The Carbanion Mechanism of Olefin-forming Elimination. Part V.[1,2] Evidence from Linear Free Energy Relationships for *E*1cB Dehydrochlorination of 1,1-Diaryl-2,2,2-trichloroethanes

By **Duncan J. McLennan** * and **Ronald J. Wong,** Department of Chemistry, University of Auckland, Private Bag, Auckland, New Zealand

Rate constants for dehydrochlorination of the title compounds by NaOMe in MeOH may be fitted to the Brønsted equation appropriate to carbanion formation from hydrocarbons in the same medium. The identity of elimination and carbanion formation rates provides further evidence for the operation of an ' irreversible ' *E*1cB mechanism in the dehydrochlorination. A basicity function approach leads to the same mechanistic conclusion. The high Hammett ρ values (2—3) for eliminations in OR^-–ROH (R = Me and Bu^t) are diagnostic of a carbanion-like transition state, and consideration of the effect of base strength on ρ leads to the conclusion that stronger bases cause the proton to be more extensively transferred at the transition state, contrary to predictions based on the Hammond postulate.

IN Part IV [1] we presented evidence which suggested that the mechanism of base-induced dehydrochlorination [reactions (1) and (2)] of 1,1-diaryl-2,2,2-trichloroethane (DDT) derivatives in alcoholic solvents is *E*1cB carbanionic elimination,[3] with the initial proton transfer step being irreversible and rate-determining ($k_2 \gg k_{-1}$[BH] so that the second-order $k_{obs} = k_1$). This evidence is somewhat inferential as far as the observance of an isotope effect maximum at Δp*K* *ca.* 0 is concerned for the reasons that first, Δp*K* values must be estimated and secondly, little is known about the behaviour of authentic *E*2 reactions under such conditions. With regard to the observed decrease in isotope effect when the base is changed from NaOMe in MeOH to Bu^tOK in Bu^tOH, it can only be stated that this behaviour is contrary to that invariably observed with reasonably well established *E*2 reactions.

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

$$Ar_2\overline{\ddot{C}}\cdot CCl_3 \xrightarrow{k_2} Ar_2C{:}CCl_2 + Cl^- \qquad (2)$$

In the present work we examine approaches using linear free energy relationships (l.f.e.r.) to the $Ar_2CH\cdot CCl_3$ system, and provide more direct evidence in favour of the *E*1cB mechanism.

RESULTS AND DISCUSSION

Rates of Carbanion Formation in the $Ar_2CH\cdot CCl_3$–NaOMe–MeOH *System.*—If the ' irreversible ' carbanion mechanism (1) and (2) is operative, a necessary condition is that the rates of olefin formation and of carbanion formation must be equal. The aim has been to provide estimates of the latter quantities and to compare them with the measured elimination rates.

Streitwieser and his co-workers [4] have recently demonstrated the existence of a Brønsted correlation between log k_2^T, the second-order rate constants for protodetritiation of indene and fluorene-type hydrocarbons by NaOMe in MeOH at 45°, and the hydrocarbon pK_a values referred to dilute aqueous solution. Their plot is shown in Figure 1. The second-order rate constants were identified as pertaining to carbanion formation, and internal return was shown to be insignificant.[4,5]

The pK_a values of four $Ar_2CH\cdot CCl_3$ compounds have been calculated by the l.f.e.r. method described earlier.[1] The same ρ and ρ^* parameters have been assumed, and the pK_a of diphenylmethane referred to dilute aqueous solution (33·45) [5] has been used as the basis for the calculations. Uncertainty as to whether σ or σ^- is the appropriate substituent parameter for the *p*-nitro-group in the

---

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

[2] Preliminary communication, D. J. McLennan and R. J. Wong, *Tetrahedron Letters*, 1972, 2891.

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

[4] 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.

[5] A. Streitwieser, W. B. Hollyhead, G. Sonnichsen, A. H. Pudjaatmaka, C. J. Chang, and T. L. Kruger, *J. Amer. Chem. Soc.*, 1971, **93**, 5096.

