The Carbanion Mechanism of Olefin-forming Elimination. Part IV.[1,2] Isotope Effects in the Dehydrochlorination of 1,1-Diaryl-2,2,2-trichloroethanes by Anionic Bases in Alcoholic Solvents

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Deuterium isotope effects (k_H/k_D) have been measured for the dehydrochlorination of $(p\text{-}ClC_6H_4)_2CH\cdot CCl_3$ (DDT) induced by the bases PhS^-, $p\text{-}NO_2\cdot C_6H_4\cdot O^-$, PhO^-, and OEt^- (in EtOH), and OMe^- (in MeOH). The isotope effect passes through a maximum as the base strength increases. The maximum corresponds to the estimated pK_a value of DDT (17) and it is suggested that the rate-determining step is simple proton transfer, so that the mechanism is ' irreversible ' *E*1c*B*. Values of k_H/k_D are also reported for the reactions of four compounds of the type $Ar_2CH\cdot CCl_3$ with OMe^-–MeOH and Bu^tO^-–Bu^tOH. The isotope effect is independent of the nature of the *para*-substituent, but in all cases it is smaller for Bu^tO^- than for OMe^-. This pattern is opposite to that which has been established for *E*2 reactions.

FOR some years we have assumed that the dehydrochlorination of compounds of the type $Ar_2CH\cdot CCl_3$ (DDT and analogues) by alkali and other bases in alcoholic solvents proceeds by a concerted *E*2 mechanism involving a paenecarbanion[3] transition state (I) in which C_β–H bond cleavage is more advanced than C_α–Cl breaking, so that C_β bears an excess of negative

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[2] Preliminary communications, ref. 1 and D. J. McLennan and R. J. Wong, *Tetrahedron Letters*, 1972, 2887 (Part II).

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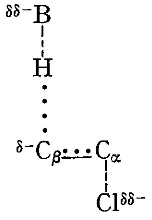
charge.[4-6] Such a process is in accord with the second-order kinetics,[4-7] the large positive Hammett ρ value,[7]



(I)

the low primary deuterium isotope effects observed when benzenethiolate and ethoxide are the bases in solvent ethanol,[4] and the fact that the hydrogen nucleophilicity order $OR^- \gg SR^-$ parallels the thermodynamic basicity order.[4,8]

We had earlier dismissed a variant of the carbanion (*E*1*cB*) mechanism [9] (Scheme) in which the carbanion is in equilibrium with the substrate, and ejection of Cl^- is the rate-determining step. This is the ' pre-equilibrium ' *E*1*cB* mechanism and corresponds to $k_{-1}[BH] \gg k_2$ in the Scheme.[9,10] The grounds for dismissal were first that general base catalysis was observed and secondly that base-catalysed hydrogen exchange between substrate and solvent was undetectable.[4]

$$Ar_2CH{\cdot}CCl_3 + B^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Ar_2\overset{-}{\ddot{C}}{\cdot}CCl_3 + BH$$

$$Ar_2{\cdot}\overset{-}{\ddot{C}}Cl_3 \xrightarrow{k_2} Ar_2C{:}CCl_2 + Cl^-$$

$$\text{rate} = \frac{k_1k_2[Ar_2CH{\cdot}CCl_3]\,[B^-]}{k_1[BH] + k_2}$$

SCHEME

Less easily rejected is that variant in which carbanion formation is rate-determining ($k_2 \gg k_{-1}[BH]$ in the Scheme, whence the second-order $k_{obs} = k_1$). In this case the transition state will be characterized by a well-broken C_β–H bond, an excess of negative charge on C_β, and an intact C_α–Cl bond, and will therefore be similar in nature to a paenecarbanion *E*2 transition state (I). There is a distinct border between the two mechanisms, except in cases where reactions of the carbanion are diffusion-controlled.[11]

We now report that as a result of more extensive investigation of DDT dehydrochlorination, the firm conclusion that the mechanism is ' irreversible ' *E*1*cB*($k_2 \gg k_{-1}[BH]$) has been reached. In 1953 it was implied that mechanism *E*1*cB* was a comparative rarity compared with *E*2 in that it warranted little attention in the classic text of the time. By 1967, when one of us reviewed the field [9] it was considered that several reasonably well-authenticated examples of *E*1*cB* elimination had been provided, although a large number of other claims to this effect rested on unsure grounds. The subsequent availability of a large number of soundly based examples of various forms of carbanionic elimination [10,12] can be taken to mean that the mechanism can no longer be regarded as a novelty, and in fact it has been proposed that concerted *E*2 elimination may be the mechanistic rarity.[10] However, we believe that the proliferation of *E*1*cB* examples arises more from better critical application of a wider range of experimental tests, and the relative demise of the *E*2 mechanism is not necessarily a consequence of its intrinsic rarity or non-existence.

