effect is still clearly larger than any of those mentioned in Table 4 (to which a maximum uncertainty of 5% may be attached). The isotope effect maximum is thus real and we now enquire as to its origin.

Search for Proton Tunnelling.—The data in Tables 3 and 4 are now scrutinized in order to see if any support for the contention of Bell and his co-workers [7] that isotope effect maxima at $\Delta pK = 0$ arise from proton tunnelling effects having a maximal influence at this ΔpK value (where a symmetrical transition state is expected) can be adduced. Four interdependent criteria for significant tunnelling are commonly employed: (i) abnormally high

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* For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Perkin II*, 1975, Index issue. Items less than 10 pp. are supplied as full-size copies.

[8] J. F. Bunnett and L. Rettallick, *J. Amer. Chem. Soc.*, 1967, **89**, 423.

[9] B. D. England and D. J.McLennan, *J. Chem. Soc.* (*B*), 1966, 696.

[10] B. D. England and D. A. House, *J. Chem. Soc.*, 1962, 4421.

TABLE 5

Activation parameters for the reactions of $Ar_2CH{\cdot}CCl_3$ and $Ar_2CD{\cdot}CCl_3$ with various bases

Base	$(E_a)_H$ kcal mol^{-1}	log A_H	$(E_a)_D - (E_a)_H$ kcal mol^{-1}	log A_D/A_H	$\Delta H^{\ddagger}$ [a] kcal mol^{-1}	$\Delta S^{\ddagger}$ [b] cal K^{-1} mol^{-1}
OEt^-	18.8 ± 0.1	12.5 ± 0.1	1.1 ± 0.2	0.2 ± 0.2	18.2	-5.4
OMe^- [c]	19.3 ± 0.3	11.9 ± 0.2	1.4 ± 0.5	0.3 ± 0.3	18.7	-7.9
OPh^-	22.6 ± 0.3	11.8 ± 0.4	1.0 ± 0.6	-0.1 ± 0.6	22.0	-8.8
SPh^-	24.9 ± 0.1	12.5 ± 0.1	0.9 ± 0.2	0.1 ± 0.2	24.3	-5.5

[a] Enthalpy of activation for $Ar_2CH{\cdot}CCl_3$. [b] Entropy of activation for $Ar_2CH{\cdot}CCl_3$. [c] In methanol.

isotope effects; (ii) values of $(E_a)_D - (E_a)_H$ greater than the zero-point energy difference between C–D and C–H stretching modes, which is *ca.* 1.15 kcal mol^{-1}; (iii) values of A_D/A_H (ratio of Arrhenius pre-exponential factors) >2; and (iv) curvature of Arrhenius plots.[11,12]

None of the isotope effects in Tables 3 and 4 are abnormally large. All Arrhenius plots of $\log k_2$ against $1/T$ are strictly linear and have correlation coefficients $>0.998\,9$. Deviations from linearity symptomatic of proton tunnelling are considered to be of greater magnitude at lower temperatures,[11a,b,12] but for practical reasons the reaction between PhO^- and $Ar_2CH{\cdot}CCl_3$ could not be studied at temperatures lower than 35° without using higher base concentrations, which could give rise to salt effects.

Arrhenius parameters and derived data for all reactions are given in Table 5. The magnitudes of the experimental uncertainties (based on the standard deviations in the slopes of the Arrhenius plots) cloud the issue as far as $(E_a)_D - (E_a)_H$ is concerned, but it can be seen that none of the activation energy differences are particularly large, and that all could have values of 1.15 kcal mol^{-1} or less. It is unfortunate that, since k_{PhO} is not determined directly, the largest uncertainty is associated with phenoxide as base. However there is no evidence from the values presented that tunnelling influences reach a maximum around $\Delta pK = 0$. Experimental uncertainties also obscure interpretation of the A_D/A_H values, and again the greatest uncertainty occurs with phenoxide. However, $A_D/A_H < 2$ ($\log A_H/A_D < 0.3$) is a permitted result in all cases. In fact it may be shown that the experimental finding of $A_H > A_D$ for PhO^- is real. Calculation (Table 6) of rate constants for the reaction of $Ar_2CD{\cdot}CCl_3$ assuming $A_D = A_H$ and using the measured $(E_a)_D$ gives values that are significantly higher than the observed rate constants. This can only be so if A_H is greater than A_D by a small amount. There can thus be little doubt that tunnelling is unimportant in this reaction.

In summary, the view that differential degrees of tunnelling are primarily responsible for the isotope effect maximum is not sustained by the Arrhenius equation treatment, particularly for the base generating the largest isotope effect.

