# Model Calculations of Heavy Atom Isotope Effects for *E*2 and *E*1cB Dehydrochlorination of 1,1-Diaryl-2,2-dichloroethanes

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Calculations of heavy atom kinetic isotope effects for the alkoxide-induced dehydrochlorination of $Ar_2CH{\cdot}CHCl_2$ are presented. Previously employed cut-off methods and transition state models are used, and the atoms concerned are: α-chlorine ($k_{35}/k_{37}$ for primary intermolecular and intramolecular effects, and for the secondary effect) and $C_\alpha$ and $C_\beta$ primary carbon isotope effects, $k_{12}/k_{14}$). Changes in kinetic isotope effect with simulated variations in transition state structure are discussed. The effect of simulating partial solvation of the incipient anionic leaving group in the transition state is investigated. Theoretical isotope effects are compared with preliminary experimental results, and tentative transition state structures are proposed.

WE have previously detailed the results of computer-calculated model kinetic isotope effects (KIEs) for alkoxide-induced dehydrochlorinations of 1,1-diaryl-2,2-dichloroethanes (DDDs) [equation (1)].[1] We now consider heavy atom isotope effects with a preliminary view to the transition state (TS) mapping [2] of the *E*2 reaction. Thus we have studied the response of various

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

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[1] G. W. Burton, L. B. Sims, and D. J. McLennan, *J.C.S. Perkin II*, 1977, 1763.

[2] D. A. Winey and E. R. Thornton, *J. Amer. Chem. Soc.*, 1975, **97**, 3102.

heavy atom KIEs to changes in structure of the TS model. This work is complementary to calculations by Saunders for the elimination reactions of EtX with $^{-}$OH,[3] but has the advantage that the calculated KIEs are directly applicable to a system that is currently under experimental investigation. Hydrogen[4,5] and chlorine[6] KIEs have already been reported. As described earlier,[1] our initial state (IS) and TS models differ in some respects from those of Saunders. The procedure for calculating vibrational frequencies is likewise a little different, and minor differences in the predicted behaviour of $k_H/k_D$ have been reported.

## CALCULATIONS

The geometric models for IS and the variable TS structures, together with the force fields, have been described.[1] Changes in TS structure are again simulated by varying appropriate bond angles and the lengths and bond orders of reacting bonds, as depicted in the Figure in ref. 1, with the same provisos; namely $1.0 \geqslant n_4 \geqslant 0.5$ and $n_4 \geqslant n_2$, so that only paenecarbanionic or central ($n_4 = n_2$) TSs are considered. The earlier alternative formulations of the reaction co-ordinate decomposition mode are employed. All KIEs reported here are for a temperature of 25 °C, and incorporate the simple Bell tunnel correction, small though it is for heavy atom KIEs, unless otherwise noted. In displaying and discussing the results the previous transition state structure codes are used.

We have also KIE data for 50 °C, but since Saunders has recently treated temperature effects in some depth[3b] it suffices to state that in cases where comparison is possible there is no essential disagreement between his results and ours.

## RESULTS AND DISCUSSION

*Chlorine Isotope Effects.*—Because there are two potentially reactive chlorine atoms in $Ar_2CH{\cdot}CHCl_2$ there are four isotopically distinguishable processes. In Table 1 we show the primary intermolecular chlorine KIE for loss of $^{35}Cl$ from $Ar_2CH{\cdot}CH^{35}Cl_2$ *vs.* loss of $^{37}Cl$ from $Ar_2CH{\cdot}CH^{35}Cl^{37}Cl$. Secondary and primary intramolecular KIEs will be discussed later.

Reading down the columns of Table 1 establishes the KIE pattern for an increase in the degree of $C_\alpha \cdots Cl$ bond breaking at a constant degree of proton transfer. The KIEs increase regularly, irrespective of whether substantial chlorine motion in the reaction co-ordinate mode is permitted, as in (A) and (E), or is minimized, as in (B)—(D). This is as expected, and the values of $k_{35}/k_{37}$ correspond reasonably well, with the exception of those in series (E), with those calculated by Saunders for EtCl plus $^{-}$OH.[3] The immediate molecular environment of the departing chlorine nucleus is of little consequence in this regard. The KIEs are, however, smaller than those calculated[7] for $S_N2$ displacement on benzyl chloride for $C \cdots Cl$ bond orders of 0.5, and this is clearly a consequence of a difference in barrier curvature and in reaction co-ordinate formulation.

