The Carbanion Mechanism of Olefin-forming Elimination. Part 10.[1] Isotope Effects in the Dehydrochlorination of 1,1-Diaryl-2,2-dichloroethanes

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Intramolecular primary chlorine isotope effects have been measured for the base-induced dehydrochlorination reactions of $(p\text{-}YC_6H_4)_2CH{\cdot}CHCl_2$ (Y = MeO, H, or Cl) in $^-$OMe–MeOH, $^-$OMe–MeOH–Me$_2$SO, and Bu^{t}O$^-$–Bu^{t}OH. All isotope effects are small (*ca.* 0.14—0.37%), suggesting that the *E*2 transition states have nearly intact C$_\alpha$–Cl bonds. Trends in k_{35}/k_{37} with changing substituent, base, and solvent are interpreted in terms of current theories of *E*2 transition-state character. An isotope effect of unity for the reaction of $(p\text{-}NO_2C_6H_4)_2CH{\cdot}CHCl_2$ with $^-$OMe–MeOH confirms an earlier suggestion that the mechanism here is *E*1cB with rate-determining proton transfer.

PRIMARY isotope effect studies have been widely employed in investigations of mechanism and transition state character in olefin-forming eliminations.[2,3] Most work concerns β-hydrogen isotope effects. With regard to the leaving group X in equation (1), relatively few

$$B^- + H\text{–}C_\beta\text{–}C_\alpha\text{–}X \longrightarrow BH + C{=}C + X^- \quad (1)$$

systematic studies of heavy atom isotope effects have been reported, and these have involved S and N isotope effects pertaining to X = SMe$_2^+$ and NMe$_3^+$ respectively.[4] A ^{14}C study of *E*1cB elimination with X = CN is the only neutral leaving group example.[5]

Despite the fact that dehydrochlorinations (X = Cl) comprise an important part of solution elimination chemistry, no work on chlorine isotope effects, k_{35}/k_{37}, has been reported for such reactions. In fact only a few studies of chlorine isotope effects have been described,[6-16] and almost all pertain to nucleophilic substitutions. Our interest in this matter arose as a result of apparent differences in behaviour between DDD-type substrates, equation (2), and DDT-type substrates, Ar$_2$CH·CCl$_3$, in

$$Ar_2CH{\cdot}CHCl_2 + B^- \longrightarrow Ar_2C{:}CHCl + Cl^- + BH \quad (2)$$

dehydrochlorinations. The latter are believed to undergo elimination *via* the *E*1cB mechanism with rate-

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[1] Part 9, D. J. McLennan, preceding paper; preliminary communication, A. Grout, D. J. McLennan, and I. H. Spackman, *J.C.S. Chem. Comm.*, 1976, 775.

[2] W. H. Saunders and A. F. Cockerill, 'Mechanisms of Elimination Reactions,' Wiley–Interscience, New York, 1973, pp. 71—92.

[3] A. Fry, *Chem. Soc. Rev.*, 1972, **1**, 163.

[4] Ref. 2, pp. 90—91.

[5] F. M. Fouad, P. G. Farrell, and A. G. Abdal-Reheim, *Tetrahedron Letters*, 1974, 3355.

[6] R. M. Bartholomew, F. Brown, and M. Lounsbury, *Canad. J. Chem.*, 1954, **32**, 979.

[7] J. W. Hill and A. Fry, *J. Amer. Chem. Soc.*, 1962, **84**, 2763.

[8] A. Fry, *Pure Appl. Chem.*, 1964, **8**, 409.

[9] K. D. Reppond and A. Fry, Abstracts of Papers, A.C.S. 167th National Meeting, 1974, ORGN 135.

[10] E. P. Grimsrud and J. W. Taylor, *J. Amer. Chem. Soc.*, 1970, **92**, 739.

[11] C. R. Turnquist, J. W. Tayor, E. P. Grimsrud, and R. C. Williams, *J. Amer. Chem. Soc.*, 1973, **95**, 4133.

[12] D. G. Graczyk and J. W. Taylor, *J. Amer. Chem. Soc.*, 1974, **96**, 3255.