RESULTS

All reactions studied had the stoicheiometry of equation (1). Kinetics were generally investigated spectrophotometrically (wavelength range 240—300 nm) under conditions such that first-order kinetics obtained ($[B^-]_0 \gg [Ar_2CH{\cdot}CCl_3]_0$ so that rate $= k_\psi[Ar_2CH{\cdot}CCl_3]$). For dilute basic solutions, second-order rate constants k_2 as calculated from equation (2) were effectively constant over a range of base concentrations. An exception occurred in reactions involving phenoxide as base in ethanol, when competing attack by ethoxide caused the depression of k_2 by added phenol. Linear plots of k_2 *vs.* $[PhOH]^{-1}$ were extrapolated to $[PhOH]^{-1} = 0$ as before [4,13] in order to obtain the true rate constant for PhO^- attack. From the slopes of such plots and the separately evaluated k_2 values for the ethoxide-induced reactions, a value of 15·8 could be derived for the pK_a of phenol in ethanol This is identical with that from an independent determination.[14] The very slow reactions involving p-$NO_2{\cdot}C_6H_4{\cdot}O^-$ were run with $[\text{base}]_0 \ll [Ar_2CH{\cdot}CCl_3]_0$, and the disappearance of base was monitored spectrophotometrically.

$$Ar_2CH{\cdot}CCl_3 + B^- \longrightarrow Ar_2C{:}CCl_2 + BH + Cl^- \quad (1)$$

$$k_2 = k_\psi/[B^-] \quad (2)$$

In none of the reactions of the compounds $Ar_2CD{\cdot}CCl_3$ was an induction period observed. This fact, combined with the observation of substantial isotope effects, rules out the possibility of hydrogen exchange competing with elimination.[15]

The fast reactions of $(p\text{-}NO_2{\cdot}C_6H_4)_2CH{\cdot}CCl_3$ and its 1-deuterio-analogue with NaOMe–MeOH and Bu^{t}OK–Bu^{t}OH at 30 and 45 °C were investigated by stopped-flow spectrophotometry. Facilities, advice, and assistance were kindly provided by Dr. M. J. Hardman and Dr. L. F. Blackwell of Massey University. The rates of these reactions were extremely sensitive to traces of basic impurities in the

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TABLE 1

Rate constants for the reactions of $Ar_2CH{\cdot}CCl_3$ and $Ar_2CD{\cdot}CCl_3$ with various bases in alcoholic solvents