Ar_2CH_2 ionization series leads to the pK_a of (p-$NO_2C_6H_4)_2$-$CH{\cdot}CCl_3$ lying within the range 9·9—14·8. However, we may estimate the acidity of this compound a little more precisely. The pK_a values of Ph_2CH_2 and (p-$MeC_6H_4)_2$-CH_2 correspond[6] to a ρ value of 4·85. If the same ρ pertains to the ionization of 4,4′-dinitrodiphenylmethane, and 3,4′-dinitrodiphenylmethane, an effective *para*-σ-value of 1·08 for nitro is needed to correlate the quoted acidities.[7] This lies between the σ and σ^- limits, which is a not unprecedented situation.[8] On this basis we calculate a pK_a of 11·8 for (p-$NO_2C_6H_4)_2CH{\cdot}CCl_3$. Other p$K_a$ values are shown in Table 1.

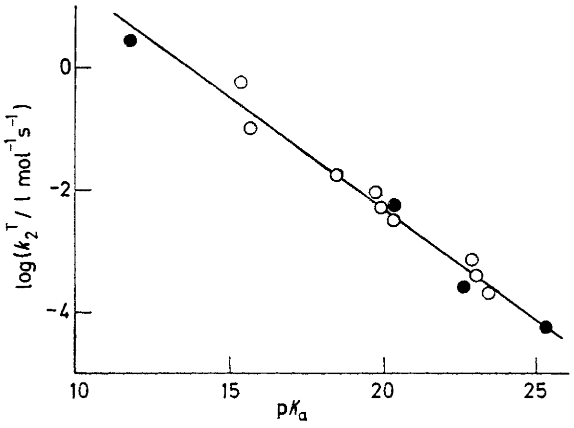

FIGURE 1 Brønsted plot for carbanion formation: open circles, hydrocarbon points from ref. 4, filled circles, $Ar_2CH{\cdot}CCl_3$ points from this work

TABLE 1

Values of pK_a for (p-$RC_6H_4)_2CH{\cdot}CCl_3$ compounds referred to dilute aqueous solution as standard state

R	MeO	H	Cl	NO_2
pK_a (l.f.e.r.)	25·3	22·6	20·3	11·8
pK_a (calc.) [a]	25·4	23·8	20·0	12·7

[a] Calculated from equation (4); see text.

TABLE 2

Rate constants and activation parameters for the reactions of various substrates (p-$RC_6H_4)_2CH{\cdot}CCl_3$ with NaOMe in MeOH

R	10^5k_2/l mol^{-1} s^{-1} 30°	45°	$\Delta H^‡$/kcal mol^{-1} [a]	$\Delta S^‡$/cal K^{-1} mol^{-1} [b]
MeO	8·71	50·4	21·8	−3
Me	12·7	77·6	22·8	1
H	47·6	197	17·5	−13
F	181	1080	22·2	5
Cl	1130	5230	18·8	−3
Br	1230	6810	21·2	5
NO_2	6·05 × 10^5	2·51 × 10^6	17·6	6

[a] Experimental uncertainty *ca.* ±1·0 kcal mol^{-1}. [b] Experimental uncertainty *ca.* 2·5 cal K^{-1} mol^{-1}.

Rate constants for detritiochlorination of $Ar_2CT{\cdot}CCl_3$ compounds by NaOMe in MeOH have not been measured, but they can be estimated from the rate constants at 45° in Table 2, and the deuterium isotope effects at 45°[1]

$$\log (k_H/k_T) = 1{\cdot}44 \log (k_H/k_D) \qquad (3)$$

via equation (3).[9] They are plotted with respect to the relevant pK_a values in Figure 1.

The points for (p-$MeOC_6H_4)_2CH{\cdot}CCl_3$ and (p-$ClC_6H_4)_2$-$CH{\cdot}CCl_3$ lie almost directly on the Brønsted plot for hydrocarbon into carbanion conversions. The $Ph_2CH{\cdot}$-CCl_3 point deviates slightly in the negative sense, but this is not regarded as a serious deviation for the reason that $\Delta S^‡$ for this compound's dehydrochlorination is anomalously low (Table 2). A negative deviation is also apparent for (p-$NO_2C_6H_4)_2CH{\cdot}CCl_3$, but in view of the extra assumptions employed in estimating the pK_a of this compound, neither is this regarded as a serious discrepancy. It is in fact satisfying that the hydrocarbon Brønsted line passes almost through the mid-point of the aforementioned pK_a range of 9·9—14·8.