[13] T. M. Bare, N. D. Hershey, H. O. House, and C. G. Swain, *J. Org. Chem.*, 1972, **37**, 997.

[14] C. G. Swain and N. D. Hershey, *J. Amer. Chem. Soc.*, 1972, **94**, 1901.

[15] T. H. Cromartie and C. G. Swain, *J. Amer. Chem. Soc.*, 1976, **98**, 575, 2962.

[16] J. R. Christie, W. D. Johnson, A. G. Loudon, A. Macoll, and M. N. Mruzek, *J.C.S. Faraday I*, 1975, 1937.

determining proton transfer.[17] The concerted $E2$ mechanism is thought to prevail for the DDD series except in the case Ar = p-$NO_2C_6H_4$, for which a shift to E1cB appears to occur.[1,18]

Bimolecular $E2$ eliminations *must* exhibit leaving group isotope effects since the $C_\alpha \cdots X$ bond is stretched at the transition state. The situation is not so clearcut for E1cB processes, however. If proton transfer is rate-determining, equations (3) and (4) show that $k'_2 \geqslant$

$$\mathrm{B^- + H{-}C{-}C{-}X \underset{k_{-1}'}{\overset{k_1'}{\rightleftharpoons}} BH + \overset{-}{\ddot{C}}{-}C{-}X} \qquad (3)$$

$$\mathrm{\overset{-}{\ddot{C}}{-}C{-}X \xrightarrow{k_2'} C{=}C + X^-} \qquad (4)$$

k_1'[BH] is a necessary condition. No X isotope effect will be observed if direct kinetic methods (experimentally unlikely) are employed in determining leaving group isotope effects. The more usual competitive methods for heavy atom isotope effects will give, for X = Cl, a measured k_{35}/k_{37} equal to $(k_2')_{35}/(k_2')_{37}$ if the secondary isotope effect on the k_1' step is negligible. If the carbanion is highly unstable and k_2' is very large, the transition state for reaction (4) will be carbanion-like, and the lack of C–Cl bond weakening may result in a low isotope effect. However, if the k_{-1}' step is not diffusion-controlled, the inequality $k_2' \gg k_{-1}'$[BH] allows the k_2' step to be activation-controlled. If the carbanion is reasonably stable with respect to the products, and since the C–Cl bond may thus be reasonably well broken,[19] a substantial competitive isotope effect may be observed.

In the present work we examine chlorine isotope effects in DDD dehydrochlorination [equation (2)].

RESULTS

Isotopic Fractionation and the Isotope Effect.—The presence of two equivalent potentially reactive chlorines in $Ar_2CH{\cdot}CHCl_2$ complicates matters as far as the conversion of measured chlorine isotope ratios into isotope effects is concerned. The system can be symbolized by equations (5)—(8), in which ABA species represent the substrate, A species represent the released chloride ion, and AB species the chlorine-containing olefin. The heavy isotopes are denoted by primes. The quotient $k_1/2k_3$ is the primary

$$\mathrm{ABA} \xrightarrow{k_1/2} \mathrm{AB + A} \qquad (5)$$

$$\mathrm{ABA'} \xrightarrow{k_2} \mathrm{A'B + A} \qquad (6)$$

$$\mathrm{ABA'} \xrightarrow[k_3]{} \mathrm{AB + A'} \qquad (7)$$

$$\mathrm{A'BA'} \xrightarrow{k_1/2} \mathrm{A'B + A'} \qquad (8)$$

intermolecular isotope effect, k_2/k_3 is the primary intramolecular isotope effect, and $k_1/2k_2$ is the secondary isotope effect. Solutions for the isotope effects have been given for cases where A′BA′ is negligible,[20] but for chlorine, ABA comprises 57.41% of the total, ABA′ 36.72%, and A′BA′ comprises 5.87% of the total molecules present in a natural abundance sample.