Substrate	Base	Solvent	T/°C	10^5k_2/l mol^{-1} s^{-1}
$(p\text{-}MeO{\cdot}C_6H_4)_2CH{\cdot}CCl_3$	NaOMe	MeOH	30	8·71
$(p\text{-}MeO{\cdot}C_6H_4)_2CH{\cdot}CCl_3$	NaOMe	MeOH	45	50·4
$Ph_2CH{\cdot}CCl_3$	NaOMe [a]	MeOH	30	47·6
$Ph_2CH{\cdot}CCl_3$	NaOMe	MeOH	45	197
$(p\text{-}ClC_6H_4)_2CH{\cdot}CCl_3$	NaOMe	MeOH	30	1130
$(p\text{-}ClC_6H_4)_2CH{\cdot}CCl_3$	NaOMe	MeOH	45	5230 [b]
$(p\text{-}NO_2{\cdot}C_6H_4)_2CH{\cdot}CCl_3$	NaOMe	MeOH	30	$6{\cdot}05 \times 10^5$
$(p\text{-}NO_2{\cdot}C_6H_4)_2CH{\cdot}CCl_3$	NaOMe	MeOH	45	$2{\cdot}51 \times 10^6$
$(p\text{-}MeO{\cdot}C_6H_4)_2CD{\cdot}CCl_3$	NaOMe	MeOH	30	1·67
$(p\text{-}MeO{\cdot}C_6H_4)_2CD{\cdot}CCl_3$	NaOMe	MeOH	45	10·4
$Ph_2CD{\cdot}CCl_3$	NaOMe [a]	MeOH	30	9·37
$Ph_2CD{\cdot}CCl_3$	NaOMe	MeOH	45	42·8
$(p\text{-}ClC_6H_4)_2CD{\cdot}CCl_3$	NaOMe	MeOH	30	219
$(p\text{-}ClC_6H_4)_2CD{\cdot}CCl_3$	NaOMe	MeOH	45	1100
$(p\text{-}NO_2{\cdot}C_6H_4)_2CD{\cdot}CCl_3$	NaOMe	MeOH	−0·4	$1{\cdot}01 \times 10^4$
$(p\text{-}NO_2{\cdot}C_6H_4)_2CD{\cdot}CCl_3$	NaOMe	MeOH	30	$1{\cdot}22 \times 10^5$
$(p\text{-}NO_2{\cdot}C_6H_4)_2CD{\cdot}CCl_3$	NaOMe	MeOH	45	$5{\cdot}45 \times 10^5$ [c]
$(p\text{-}MeO{\cdot}C_6H_4)_2CH{\cdot}CCl_3$	Bu^{t}OK	Bu^{t}OH	30	94·8
$(p\text{-}MeO{\cdot}C_6H_4)_2CD{\cdot}CCl_3$	Bu^{t}OK	Bu^{t}OH	30	26·7
$Ph_2CH{\cdot}CCl_3$ [d]	Bu^{t}OK	Bu^{t}OH	30	262
$Ph_2CD{\cdot}CCl_3$ [d]	Bu^{t}OK	Bu^{t}OH	30	66·0
$(p\text{-}ClC_6H_4)_2CH{\cdot}CCl_3$	Bu^{t}OK	Bu^{t}OH	30	$2{\cdot}22 \times 10^4$
$(p\text{-}ClC_6H_4)_2CD{\cdot}CCl_3$	Bu^{t}OK	Bu^{t}OH	30	6850
$(p\text{-}NO_2{\cdot}C_6H_4)_2CH{\cdot}CCl_3$	Bu^{t}OK	Bu^{t}OH	30	$2{\cdot}19 \times 10^7$
$(p\text{-}NO_2{\cdot}C_6H_4)_2CD{\cdot}CCl_3$ [d]	Bu^{t}OK	Bu^{t}OH	30	$5{\cdot}73 \times 10^6$
$(p\text{-}ClC_6H_4)_2CH{\cdot}CCl_3$	NaSPh	EtOH	45	2·61 [e]
$(p\text{-}ClC_6H_4)_2CD{\cdot}CCl_3$	NaSPh	EtOH	45	0·834 [e]
$(p\text{-}ClC_6H_4)_2CH{\cdot}CCl_3$	$p\text{-}NO_2{\cdot}C_6H_4{\cdot}ONa$	EtOH	45	0·145
$(p\text{-}ClC_6H_4)_2CD{\cdot}CCl_3$	$p\text{-}NO_2{\cdot}C_6H_4{\cdot}ONa$	EtOH	45	0·030
$(p\text{-}ClC_6H_4)_2CH{\cdot}CCl_3$	NaOPh	EtOH	45	17·4 [e,f]
$(p\text{-}ClC_6H_4)_2CD{\cdot}CCl_3$	NaOPh	EtOH	45	93·0 [g]
$(p\text{-}ClC_6H_4)_2CD{\cdot}CCl_3$	NaOPh	EtOH	45	61·6 [h]
$(p\text{-}ClC_6H_4)_2CD{\cdot}CCl_3$	NaOPh	EtOH	45	45·2 [i]
$(p\text{-}ClC_6H_4)_2CD{\cdot}CCl_3$	NaOPh	EtOH	45	2·8 [f]

[a] [NaOMe] = 0·472 mol l^{-1}. [b] Ref. 4 reports 10^5k_2 = 5140 l mol^{-1} s^{-1}. [c] Extrapolated from − 0·4 and 30 °C results. [d] From competitive run. [e] From ref. 4. [f] Extrapolated to [PhOH]$^{-1}$ = 0. [g] [PhOH] = 0·1996 mol l^{-1}. [h] [PhOH] = 0·3067 mol l^{-1}. [i] [PhOH] = 0·424 mol l^{-1}.

solvent, and k_2 values often varied between different solvent batches. Rates and isotope effects in some cases were therefore obtained by using a competitive technique in which reactions of mixtures of the two compounds with the alkoxide were studied.[16,17] There is thus a greater than usual uncertainty in the actual rate constants, but the isotope effects are considered to be no less accurate than others obtained from separate runs. Rate constants for the protium and the deuterium compound were always compared for runs in which the base concentrations were identical.

Second-order rate constants are shown in Table 1. They are in the main mean values of two or more concordant results.

DISCUSSION

Effect of Base Strength.—In Table 2 we show isotope effects for the reactions of various bases in ethanol at 45 °C with DDT itself. We also include the appropriate NaOMe–MeOH isotope effect, on the grounds that methanol and ethanol have similar properties as far as rates of such reactions are concerned,[4] and that NaOMe–MeOH is only a little less basic than is NaOEt–EtOH, as shown by the respective basicity functions for a given base concentration.[18]

It is clear that k_H/k_D passes through a distinct maximum as the base strength increases. Such an effect is theoretically respectable,[19] but has only rarely been realized experimentally,[20] even under conditions where it might have been expected.[21-24] We shall discuss the paucity of observations of maximal isotope effects in a series of related reactions later.