Another way of looking at the situation is to use the kinetic acidities of the substrates to calculate their equilibrium acidities. From equation (4) pertaining to the hydrocarbon Brønsted plot[4] and the k_2^T values for detritiochlorination of the $Ar_2CH{\cdot}CCl_3$ compounds we calculate kinetically-derived pK_a values, which are also shown in Table 1. Agreement between them and the independently estimated l.f.e.r. acidities is impressive, bearing in mind the necessary assumptions inherent in calculation of the latter.

$$\log k_2^T = 5{\cdot}1085 - 0{\cdot}369\ pK_a \qquad (4)$$

It may then be concluded that, within the limits of uncertainty in the estimated pK_a values, the rate constants for elimination and carbanion formation from four $Ar_2CH{\cdot}CCl_3$ compounds are indeed equal. Strong evidence for the 'irreversible' *E*1cB mechanism is thus provided.

TABLE 3

Rate constants for the reactions of $Ph_2CH{\cdot}CCl_3$ in MeOH with varying concentrations of NaOMe at 30°

[NaOMe]/M	10^5k_ψ/s^{-1}	10^5k_2/l mol^{-1} s^{-1}
0·112	4·87	4·37
0·226	9·93	4·39
0·472	22·7	4·76
0·707	34·6	4·89
0·944	53·9	5·70
1·410	115	8·13
1·888	205	10·9

Basicity Function Correlation.—In Table 3 is shown the effect of base concentration on the observed first-order rate constant (k_ψ) for the reaction of $Ph_2CH{\cdot}CCl_3$ with NaOMe in MeOH, obtained using $[NaOMe]_0 \gg [Ph_2CH{\cdot}CCl_3]_0$. Also displayed are second-order rate

---

[6] A. Streitwieser, J. R. Murdoch, G. Häfelinger, and C. J. Chang, *J. Amer. Chem. Soc.*, 1973, **95**, 4248.

[7] K. Bowden and R. Stewart, *Tetrahedron*, 1965, **21**, 265.

[8] L. P. Hammett, 'Physical Organic Chemistry,' McGraw-Hill, New York, 1970, 2nd edn., p. 362; H. van Bekkum, P. E. Verkade, and B. M. Wepster, *Rec. Trav. chim.*, 1959, **78**, 815; F. G. Bordwell and H. M. Anderson, *J. Amer. Chem. Soc.*, 1953, **75**, 6019.

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

coefficients k_2 as calculated from equation (5). It is clear that this equation is applicable only at low base concentrations, since k_2 increases markedly at base concentrations greater than *ca.* 0·5M. A similar phenomenon has been observed in the protodetritiation of [9-^{3}H]fluorene by NaOMe in MeOH.[4]

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

Following Cram and Kollmeyer [10] we attempt to correlate log k_ψ with a basicity function for NaOMe in MeOH. Fortunately, the ideal function for our purposes has recently been provided by Streitwieser *et al.*[11] whose H_M function for NaOMe in the 0—2·5M range is anchored in dilute methanolic solution and is based on the ionization of a carbon acid indicator, 1,3-diphenylindene. A plot of log k_ψ for [9-^{3}H]fluorene protodetritiation in NaOMe–MeOH against H_M is linear,[11] with slope 0·847 ± 0·006. We adopt this as the model slope for carbanion-forming processes in which simple proton transfer is rate-determining, recalling that the point for [9-^{3}H]fluorene lies on the Brønsted plot in Figure 1.

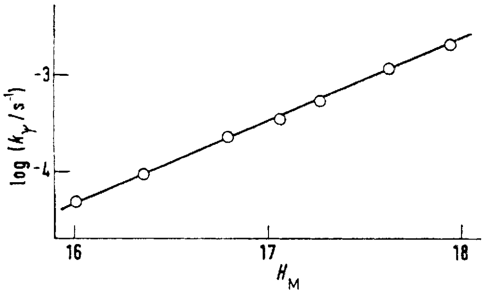

FIGURE 2 Plot of log k_ψ for the NaOMe-induced dehydrochlorination of $Ph_2CH{\cdot}CCl_3$ in MeOH against the H_M function for NaOMe–MeOH from ref. 11

Figure 2 shows the log k_ψ against H_M plot for $Ph_2CH{\cdot}CCl_3$ dehydrochlorination. The linearity is impressive (r 1·000) but the mere fact of linearity is not significant. Plots of log k_ψ for various reactions (including *E*2, *E*1*cB*, hydrogen exchange, and even S_N2) in NaOMe–MeOH [12] against H_M are also linear. The significant point is that the slope of the plot in Figure 2 (0·853 ± 0·008) is identical with the [9-^{3}H]fluorene slope. This result strongly implies (although it does not absolutely demand) that the rate-determining step in $Ph_2CH{\cdot}CCl_3$ dehydrochlorination is carbanion formation, in agreement with the conclusion reached in the previous section.