In deriving expressions for the intramolecular isotope effect, k_2/k_3, we neglect isotopic inhomogeneity of C_α. If the reaction is taken to completion, product concentrations refer to $t = \infty$. Consider the measurable isotopic quotient, $R_A = [A']/[A]$ at $t = \infty$. Isotope A arises from reactions (5) and (6) whilst A′ arises from reactions (7) and (8), so equations (9) and (10) follow. It is obvious that $[A_5] = [ABA]_0$ and $[A'_8] = [A'BA']_0$, where the zeros refer to

$$[A] = [A_5] + [A_6] \qquad (9)$$

$$[A'] = [A'_7] + [A'_8] \qquad (10)$$

initial reactant composition. The species ABA′ decomposes selectively according to equations (11) and (12). Substitution into equations (9) and (10) followed by division

$$[A_6] = k_2[ABA']_0/(k_2 + k_3) \qquad (11)$$

$$[A_7'] = k_3[ABA']_0/(k_2 + k_3) \qquad (12)$$

leads to equation (13). With attention to the following

$$R_A = [A']/[A] = \frac{k_2[A'BA']_0 + k_3[A'BA']_0 + k_3[ABA']_0}{k_2[ABA]_0 + k_2[ABA']_0 + k_3[ABA]_0} \qquad (13)$$

relationships:[20] $[ABA]_0 = [\text{substrate}]_0/(1 + R_0)^2$, $[ABA']_0 = 2R_0[\text{substrate}]_0/(1 + R_0)^2$, and $[A'BA']_0 = R_0^2[\text{substrate}]_0/(1 + R_0)^2$, where R_0 is the isotopic quotient of the original substrate (natural abundance in the present case), rearrangement of equation (13) yields equation (14)

$$\frac{k_2}{k_3} = \frac{R_0(R_0 + 2) - R_A}{R_A(2R_0 + 1) - R_0^2} \qquad (14)$$

for k_2/k_3. A similar derivative based on R_{AB}, the $^{37}Cl/^{35}Cl$ quotient in the AB–A′B product mixture at $t = \infty$, gives equation (15) as an equivalent expression, which serves as an experimental consistency check.

$$\frac{k_2}{k_3} = \frac{R_{AB}(2R_0 + 1) - R_0^2}{R_0(R_0 + 2) - R_{AB}} \qquad (15)$$

Experimental Results.—For all substrate–base solvent systems, independent determinations of R_A and R_{AB} were made in order to obtain the intramolecular isotope effect. Treatment of Ar_2C⁚CHCl with Bu^{t}OK–Bu^{t}OH yielded 1 equiv. of chloride ion, and presumably ArC⁚CAr, for the measurement of R_{AB}. Chloride ion samples were converted into MeCl by the method of Taylor and Grimsrud,[21] and analysis was performed by mass spectrometry (positive ion measurements).

Results for OMe$^-$–MeOH are shown in Table 1. Each value of R_A and R_{AB} is the mean of at least six recordings of the MeCl isotope quotient for a given MeCl sample, and the uncertainties are standard deviations. Values of k_2/k_3 are essentially the same whether calculated *via* R_A[equation (14)] or R_{AB} [equation (15)]. The natural abundance quotient,[22] 0.319 77, was used for R_0.

An attempt was made to measure the intermolecular

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[17] D. J. McLennan and R. J. Wong, *J.C.S. Perkin II*, 1974, (*a*) p. 526; (*b*) p. 1373.

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

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

[20] J. Bigeleisen and M. Wolfsberg, *Adv. Chem. Phys.*, 1958, **1**, 15.

[21] J. W. Taylor and E. P. Grimsrud, *Analyt. Chem.*, 1969, **41**, 805.