The reaction of phenylnitromethane with various bases in water exhibits a maximum k_H/k_D value at ΔpK *ca.* 0. An inspection of Arrhenius parameters shows that tunnelling is significant in some reactions, but there is no correlation between the magnitudes of k_H/k_D and the tunnel correction,[13] the latter being taken as the discrepancies between $(E_a)_D - (E_a)_H$ and $\log A_D/A_H$, and their respective 'classical' values. Unambiguous experimental verification of the essential correctness of the Bell model [7] has yet to be provided.

TABLE 6

Comparison of calculated and experimental rate constants for the reaction of $Ar_2CD{\cdot}CCl_3$ with NaOPh in ethanol

		10^5k_2(calc)/l mol^{-1} s^{-1}	
T/°C	10^5k_2(obs)/l mol^{-1} s^{-1}	A [a]	B [b]
45.0	3.17 ± 0.11	3.11	3.68
54.9	9.29 ± 0.31	9.59	11.3
60.4	17.9 ± 0.7	17.4	20.6
65.2	28.5 ± 1.0	28.9	34.1
75.5	78.9 ± 2.5	81.4	96.3

[a] Calculated from $\log k_2 = 11.707 - 23\,610/2.303RT$. [b] Calculated from $\log k_2 = 11.780 - 23\,610/2.303RT$.

An alternative explanation for the isotope effect maximum comes readily to hand. Measurement of Hammett ρ constants indicates that the transition state for $Ar_2CH{\cdot}CCl_3$ deprotonation becomes more carbanionic as the strength of the base increases.[3] Transition state symmetry is thus changing, and so long as a symmetrical (in terms of $B \cdots H$ and $H \cdots C$ force constants) transition state occurs within the range of bases employed, the maximum in k_H/k_D can be understood. The way in which transition state structure appears to change with increasing base strength is opposite to what is considered normal behaviour,[4d,14–16] but it can be accounted for in terms of the steric consequences of base solvation.[17] The structural variation in the bases considered here is too great to permit application of the Marcus theory of proton transfer.[4d] This point is to be further elaborated. However the isotope effects do provide information as to transition state structure, with the proviso that without additional information one does not know whether a small isotope effect is indicative of little or much proton transfer.

EXPERIMENTAL

General preparative and kinetic details have been published previously.[1,2,9] The following analytical pro-

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[11] (*a*) R. P. Bell, 'The Proton in Chemistry,' Chapman and Hall, London, 1973, 2nd edn., ch. 12; (*b*) E. F. Caldin, *Chem. Rev.*, 1969, **69**, 135; (*c*) E. S. Lewis and L. H. Funderburk, *J. Amer. Chem. Soc.*, 1967, **89**, 2322; (*d*) E. S. Lewis and J. K. Robinson, *ibid.*, 1968, **80**, 4337; (*e*) H. Wilson, J. D. Caldwell, and E. S. Lewis, *J. Org. Chem.*, 1973, **38**, 564.

[12] J. R. Hulett, *Quart. Rev.*, 1964, **18**, 227.

[13] J. R. Keefe and N. H. Munderloh, *J.C.S. Chem. Comm.*, 1974, 17.

[14] E. R. Thornton, *J. Amer. Chem. Soc.*, 1967, **89**, 2915.

[15] R. A. Marcus, *J. Phys. Chem.*, 1968, **72**, 891; J. R. Murdoch, *J. Amer. Chem. Soc.*, 1972, **94**, 4410.

[16] A. J. Kresge, *Chem. Soc. Rev.*, 1973, **2**, 475.

[17] D. J. McLennan, *J.C.S. Faraday I*, 1975, 1516.

cedure was used for the phenoxide-induced reactions. At various times aliquot portions of reaction mixture were cooled and run into water containing excess of NaOH so as to neutralise all the phenol present. An accurately measured quantity of n-hexane (usually 10 ml) was then introduced and the product olefin plus remaining substrate were quantitatively extracted. The n-hexane extract was washed two further times with aqueous NaOH then with water. Checks showed that no detectable phenol remained and that the substrate was inert to the alkaline washings. The u.v. absorbance of the n-hexane extract was measured at 255 nm and rate constants were reckoned as usual from plots of $\log(A_\infty - A_t)$ against time.

A similar procedure was tried for those reactions where PhS^- was the base. However, sulphur-containing material (probably diphenyl disulphide) remained in the n-hexane extracts and interfered with absorbance measurements in the 240—260 nm region. Hence rate constants were determined by the previously described titration method.[9]

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