Internal return is held to be insignificant in [9-^{3}H]fluorene protodetritiation catalysed by NaOMe in MeOH,[4,5] but it is an important component in the hydrogen exchange reactions of polyfluorobenzenes in this medium.[13] The linear plot of log k_ψ for tritiodeprotonation of 1,2,3,5-tetrafluorobenzene by NaOMe in MeOH(T) [12] against H_M has a slope of 1·125. This is significantly different from the above slopes, and assists in allowing rejection of a significant degree of internal return in the elimination process. It has been suggested that $\Delta S^\ddagger$ values of *ca.* 0 for base-catalysed hydrogen exchange reactions might be diagnostic of internal return mechanisms whilst values in the range −20 to −10 cal K^{-1} mol^{-1} might indicate rate-determining proton transfer.[10,13] Later work has shown that $\Delta S^\ddagger$ is not a reliable criterion of mechanism, there being no such grouping for fluorene-type hydrocarbon exchanges on one hand,[4] and diaryl- and triaryl-methanes (internal return important) on the other.[5] Neither do the entropies of activation for $Ar_2CH{\cdot}CCl_3$ dehydrochlorinations (Table 1) permit mechanistic speculation.

Hammett Equation Studies.—The data in Tables 2 and 4 enable Hammett plots to be constructed. As has been noted previously, it is necessary to plot log k_2 against $2\sigma_I + (1 + \alpha)\sigma_R$ $(0 \leqslant \alpha \leqslant 1)$ and to adjust α in order to obtain good linear plots.[14,15] Results of this treatment, and parameters for a relevant related reaction,[14] are shown in Table 5. Several noteworthy points emerge.

TABLE 4

Rate constants for the reactions of various substrates $(p\text{-}RC_6H_4)_2CH{\cdot}CCl_3$ with Bu^{t}OK in Bu^{t}OH at 30°

R	10^5k_2/l mol^{-1} s^{-1}
MeO	94·8
Me	113
H	262
F	2050
Cl	$2{\cdot}22 \times 10^4$
Br	$3{\cdot}09 \times 10^4$
NO_2	$2{\cdot}19 \times 10^7$

TABLE 5

Hammett equation parameters for the reactions of $Ar_2CH{\cdot}CCl_3$ compounds in various media

Base	Solvent	T/°C	ρ	r [a]	s [b]	α
NaOMe	MeOH	30	2·54	0·998	0·07	0·76
NaOMe	MeOH	45	2·49	0·996	0·08	0·72
NaOMe [c]	MeOH	65	2·30	0·995	0·08	0·60
NaSPh [d]	EtOH	65	2·11	0·999	0·02	0·37
Bu^{t}OK	Bu^{t}OH	30	2·99	0·993	0·14	0·62

[a] Correlation coefficient. [b] Standard deviation of slope. [c] Parameters obtained by extrapolating individual 30 and 45° rate constants to 65°. [d] From ref. 14.

The σ_R value needed to correlate the *para*-nitro-points in all reaction series in Table 5 was obtained from $\sigma_R = \sigma - \sigma_I$ rather than from $\sigma_R = \sigma^- - \sigma_I$. This implies that direct resonance interaction between the carbanionic benzylic β-carbon atom and the substituent is unimportant in the transition state, which in turn suggests that the β-carbon atom is substantially pyramidal in the transition state rather than being sp^2 hybridized as it will surely be in the delocalised carbanion. Other kinetic results pertaining to diarylmethyl carbanions have

---

[10] D. J. Cram and W. D. Kollmeyer, *J. Amer. Chem. Soc.*, 1968, **90**, 1784.

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

[12] R. A. More O'Ferrall, *J.C.S. Perkin II*, 1972, 976.