[22] W. R. Shields, T. J. Murphy, E. L. Garner, and V. H. Dibeler, *J. Amer. Chem. Soc.*, 1962, **84**, 1519.

isotope effect. Measurement of R_{AB} and R_{ABA} after partial reaction requires separation of $Ar_2CH\cdot CHCl_2$ and $Ar_2C{:}CHCl$ and quantitative recovery. Various chromatographic methods were inadequate or inconvenient. Benzenethiolate ions in EtOH react at vastly different rates with the two components, releasing 2 equiv. of Cl^- from the former slowly and 1 equiv. of Cl^- from the latter rapidly (in the presence of an excess of PhSH).[23] While this allowed selective and quantitative recovery of Cl^- from standard samples, the AgCl consequently obtained [21] did not react quantitatively with MeI in the step producing MeCl. Various yields (<50%) were obtained, and surface contamination of the AgCl by unextractable sulphur-containing materials (which could be smelled) was thought to be the cause.

TABLE 1

Intramolecular chlorine isotope effects in reactions of $(p\text{-}YC_6H_4)_2CH\cdot CHCl_2$ with NaOMe (0.25M) in MeOH at 30 °C

Y	R_A [a]	R_{AB} [a]	k_{35}/k_{37}	Mean k_{35}/k_{37} [b]
MeO	0.319 16		1.003 82	
MeO		0.320 37	1.003 76	1.003 79 ±0.000 19
H	0.319 22		1.003 45	
H		0.320 34	1.003 63	1.003 54 ±0.000 15
Cl	0.319 40		1.002 25	
Cl		0.320 15	1.002 39	1.002 32 ±0.000 20
NO_2 [c]	0.319 86		0.999 43	
NO_2 [c]	0.319 75		1.000 12	
NO_2 [c]		0.319 72	0.999 88	
NO_2 [c]		0.319 83	1.000 38	0.999 95 ±0.000 26

[a] Corrected for fragmentation as described in Experimental section; accurate to within ±0.000 05 at the most. [b] Uncertainty based on standard deviation of the six individual readings of R_A or R_{AB} from the mean. [c] [NaOMe] = 0.05M.

TABLE 2

Intramolecular chlorine isotope effects in the reaction of $Ph_2CH\cdot CHCl_2$ with NaOMe (0.1M) in MeOH–Me_2SO at 30 °C

Mole % Me_2SO	R_A [a]	R_{AB} [a]	k_{35}/k_{37}	Mean k_{35}/k_{37} [b]
0	0.319 22	0.320 34		1.003 54 ±0.000 15 [c]
12.45	0.319 28		1.003 07	
12.45		0.320 24	1.002 94	1.003 00 ±0.000 23
27.35	0.319 43		1.002 12	
27.35		0.320 10	1.002 07	1.002 10 ±0.000 21

[a,b] As Table 1. [c] From Table 1.

TABLE 3

Intramolecular chlorine isotope effect in the reaction of $(p\text{-}YC_6H_4)_2CH\cdot CHCl_2$ with Bu^tOK (0.12M) in Bu^tOH at 30 °C

Y	R_A [a]	R_{AB} [a]	k_{35}/k_{37}	Mean k_{35}/k_{37} [b]
H	0.319 44		1.002 06	
H		0.320 08	1.001 95	1.002 00 ±0.000 22
Cl	0.319 54		1.001 37	
Cl		0.319 99	1.001 37	1.001 40 ±0.000 17

[a,b] As Table 1.

In a second series of experiments the effect on the intramolecular isotope effect of adding Me_2SO to the ^-OMe–MeOH reaction medium was investigated, and the results are shown in Table 2. Finally, the intramolecular isotope effect for the dehydrochlorination of $Ph_2CH\cdot CHCl_2$ by Bu^tOK–Bu^tOH was measured (Table 3).

DISCUSSION

Mechanisms of Elimination.—The chlorine isotope effects found in these reactions are the lowest that have yet been recorded as far as leaving groups are concerned. To show that no bias towards low isotope effects arose as an experimental artifact, k_{35}/k_{37} for the S_N2 reaction of $PhCH_2Cl$ with LiOMe in MeOH was measured (see Experimental section); the result compared favourably with the literature value of 1.008 0.[10] The method used here gives intramolecular isotope effects, whereas all previous chlorine isotope effect work has yielded primary intermolecular effects. Theoretical calculations reported in the following paper suggest, however, that the secondary isotope effect is small (no greater than 1.000 55 for a physically unreasonable model) so that the primary intermolecular and intramolecular isotope effects will be approximately equal.