A central-atom isotope effect maximum is to be expected in a three-centre process such as a proton transfer when the strengths of the partial C · · · H and H · · · B bonds in the transition state are equal.[19] An approximate corollary of this is that, if the activation

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TABLE 2

Primary deuterium isotope effects for the reactions of bases with $(p\text{-ClC}_6\text{H}_4)_2\text{CH}\cdot\text{CCl}_3$ in ethanol at 45 °C

Base	PhS^-	$p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{O}^-$	PhO^-	$\text{OMe}^{-\,a}$	OEt^-
k_H/k_D	3·13	4·83	6·21	4·75	3·40
$\mathrm{p}K_a$ (of BH in EtOH	9·3 [b]	13·3 [c]	15·8 [d]	18·3 [a,e]	20·3 [f]

[a] In methanol solvent. [b] From ref. 4. [c] From ref. 13. [d] From ref. 14. [e] R. Schaal and G. Lambert, *J. Chim. phys.*, 1962, **59**, 1151. [f] P. S. Danner, *J. Amer. Chem. Soc.*, 1962, **44**, 2832.

process in a given reaction involves *only* proton transfer, the maximum should be observed when the $\mathrm{p}K_a$ of the proton donor is about equal to the $\mathrm{p}K_a$ of the conjugate acid of the proton acceptor.[20] The $\mathrm{p}K_a$ values for DDT and its analogues cannot of course be measured, but they can be estimated by a linear free energy relationship technique.

The $\mathrm{p}K_a$ value for Ph_2CH_2 has been estimated in a number of ways by using measurements in a variety of base-solvent systems. The most appropriate value for the present purposes is 30·2, which is based partly on rate measurements in methanolic solution.[25] We adopt this $\mathrm{p}K_a$ for ionization in ethanol on the basis that the numerical values of $\mathrm{p}K_a$ for benzenethiol,[4] phenol,[14] and acetic acid[26] are about the same in methanol and ethanol, with reference to dilute solutions in the respective pure solvents as standard states. The $\mathrm{p}K_a$ values of *meta*- and *para*-disubstituted diarylmethanes can then be calculated from equation (3), in which σ

$$\mathrm{p}K_a(\text{Ar}_2\text{CH}_2) = 30{\cdot}2 - 2\rho\sigma \tag{3}$$

is the appropriate Hammett substituent constant. A well-established value of ρ for diarylmethane ionization is not available, but an estimate of 5·0, based on ρ values for carbanion formation in other systems,[27] is in order. A further assumption implicit in equation (3) is that the substituents act additively, which is not always the case,[6,28] but the assumption cannot be avoided. The $\mathrm{p}K_a$ values for DDT derivatives may now be calculated from the Taft equation (4). Again a value for the

$$\mathrm{p}K_a(\text{Ar}_2\text{CH}\cdot\text{CCl}_3) = \mathrm{p}K_a(\text{Ar}_2\text{CH}_2) - \rho^*[\sigma^*(\text{CCl}_3) - \sigma^*(\text{H})] \tag{4}$$

reaction parameter ρ^* has to be estimated and again we choose $\rho^* = 5{\cdot}0$ on the basis of measurements pertaining to carbanion formation.[27b,29] The CCl_3 and H σ^* polar constants given by Taft[30] lead to the $\mathrm{p}K_a$ values in Table 3. It is impossible accurately to assess the uncertainty in each $\mathrm{p}K_a$. However, we note that the approximation that $\mathrm{p}K_a$ values of carbon acids in methanol and ethanol (based on dilute solution in the pure solvent as standard state) are numerically equal may be in error by up to 1·5 pK units if oxygen and sulphur acids are taken as a guide.[4,14,26] Similarly if ρ and ρ^* are assigned values of $5{\cdot}0 \pm 1{\cdot}0$ then the uncertainty in the derived $\mathrm{p}K_a$ values is $\pm 2{\cdot}5$. This is, however, adequate for the present purposes. The range of $\mathrm{p}K_a$ values given for $(p\text{-NO}_2\cdot\text{C}_6\text{H}_4)_2\text{CH}\cdot\text{CCl}_3$ arises from uncertainty as to whether σ (0·78) or σ^- (1·27) is the correct substituent parameter to be used in equation (3).

The $\mathrm{p}K_a$ of DDT itself is, within the bounds of reasonable uncertainty, equal to the $\mathrm{p}K_a$ of phenol, so that $\Delta \mathrm{p}K = 0$ in the vicinity of the maximum isotope effect in Table 2. This implies, although it does not demand, that the rate-determining step in the dehydrochlorination involves solely proton transfer, so that the ' irreversible ' *E*1c*B* mechanism is a strong possibility.