[13] A. Streitwieser, J. A. Hudson, and F. Mares, *J. Amer. Chem. Soc.*, 1968, **90**, 648.

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

[15] O. R. Jackson, D. J. McLennan, S. A. Short, and R. J. Wong, *J.C.S. Perkin II*, 1972, 2308.

been similarly interpreted.[5,16] The Brønsted plot in Figure 1 yields the relatively low Brønsted α value of 0·369. This is apparently at variance with the high ρ values in Table 5, which are suggestive of extensive proton transfer at the transition state. But since there is little structural continuity on proceeding from reactants, through the transition state, to products, it is not in order to identify α with the degree of proton transfer.[16]

All ρ parameters in Table 2 are large. This is a necessary but not a sufficient condition for *E*1cB elimination. The fact that none of them are as large as some of the ρ values found for *E*2 reactions in the $ArCH_2{\cdot}CH_2X$ system [17] can be understood by the fact that in the latter compounds the negative charge (apart from that relayed to the leaving group) is dissipated by the aryl group alone, whereas in the present cases this charge is also dissipated to some extent by the non-reacting α-chlorine atoms. No mechanistic significance is claimed for the observation that $\rho(\mathrm{Bu^tO^-} - \mathrm{Bu^tOH}) > \rho(\mathrm{OMe^-} - \mathrm{MeOH})$, since such an ordering is predicted on the basis of the change in solvent polarity,[18] and the effect of the concommitant increase in base strength cannot be isolated. This order is also observed in *E*2 reactions.[17]

It was mentioned in Part IV [1] that an overall mechanistic change with change in base strength could be responsible for the observed isotope effect maximum. However the essential similarity of ρ values for the eliminations induced by PhS^- and OMe^- (basicity difference of 9 p*K* units) argues against this, and instead suggests that there is a difference in transition state character within the framework of a common mechanism.

The most important observation is that ρ for NaOMe–MeOH reactions is significantly greater than ρ for the eliminations induced by the weaker base NaSPh in EtOH. The solvent difference is of no consequence since ρ for PhS^- in MeOH would be, if anything, less [18] than 2·11. This means that the stronger is the base, the more extensively is the proton transferred, which is contrary to the predictions of the Hammond postulate.[19] However, a three-centre proton transfer must be described in terms of a three-dimensional potential energy surface, whereas the Hammond postulate is concerned with motions parallel to the reaction co-ordinate only. 'Anti-Hammond' behaviour is expected if substituent effects are manifested in motions perpendicular to the reaction co-ordinate,[20] and a small number of items of evidence, based on slopes of l.f.e.r. plots,[21] suggests that perpendicular effects may dominate in some cases. A theoretical rationale has been given for this type of behaviour,[22] which was originally predicted by Bunnett to apply to elimination reactions.[23]

In any case the Hammond postulate does not apply to the present system for the reason that the intermediate carbanions are not relatively high energy species. We calculate, *via* the pK_a values of $(p\text{-}ClC_6H_4)_2CH{\cdot}CCl_3$ and PhSH in EtOH,[1] that $\Delta G^0 = 11{\cdot}3$ kcal mol^{-1} for the equilibrium in equation (6). The free energy of activation ($\Delta G_f^{\ddagger}$) for the forward reaction is [24] 25·3 kcal mol^{-1} so that $\Delta G_r^{\ddagger} = 14{\cdot}0$ kcal mol^{-1}, meaning that the hypothetical reprotonation of the carbanion is activation controlled. This situation is even more pronounced when OEt^- in EtOH is the base. Here, $\Delta G_f^{\ddagger} = 19{\cdot}9$ (ref. 24) whilst $\Delta G^0 = -4{\cdot}7$ kcal mol^{-1} (ref. 1), so that carbanion formation is actually exoenergetic. The carbanions are thus not of high energy relative to reactants, and so the transition states leading to and from them need not resemble them closely. Similarly we may question the applicability of the 'extended Hammond postulate' which is intended to cover reaction steps that are neither highly exo- nor endo-energetic,[25] since it too considers only parallel effects. It has already been mentioned that a largely pyramidal transition state lies on the pathway to a near-planar delocalised carbanion product, and thus as no smooth and continuous structural conversion of reactant into product occurs, the extension must also be invalid.[16]

$$(p\text{-}ClC_6H_4)_2CH{\cdot}CCl_3 + PhS^- \rightleftharpoons (p\text{-}ClC_6H_4)_2\overset{-}{\ddot{C}}{\cdot}CCl_3 + PhSH \quad (6)$$