Table 1 shows that k_{35}/k_{37} falls as Y in $(p\text{-}YC_6H_4)_2CH\cdot CHCl_2$ becomes more powerfully electron-withdrawing, to the point where it effectively equals unity for Y = NO_2. An attractive explanation is that the $E2$ mechanism dominates for Y = MeO, H, or Cl, and the already relatively small degree of $C_\alpha \cdots Cl$ stretching in the transition state is diminished in this order, as earlier suggested.[1] This is in accordance with substituent effect results based on reactions of 2-phenethylarenesulphonates.[24] When Y = NO_2 the $E1cB$ mechanism is operative and the C_α–Cl bond is not significantly stretched in the transition state for carbanion destruction. This reasoning is based on the theoretically demonstrable principle that k_{35}/k_{37} is a roughly linear function of the degree of breaking of the $C_\alpha \cdots Cl$ bond.[25,26] This applies strictly only for a fixed degree of proton transfer, and while the *para*-substituent change does cause the degree of proton transfer to vary,[1] deviations of k_{35}/k_{37} should occur only for extremely small or large amounts of $H \cdots C_\beta$ breaking, as is shown in the following paper. There is no evidence for this in the present system.

But neither are the results, at first sight, incompatible with $E1cB$ eliminations for all substrates, for reasons mentioned in the Introduction. All that is needed is a k'_2 step that is activation-controlled, with $k_2' \gg k'_{-1}$[BH], for observable competitive chlorine isotope effects to attend an $E1cB$ process. This means that k_{-1}'[BH] must be lower than the diffusion-controlled limit, and in fact there is some evidence available suggesting that this

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

[24] J. Banger, A. F. Cockerill, and G. L. O. Davies, *J. Chem. Soc.* (*B*), 1971, 498.

[25] L. B. Sims, A. Fry, L. T. Netherton, J. C. Wilson, K. D. Reppond, and S. W. Crook, *J. Amer. Chem. Soc.*, 1972, **94**, 1364.

[26] W. H. Saunders, *Chemica Scripta*, 1975, **8**, 27.

is the case for *E*1cB elimination in the DDT series.[27] But predictions based on an *E*1cB hypothesis for the DDD series are at variance with the present results. One would predict the order of carbanion stability to decrease in the order of Y groups; $NO_2 > Cl > H >$ MeO, and as the substituents should have little effect on the stability of the product olefin, the exothermicity of the hypothetical carbanion decomposition step should decrease along the series from MeO to NO_2. Thus the k_2' values should decrease in the same order, and evidence for this type of behaviour is available.[28] It then follows *via* the Hammond postulate [19] that the $C_\alpha \cdots Cl$ bond should be more stretched for $Y = NO_2$ than for $Y = MeO$, with chlorine isotope effects decreasing in the same order. This is contrary to fact, and so an all-*E*1cB explanation must be rejected. It is more reasonable to assume that the *E*1cB mechanism does prevail for $Y = NO_2$ and that k_2' is close to the vibrational limit (6.3×10^{12} s^{-1} at 45 °C). If there is then no intramolecular chlorine isotope effect in this carbanion decomposition step, neither will there be any in the minor *E*1cB components [1] of the other reactions. The k_{35}/k_{37} values recorded for Y = MeO, H, or Cl then pertain to the major *E*2 (paenecarbanion) components.*

The *para*-substituent effect on the *E*2 k_{35}/k_{37} values is of interest. The decrease on going from Y = MeO to Y = Cl is outside the limits imposed by experimental uncertainty. Application of the *E*2 transition state rules for carbanion-like species [29] allows the prediction that the degree of rupture of the $C_\alpha \cdots Cl$ bond should decrease somewhat as substituents on C_β are made more electron-attracting. The present results indicate that this is indeed the case, and thus provide evidence for an *E*2 interpretation. A similar decrease in the leaving group isotope effect has been reported for the *E*2 reactions of $ArCH_2{\cdot}CH_2NMe^+$ induced by ^-OEt in EtOH, and a similar interpretation has been advanced.[30]

Effect of Dimethyl Sulphoxide.—There is a clear decrease in k_{35}/k_{37} as the Me_2SO content of the medium is increased (Table 2). A change in transition state character is clearly responsible since the tunnelling explanation used to rationalise trends in k_H/k_D[1] is inappropriate for heavy atom isotope effects.