On the other hand there is the coincidental possibility that the isotope effect could reach such a maximum at $\Delta \mathrm{p}K = 0$ were the mechanism *E*2, and such a coincidence cannot be dismissed lightly for the good reason that little is known about such maxima in *E*2 reactions. One well-founded example can be tested, however. In the reaction of $\text{PhCH}_2\cdot\text{CH}_2\cdot\text{SMe}_2^+$ with OH^- to produce styrene in $\text{Me}_2\text{SO–H}_2\text{O}$ solvent mixtures, k_H/k_D passes through a maximum dependent on the Me_2SO content of the solvent.[20b] Values of $\Delta \mathrm{p}K$, equal to $\mathrm{p}K_a(\text{PhCH}_2\cdot\text{CH}_2\cdot\text{SMe}_2^+) - \mathrm{p}K_a(\text{H}_2\text{O})$ in each solvent mixture can be calculated by the method of Bell and Cox[20c] if the $\mathrm{p}K_a$ of the sulphonium ion can be estimated. Again we use a linear free energy relationship approach. The $\mathrm{p}K_a$ of toluene relative to dilute aqueous solution as standard state has been given[24] as 40·9. Use of the σ^* value for the $\text{CH}_2\text{SMe}_2^+$ group[32] and $\rho^* = 5{\cdot}0$ leads to $\mathrm{p}K_a = 36{\cdot}8$ for $\text{PhCH}_2\cdot\text{CH}_2\cdot\text{SMe}_2^+$. In Table 4 are arranged the isotope effects for the elimination and the appropriate $\Delta \mathrm{p}K$ values. The isotope effect does not pass through its maximum value anywhere near $\Delta \mathrm{p}K = 0$. Thus a

TABLE 3

Calculated $\mathrm{p}K_a$ values of $(p\text{-RC}_6\text{H}_4)_2\text{CH}\cdot\text{CCl}_3$ in ethanol

R	MeO	H	Cl	NO_2
$\mathrm{p}K_a$	22·1	19·4	17·1	6·7—11·6

TABLE 4

Isotope effects as a function of $\Delta \mathrm{p}K$ in elimination from $\text{PhCH}_2\cdot\text{CH}_2\cdot\text{SMe}_2^+$ induced by hydroxide in $\text{H}_2\text{O–Me}_2\text{SO}$ mixtures

Me_2SO (mole %)	k_H/k_D [a]	$\Delta \mathrm{p}K$ [b]	$\Delta \mathrm{p}K$ [c]
0	5·03	24·4	23·3
19·4	5·29	22·3	21·2
26·3	5·55	21·8	20·7
38·0	5·73	21·0	19·9
50·2	5·61	20·1	19·0
60·3	5·63	19·2	18·2
71·8	4·79	18·2	17·1

[a] From ref. 20*b*, at 50 °C. [b] Based on the H_- scale in ref. 18. [c] Based on the H_- values in ref. 31.

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single example of *E*2 behaviour must serve to illustrate the point that maximal isotope effects are not observed at $\Delta pK = 0$ when proton transfer is coupled to other bond-making and bond-breaking processes. The possibility of coincidence in the DDT result and an *E*2 mechanism for this substrate is therefore diminished.

A further mechanism that can be dismissed is that variant of the *E*1c*B* mechanism in which internal return of the proton to the substrate occurs, so that while Cl^- ejection is rate-determining, no hydrogen exchange with a protic solvent is observed.[12g,33,34] In such cases, hydrogen isotope effects close to unity are expected and have been observed,[12g,33] but there is no such behaviour in the present reactions. An exception to the rule of low isotope effects is the hydrogen exchange reaction of triphenylmethane with lithium cyclohexylamide–cyclohexylamine,[35] but evidence to be presented in a later paper further rules out the possibility of internal return. The varying isotope effects in Table 2 can also be interpreted in terms of *E*2 elimination being induced by some of the bases and *E*1c*B* obtaining for the others, but in a later paper we report evidence that suggests that PhS^- and OMe^- promote elimination by the same basic mechanism. At one time it was thought that the similarity of the PhS^- and OEt^- isotope effects indicated similarity of transition state character.[4] It is now clear that in one case a less than half-transferred proton is involved and in the other the proton is more than half transferred, but we defer discussion as to which base produces which carbanion-forming transition state.

An apparent paradox is the fact that while the present results suggest a half-transferred proton in the phenoxide transition state: $\overset{\delta-}{C_\beta}\cdots H\cdots \overset{\delta-}{O}Ph$, the Brönsted β value of 0·88 for the DDT–OAr^- reaction series[4] implies an almost completely transferred proton at the transition state. Discrepancies of this type have been noted before[20d,j,36] and in all cases it has been concluded that β is the less reliable criterion of transition state character. The foregoing β value is arrived at by comparing rates of proton abstraction from a carbon acid by a series of bases with equilibria involving proton transfer from an oxygen acid (ethanol) to the same bases. In view of the fundamental differences between carbon and oxygen acids,[37] it is hardly surprising that such β values are not to be literally interpreted as indices of degrees of proton transfer in transition states.