Isotope Effects and Transition State Structure.—We have already mentioned that the ρ values for the eliminations induced by PhS^- and OMe^- are indicative of well-transferred protons in the transition states, and the above premise leads to the conclusion that the degree of proton transfer is greater in the latter case. Why then do the respective isotope effects [1] fall on the opposite sides of an isotope effect maximum for a half-transferred proton? The answer lies in the fact that the magnitude of such isotope effects are determined principally by the relative force constants of the partial $C \cdots H$ and $H \cdots B$ transition state bonds, and while a proton may be more than half-transferred to the base in the geometric sense (large ρ) it may still be less than half-transferred in the force constant sense. Model calculations on $C \cdots H \cdots S$ transfers show that the proton needs to be significantly more than half-transferred to sulphur,

---

[16] A. Streitwieser, M. A. Granger, F. Mares, and R. A. Wolf, *J. Amer. Chem. Soc.*, 1973, **95**, 4257.

[17] (*a*) W. H. Saunders, D. G. Bushman, and A. F. Cockerill, *J. Amer. Chem. Soc.*, 1968, **90**, 1775; (*b*) W. H. Saunders and R. A. Williams, *ibid.*, 1957, **79**, 3712; (*c*) C. H. DePuy and D. H. Froemsdorf, *ibid.*, p. 3710; (*d*) C. H. DePuy and C. A. Bishop, *ibid.*, 1960, **82**, 2532, 2535; (*e*) R. Baker and M. J. Spillett, *J. Chem. Soc.* (*B*), 1969, 481.

[18] P. R. Wells, 'Linear Free Energy Relationships,' Academic Press, New York, 1968, p. 24.

[19] G. S. Hammond, *J. Amer. Chem. Soc.*, 1955, **77**, 334.

[20] (*a*) E. R. Thornton, *J. Amer. Chem. Soc.*, 1967, **89**, 2915; (*b*) L. J. Steffa and E. R. Thornton, *ibid.*, p. 6149; (*c*) R. A. More O'Ferrall, *J. Chem. Soc.* (*B*), 1970, 274; (*d*) R. L. Schowen, *Progr. Phys. Org. Chem.*, 1972, **9**, 306.

[21] R. F. Hudson and G. Klopman, *J. Chem. Soc.*, 1964, 5; Y. Yano and S. Oae, *Tetrahedron*, 1970, **26**, 27; F. G. Bordwell and W. J. Boyle, *J. Amer. Chem. Soc.*, 1971, **93**, 511; N. Gravitz and W. P. Jencks, *ibid.*, 1974, **96**, 507; S. Alunni and E. Baciocchi, *Tetrahedron Letters*, 1973, 4665.

[22] J. E. Critchlow, *J.C.S. Faraday I*, 1972, 1774; W. P. Jencks, *Chem. Rev.*, 1972, **72**, 720.

[23] J. F. Bunnett in 'Survey of Progress in Chemistry,' ed. A. E. Scott, Academic Press, New York, 1969, p. 53.

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

[25] J. R. Murdoch, *J. Amer. Chem. Soc.*, 1972, **94**, 4410.

geometrically, before an isotope effect maximum is exhibited.[26]

We have found that primary k_H/k_D values for methoxide–methanol dehydrochlorinations of $Ar_2CH{\cdot}CCl_3$ substrates are greater than those observed when the base is Bu^tOK in Bu^tOH.[1] In both media the isotope effect is less than maximal, and this fact, considered in conjunction with the high ρ values, suggests that the proton is more than half-transferred in both cases. It follows that for such carbanion-forming processes, the stronger base should give rise to the lower isotope effect as it should exert greater control over the proton in the transition state. This is in agreement with our observation.

EXPERIMENTAL

Preparation of substrates, purification of solvent, and the kinetic procedures have been previously described.[1,14,24]

We thank Dr. M. J. Hardman and Dr. L. F. Blackwell, Massey University, for kindly allowing the use of the stopped-flow spectrophotometer and for valuable assistance.

[4/606 *Received*, 25th *March*, 1974]

---

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