The addition of Me_2SO can affect overall transition-state character in two ways, both of which arise out of its lack of solvating ability towards anions. The base strength of ^-OMe will be increased, and the incipient chloride ion in the transition state will become more poorly solvated. The *E*2 rules predict that an increase in base strength will have little if any effect on the extension of the $C_\alpha \cdots X$ bond for a paenecarbanion transition state.[29] If this is so, a leaving group solvation effect could be dominating the isotope effect trend. Such solvation would have to act in such a way as to assist bond-breaking in media that can better solvate the incipient anion, *i.e.* as a perpendicular effect operating on the stable vibrational modes connected with the $C_\alpha \cdots Cl$ bond. We have already concluded (preceding paper) that heavy leaving groups move but little in the parallel decomposition mode, thus affording an opportunity for the dominance of perpendicular substituent and solvent effects on transition state character.

However, theoretical calculations (following paper) indicate that k_{35}/k_{37} will be lowered by stronger solvational bonds to the departing chlorine atom *for a given degree of bond breaking*, and experimental results pertaining to S_N2 reactions of benzyl chlorides can be cited in support of this contention.[9] It must then be concluded that the present results arise from a combination of base strength effects and the effect of the hydrogen bond donation ability of the solvent on the degree of $C_\alpha \cdots Cl$ bond breaking. There may be some lowering of k_{35}/k_{37} in the more methanolic media as a result of a three-centre $C_\alpha \cdots Cl \cdots HOMe$ arrangement, but Reppond and Fry report such an effect as being of importance only when the bond is already well severed,[9] with a large degree of negative charge present on chlorine. The inherent lowness of the isotope effects observed here argues against this.

Element effect results (k_{Br}/k_{Cl}) are responsive to solvent composition in the same way as are the isotope effects,[31] although care should be taken in interpreting the former rate ratios.[32] The sulphur isotope effect in the $PhCH_2{\cdot}CH_2SMe_2^+$–OH^- elimination falls as dimethyl sulphoxide is added to an aqueous medium.[33] The magnitude of the isotope effect in water indicates a central transition state,[26] where base strength effects are considered to be of greater importance.[29b] Thus the trend can be rationalized without attempting to disentangle the effects of H_2O and Me_2SO solvation of sulphonium ion *vs.* incipient SMe_2 molecule. No change in the nitrogen isotope effect in the ethoxide-induced, carbonyl-forming elimination from benzyl nitrate is observed when the solvent is changed from EtOH to 80% EtOH–Me_2SO.[34] The transition state is again in the central region [34,35] and the solvent range is not as wide as that employed here.

Isotope Effects in Bu^tOK–Bu^tOH.—Comparison of results in Tables 1 and 3 shows that a medium change from NaOMe–MeOH to Bu^tOK–Bu^tOH causes a decrease in the extent of the $C_\alpha \cdots Cl$ bond breaking.

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* For discussion of the *E*2/*E*1cB borderline, see ref. 29*a*, also F. G. Bordwell, *Accounts Chem. Res.*, 1972, **5**, 374; W. H. Saunders, *ibid.*, 1976, **9**, 19.

[27] D. J. McLennan and R. J. Wong, *Austral. J. Chem.*, 1976, **29**, 787.

[28] M. Albert, S. Hoz, and Z. Rappoport, *J.C.S. Perkin II*, 1972, 1248; 1975, 628.

[29] (*a*) R. A. More O'Ferrall in ' Chemistry of Carbon–Halogen Bonds,' ed. S. Patai, Wiley, New York, 1973, ch. 9; (*b*) D. A. Winey and E. R. Thornton, *J. Amer. Chem. Soc.*, 1975, **97**, 3102.