Effect of Substrate Acidity.—Primary deuterium isotope effects have been measured for the reactions of four compounds of the type $Ar_2CH{\cdot}CCl_3$ with OMe^-–MeOH and Bu^tO^-–Bu^tOH, and results are shown in Table 5. As the substrate acidity is varied over at least 11 p*K* units (Table 3), the isotope effects in both base-solvent systems are invariant within experimental error. It has been suggested that isotope effect maxima might be observed in cases where varying ring substituents cause changes in substrate acidity,[38] but this is not so. Neither has such a phenomenon been observed for the *E*2 reactions of 2-arylethyl bromides with Bu^tOK–Bu^tOH[17] and the base-catalysed hydrogen exchange reactions of ring-substituted acetophenones.[21c] In these two cases the isotope effect increases and decreases respectively with increasing σ.

TABLE 5

Isotope effects for the reactions of $Ar_2CH{\cdot}CCl_3$ with NaOMe–MeOH and Bu^tOK–Bu^tOH

	k_H/k_D		
	NaOMe–MeOH		Bu^tOK–Bu^tOH
Substrate	30 °C	45 °C	(30 °C)
$(p\text{-}MeO{\cdot}C_6H_4)_2CH{\cdot}CCl_3$	5·21	4·75	3·55
$Ph_2CH{\cdot}CCl_3$	5·08	4·60	3·97
$(p\text{-}ClC_6H_4)_2CH{\cdot}CCl_3$	5·16	4·75	3·38
$(p\text{-}NO_2C_6H_4)_2CH{\cdot}CCl_3$	4·95	4·60	3·82

The reason why k_H/k_D does not pass through a maximum in the present case, even though $\Delta pK = 0$ falls within the acidity range in the OMe^-–MeOH system, must lie in the fact that *both* k_H and k_D are accurately described by the same linear free energy relationship (the Hammett equation—see a later paper) and that $\rho_H \simeq \rho_D$. If $\rho_D > \rho_D$ the isotope effect should increase with increasing σ,[17,39] and should decrease if $\rho_H < \rho_D$.[21c,40] However, if irregularities in some linear free energy relationships occur,[20b,d,j] or if the reaction parameter continuously varies as a function of ΔpK,[19e] or if neither k_H nor k_D is described by a linear free energy relationship, observation of a maximal isotope effect is a possibility. In the Figure we show a 'Brönsted plot' for the reactions of DDT with a series of sulphur (PhS^-, $p\text{-}Me_6H_4S^-$) and oxygen bases ($p\text{-}NO_2{\cdot}C_6H_4O^-$, PhO^-, $p\text{-}MeO{\cdot}C_6H_4{\cdot}O^-$, OMe^-–MeOH, OEt^-) in ethanol; even over the range of oxygen bases linearity does not obtain, and neither could it be expected to do so for a series of structurally unrelated bases; a series which also includes lyate ions.[36] It is therefore scarcely surprising that k_H/k_D passes through a maximum when ΔpK is varied by changing base strength along a series of unrelated bases but does not do so if the variation in ΔpK is brought about by more subtle changes along a series of closely related carbon acids.

We acknowledge that the foregoing is a description and not an explanation. In terms of the description there is no compelling reason why a k_H/k_D minimum rather than a maximum should not be observed. An explanation of the underlying causes of these various phenomena would require better understanding than is

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TABLE 6

Activation parameters for the reactions of $Ar_2CH{\cdot}CCl_3$ and $Ar_2CD{\cdot}CCl_3$ with NaOMe–MeOH

Compound	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal K^{-1} mol^{-1}
(p-MeO·C_6H_4)$_2$CH·CCl_3	21·8	−3
(p-MeO·C_6H_4)$_2$CD·CCl_3	22·7	−3
$Ph_2CH{\cdot}CCl_3$	17·5	−13
$Ph_2CD{\cdot}CCl_3$	18·8	−13
(p-ClC_6H_4)$_2$CH·CCl_3 [a]	18·8	−3
(p-ClC_6H_4)$_2$CD·CCl_3	20·0	−2
(p-$NO_2{\cdot}C_6H_4$)$_2$CH·CCl_3	17·6	6
(p-$NO_2{\cdot}C_6H_4$)$_2$CD·CCl_3	18·5	5

[a] Ref. 4 reports $\Delta H^{\ddagger}$ = 18·0 kcal mol^{-1}; $\Delta S^{\ddagger}$ = −10 cal K^{-1} mol^{-1}, based on three rate constants measured over a 20 °C temperature range.

at present available of potential energy contributions to free energies of activation.[41]

In Table 6 are shown activation parameters for reactions in OMe$^-$–MeOH. Within the limits of the rather large experimental errors in these quantities (two-point ' Arrhenius plots ' over a 15 °C range), the isotope effects are governed primarily by changes in $\Delta H^{\ddagger}$ rather than in $\Delta S^{\ddagger}$. This implies that quantum mechanical tunnelling is not an important determinant of the isotope effects.[42]

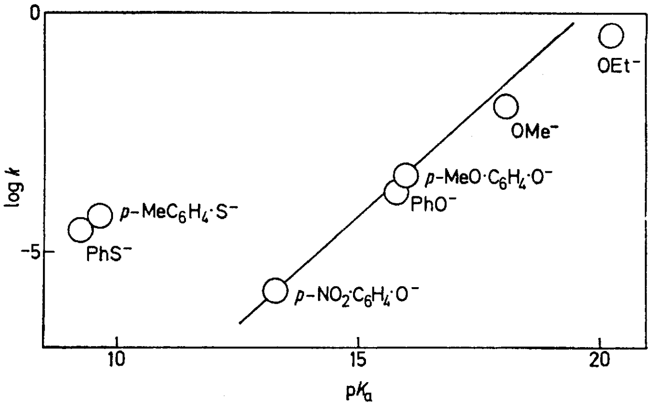
TABLE 7

Isotope effects in $E2$ reactions as a function of the base-solvent system

	Substrate	k_H/k_D OEt$^-$–EtOH	k_H/k_D Bu^{t}O$^-$–Bu^{t}OH	Temp. (°C)	Ref.
1	$PhCH_2{\cdot}ONO_2$ [a]	5·94	6·41	30	43
2	$PhCH_2{\cdot}CH_2{\cdot}NMe_3^+$	2·98 [b]	7·03	30	44
3	$PhCH_2{\cdot}CH_2{\cdot}Br$	7·11	8·0 [c]	30	17, 45
4	$PhCH_2{\cdot}CH_2{\cdot}OTs$	5·66	8·01	30	45
5	cis-PhCH:CHBr	2·9 [a]	4·6	30	46
6	cis-p-$NO_2{\cdot}C_6H_4{\cdot}$CH:CHBr	2·2 [d]	4·3	30	46
7	cis-PhCH:CHCl	2·2 [d]	3·2	30	46
8	cis-p-$NO_2{\cdot}C_6H_4{\cdot}$CH:CHCl	1·6 [d]	3·5	30	46
9	cyclo-$C_6H_{11}OTs$ [e]	4·47	7·53	49·9	47
10	$PhCH(Br)CH_3$	3·4	5·0	50	48
11	m-$BrC_6H_4{\cdot}CHMe{\cdot}CH_2{\cdot}OTs$	4·71	6·29	49·8	49
12	p-$MeC_6H_4{\cdot}CHMe{\cdot}CH_2{\cdot}OTs$	4·09	6·20	49·8	49
13	m-$BrC_6H_4CHMe{\cdot}CH_2{\cdot}Br$	7·04	7·73	49·8	49
14	p-$MeC_6H_4CHMe{\cdot}CH_2{\cdot}Br$	6·35	6·71	49·8	49
15	$PhCHMe{\cdot}\overset{+}{N}Me_3$	4·46	4·63 [f]	70	39
16	p-$CF_3{\cdot}C_6H_4{\cdot}CHMe{\cdot}\overset{+}{N}Me_3$	4·84	5·15 [f]	70	39
17	9-Bromo-9,9′-bifluorenyl	6·2 [a]	8·0	30	50
18	$MeCHBr{\cdot}CH_3Me$	3·5 [h]	4·4 [h]	70	51

[a] Carbonyl-forming elimination; PhCHO + NO_2^- are the products. [b] At 50 °C. [c] Mean of 8·12 (ref. 17) and 7·89 (ref. 45). [d] OMe$^-$–MeOH. [e] Cyclohexyl toluene-p-sulphonate. [f] Uncertainties not recorded. [g] OMe$^-$ in Bu^{t}OH. [h] For formation of $trans$-but-2-ene.