[30] P. J. Smith and A. N. Bourns, *Canad. J. Chem.*, 1974, **52**, 749.

[31] G. Marchese, F. Naso, and V. Sgherza, *Gazzetta*, 1971, **101**, 251.

[32] R. Bird and C. J. M. Stirling, *J.C.S. Perkin II*, 1973, 1221.

[33] A. F. Cockerill and W. H. Saunders, *J. Amer. Chem. Soc.*, 1967, **89**, 4985.

[34] C. A. Pollock and P. J. Smith, *Canad. J. Chem.*, 1971, **49**, 3586.

[35] P. J. Smith, C. A. Pollock, and A. N. Bourns, *Canad. J. Chem.*, 1975, **53**, 1319.

Again we believe that a base strength effect is reinforced by a solvent polarity effect on the $C_\alpha \cdots Cl$ transition state bond order. Again, the effect of H-bonding on the magnitude of the carbon–chlorine vibrational frequencies [9] seems to be relatively unimportant, since isotope effects are small. The nitrogen isotope effect in the $E2$ decomposition of $CH_3{\cdot}CH_2{\cdot}NMe_3^+$ displays the same response to change in medium from ^-OEt–EtOH to Bu^tO^-–Bu^tOH,[30] but larger relative isotope effects place the transition state in the central region which in turn suggests that the effect of base strength is relatively more important in changing transition state character.

As with reactions in NaOMe–MeOH, the replacement of *p*-H by Cl results in the diminution of the isotope effect (Table 3). No overall mechanistic switch is indicated since k_{35}/k_{37} for $(p\text{-}ClC_6H_4)_2CH{\cdot}CHCl_2$ is still substantially greater than unity. We may note that the *para*-substituent effect on leaving group isotope effects observed here and elsewhere [30] provides further evidence (if any were needed) [24,26] against Hoffmann's contention that the leaving group rate quotient k_{OTs}/k_{Br} is a valid measure of $E2$ transition state character [37] and the demonstrably incorrect corollary that $E1cB$ elimination is impossible.[38]

The most recent version of the $E2$ transition state rules predicts that central and carbanion-like transition states will respond differently as far as medium-induced and substituent-induced changes in structure are concerned.[29b] That this is necessary is well illustrated by comparison of the present results for an initially neutral leaving group with others pertaining to 'onium ion substrates.[30,31] The identical response of leaving group isotope effects to medium changes in particular is not readily intelligible unless such a division is made and, as mentioned earlier, the general relative magnitude of the respective isotope effects allows this to be done.

EXPERIMENTAL

Sample Preparation.—Substrates and base–solvent solutions were prepared as previously described.[1,18,39] In a typical experiment NaOMe–MeOH (0.50M; 100 ml) at 30 °C was rapidly mixed with a methanolic solution of substrate (0.025M; 100 ml) thermostatted at 30 °C. The mixture was stirred under nitrogen for a time corresponding to at least 10 half-lives of the reaction, and was then poured into deionized water (500 ml). This solution was extracted with several portions of ether and the extracts were combined, dried, and set aside. The aqueous extract was concentrated to *ca.* 75 ml and AgCl was precipitated, in yields never lower than 98.6%, as described by Taylor and Grimsrud.[21] The ether of the organic layer was removed under vacuum and Bu^tOK–Bu^tOH (0.15M; 100 ml) was added. The resulting solution was refluxed for at least 24 h under nitrogen and was partitioned between ether and water. Precipitation of AgCl from the aqueous layer followed, in yields corresponding to recovery of at least 97.8% of the chloride ion from $Ar_2C{:}CHCl$.

The AgCl samples were converted almost quantitatively into methyl chloride [21] for mass spectrometric measurement of R_A and R_{AB}. Check experiments showed that no detectable isotopic fractionation attended any stage of this procedure, and the almost quantitative yields of AgCl from Cl^- and $Ar_2C{:}CHCl$ rule out the possibility of fractionation in the earlier steps.

Mass Spectrometric Analysis.—A Varian MAT CH7 instrument was used, equipped with the manufacturer's double gas inlet module and the ADB twin Faraday cup double collector module. The ratio of amplified ion currents at *m/e* 50 and 52 was read from the manufacturer's measuring bridge by tapping a measured fraction of the ion current from the *m/e* 50 collector and compensating the *m/e* 52 amplifier output almost to zero. The residual output of the latter amplifier was measured with a 25 mV recorder operating at the highest level of sensitivity.

In measurement of R_A or R_{AB} *via* a methyl chloride sample, inlet pressures of sample and reference (tank, MeCl) gas were equalized. After the amplifier zeros had become stabilized, sample gas was admitted to the ionization chamber for 2 min and the output of the *m/e* 52 amplifier was compensated to give an appropriate recorder deflection using the measuring bridge. The amplifier zero was then read for 1 min. The reference gas was admitted for 2 min. During the first minute the measuring bridge was held at the same ratio as for the sample and for the second minute a different ratio was employed so as to allow calibration of the chart paper in terms of the bridge ratio. The zero was re-established for 1 min and the entire sequence was repeated five times more. Finally, it was confirmed that sample and reference gas pressures were equal.

The *m/e* 50 ions are $CH_3{}^{35}Cl^+$ and $CH^{37}Cl$; hence correction is necessary in measuring positive ion quotients.[21] Isotopic standards were not available and so an indirect method was employed. Benzyl chloride was allowed to react to 31.6% completion with LiOMe in MeOH at 20 °C. The measured isotopic quotient of the MeCl prepared from the released chloride ion was 0.336 81 and the measured ratio for reference gas was 0.339 24. Assuming that the quotient in the reference is the natural abundance quotient, an isotope effect of 1.008 73 can be derived. This is a little higher than the literature value [11] (corrected for fragmentation) of 1.008 0. With attention to a quoted positive ion correction factor based on measurements of isotopic standards, equation (16) may be derived. Here, R_{obs} is the measured

$$R_A \text{ (or } R_{AB}) = \frac{1.036\, R_0 R_{obs}}{R_r + 0.036\, R_{obs}} \qquad (16)$$

sample ratio and R_r is the measured reference ratio. The reference is assumed to be natural abundance. Application of this correction to the benzyl chloride results leads to an isotope effect of 1.008 48, which is possibly within experimental error of the literature value. Hence equation (16) was used to correct all readings for fragmentation, although in the present system, with all sample ratios close to natural abundance, the corrections were small and caused changes no greater than the experimental error in the isotope effect.

Check Experiments.—A known quantity of tank methyl chloride was allowed to react with LiOMe–MeOH in a sealed tube, to completion. The chloride ion produced

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[36] A. F. Cockerill, *Tetrahedron Letters*, 1969, 4913; Z. Rappoport, J. Kaspi, and Y. Apeloig, *J. Amer. Chem. Soc.*, 1974, **96**, 2612; R. C. Bingham and P. von R. Schleyer, *ibid.*, 1971, **93**, 3189.

[37] G. M. Fraser and H. M. R. Hoffmann, *J. Chem. Soc. (B)*, 1967, 265.

[38] H. M. R. Hoffmann, *Tetrahedron Letters*, 1967, 4393.

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

was converted into MeCl in the usual way, and the isotopic quotient was found to be identical with that of the tank methyl chloride. That compensating fractionation in preparation and measurement was not involved was demonstrated by using tank MeCl as both sample and reference. The isotopic quotients were identical. Deliberate attempts were made to induce fractionation during vacuum line manipulations, but all failed. For instance, no effect was observed on trapping MeCl from a gaseous MeCl–MeI mixture as opposed to allowing MeCl to evaporate slowly from the frozen solid mixture. In view of a quoted precaution [40] a sample was exposed to an excess of stopcock grease (silicone) coating the interior of a vaccum line tube. No fractionation was observed.

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[40] M. P. Friedberger and E. R. Thornton, *J. Amer. Chem. Soc.*, 1976, **98**, 2861.