The magnitudes of the isotope effects and their invariance with variation in ring substituent are not in themselves mechanistically informative. We cannot tell for instance whether the less than maximal values of k_H/k_D point to a proton which is less or more than half-transferred in the transition state. However it is significant that as the basicity of the medium is increased from OMe$^-$–MeOH to Bu^{t}OK–Bu^{t}OH, k_H/k_D values for all substrates decrease. Discussion of the implications of this as far as changes in transition state structure are concerned is deferred to a later paper, but there is a strong suggestion that this phenomenon is a characteristic of eliminations that do *not* proceed by the concerted $E2$ mechanism. In support of this contention we have gathered in Table 7 all $E2$ examples known to us which pertain to this question. In all 17 cases, k_H/k_D increases as the medium basicity is increased. Evidence for the $E2$ nature of some of these reactions



Brönsted plot pertaining to the reactions of thiolate, phenoxide, and alkoxide bases in ethanol (also methoxide in methanol) with (p-ClC_6H_4)$_2$CH·CCl_3 at 45 °C; data from ref. 4 and present work

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comes from the nitrogen isotope effects that have been observed for reactions 1 and 2 and the sizeable Br : Cl leaving group rate ratios existing in the 5,7 and 6,8 pairs of reactions. Again, discussion of the basis of the isotope effect behaviour is deferred to a later paper, but we consider that the contrast between *E*1c*B* and *E*2 reactions in this context is sufficiently clear-cut to be a useful criterion for distinguishing between the rather similar paenecarbanion *E*2 and 'irreversible' *E*1c*B* processes.

EXPERIMENTAL

Materials.—Solutions of NaOMe in MeOH were made up as previously described [4] as were other base solutions. The Bu^tOH solvent and the Bu^tOK solutions were purified and made up by the method of Saunders *et al.*[21b] Preparations of the protium substrates and their properties have been described.[6] Preparations of the deuteriated substrates followed a published method,[52] but as several modifications were employed, we report a typical preparation. 2,2,2-Trichloroacetophenone and 2,2,2,4′-tetrachloroacetophenone were prepared by the unpublished method of Barry.[53] Chlorine was passed into 1 mol of acetophenone or *p*-chloroacetophenone in the presence of PCl_3 for 14 h. The temperature of the mixture was gradually raised to, and maintained at 205 °C by using a 250 W light bulb and a heating mantle. The crude product mixture was cooled and nitrogen was bubbled through. An ethereal solution was washed with $NaHSO_3$ solution and dried. Solvent removal and vacuum distillation yielded the required ketones in high yield. 2,2,2-Trichloroacetophenone (3·0 g, 0·014 mol) dissolved in ether (25 ml) was added dropwise to a suspension of $LiAlD_4$ (Fluka; >99 atom %D) (0·18 g, 0·005 mol) in ether (30 ml). The mixture was refluxed under nitrogen for 15 h, and after normal work-up, 83% of 2,2,2-trichloro-1-phenyl[1-^{2}H]ethanol was obtained. This was dissolved in a four-fold molar excess of benzene cooled to 0 °C and 5 : 1 conc. H_2SO_4–oleum was added dropwise. The solution was stirred for 2·5 h at 0 °C and poured on crushed ice (200 g). The resulting sticky solid was melted several times in boiling water, and was then recrystallised from MeOH, yielding 2,2,2-trichloro-1,1-diphenyl[1-^{2}H]-ethane (67%), m.p. 64·5—65·5° (lit.,[6] 64·5—65·5: for protium compound), δ 7·45 (5H, aromatic), deuterium content 99 atom % (Varian CH-7; 20 eV).

2,2,2-Trichloro-1,1-bis-(*p*-chlorophenyl)[1-^{2}H]ethane was similarly prepared (98·8 atom % deuterium). 2,2,2-Trichloro-1,1-bis-(*p*-nitrophenyl)[1-^{2}H]ethane was prepared by nitrating 2,2,2-trichloro-1,1-diphenyl[1-^{2}H]ethane according to the method of Delaby and Baronnet,[54] and contained 98·8 atom % deuterium.

2,2,2-Trichloro-1,1-bis-(*p*-methoxyphenyl)[1-^{2}H]ethane was prepared as described [52] and contained 99·1 atom % deuterium. No protium resonances in the δ range 4·9—5·4 were detected in the n.m.r. spectra of the four deuteriated compounds.

Kinetics.—Reaction mixtures were made up as before.[4] Depending on the rate of the reaction, samples were withdrawn from thermostatted mixtures for analysis at various times; otherwise the reaction was continuously followed with the mixture in a spectrophotometer cell in the thermostatted cell compartment of a Unicam SP 3000 spectrophotometer, and the absorbance was monitored at wavelengths previously stated.[28] The reactions involving *p*-NO_2·C_6H_4·ONa were monitored at 405 nm. Reactions involving NaOPh and NaSPh were followed by using potentiometric titration for chloride ion.[4] The very fast reactions of (p-NO_2·C_6H_4)$_2$CH·CCl_3 were followed by using a Durrum–Gibson D110 stopped-flow spectrophotometer. Rate constants were somewhat dependent on the batch of basic solution employed and so generally a competitive method was used, in which a mixture containing the protium and the deuterium compound was subjected to dehydrochlorination.[16,17]

U.v. spectra of 'infinity' samples were identical with those of the appropriate olefins.[6,28]

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