Reading across the rows in Table 1 illustrates the response of the chlorine KIE, at a constant degree of $C_\alpha \cdots Cl$ rupture, to the extent of proton transfer. Small but potentially measurable changes in $k_{35}/k_{37}$ are seen, which means that there is not a one-to-one correspondence between $n_4$ and $k_{35}/k_{37}$. The converse does not apply so emphatically—$k_H/k_D$ at a constant degree of proton transfer is but little affected by variation in $n_4$.[1] This is because the reaction co-ordinate models emphasize proton motion at the expense of heavy atom motion, even when coupling is allowed.

TABLE 1

Primary chlorine isotope effects (intermolecular)

| | | | | |
|---|---|---|---|---|
| | | Reaction co-ordinate (A) | | |
| [1 910]<br>1.000 42 | [3 710]<br>1.000 03 | [5 510]<br>1.000 06 | [7 310]<br>1.000 33 | [9 110]<br>1.001 13 |
| [199]<br>1.001 06 | [379]<br>1.000 75 | [559]<br>1.000 77 | [739]<br>1.001 06 | [919]<br>1.001 93 |
| | [377]<br>1.002 27 | [557]<br>1.002 29 | [737]<br>1.002 59 | [917]<br>1.003 64 |
| | | [555]<br>1.003 94 | [735]<br>1.004 22 | [915]<br>1.005 44 |
| | | Reaction co-ordinate (B) | | |
| [1 910]<br>1.000 39 | [3 710]<br>1.000 00 | [5 510]<br>1.000 01 | [7 310]<br>1.000 17 | [9 110]<br>1.001 06 |
| [199]<br>1.001 07 | [379]<br>1.000 68 | [559]<br>1.000 69 | [739]<br>1.000 84 | [919]<br>1.001 77 |
| | [377]<br>1.002 16 | [557]<br>1.002 16 | [737]<br>1.002 29 | [917]<br>1.003 30 |
| | | [555]<br>1.003 79 | [735]<br>1.003 88 | [915]<br>1.004 93 |
| | | Reaction co-ordinate (C) | | |
| [1 910]<br>1.000 67 | [3 710]<br>1.000 0 | [5 510]<br>1.000 2 | [7 310]<br>1.000 54 | [9 110]<br>1.001 17 |
| [199]<br>1.001 06 | [379]<br>1.000 75 | [559]<br>1.000 77 | [739]<br>1.001 06 | [919]<br>1.001 93 |
| | [377]<br>1.002 16 | [557]<br>1.002 17 | [737]<br>1.002 66 | [917]<br>1.003 46 |
| | | [555]<br>1.003 80 | [735]<br>1.004 20 | [915]<br>1.005 18 |
| | | Reaction co-ordinate (D) | | |
| [1 910]<br>1.000 91 | [3 710]<br>1.000 00 | [5 510]<br>1.000 11 | [7 310]<br>1.000 62 | [9 110]<br>1.000 95 |
| [199]<br>1.001 60 | [379]<br>1.000 68 | [559]<br>1.000 69 | [739]<br>1.001 30 | [919]<br>1.001 65 |
| | | Reaction co-ordinate (E) | | |
| [1 910]<br>1.001 04 | [3 710]<br>1.000 88 | [5 510]<br>1.001 17 | [7 310]<br>1.002 02 | [9 110]<br>1.002 59 |
| [199]<br>1.001 86 | [379]<br>1.001 67 | [559]<br>1.002 00 | [739]<br>1.002 94 | [919]<br>1.003 55 |
| | [377]<br>1.003 34 | [557]<br>1.003 68 | [737]<br>1.004 80 | [917]<br>1.005 58 |
| | | [555]<br>1.005 38 | [735]<br>1.006 66 | [915]<br>1.007 77 |

We examine the response of $k_{35}/k_{37}$ to changes in $n_2$ at constant $n_4$ in some detail, since the implication is that the leaving group isotope effect does not necessarily indicate its state of bonding in the TS. Even in those cases where the $C_\alpha$–Cl bond remains intact ($n_4 = 1.0$)

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[3] W. H. Saunders, *Chemica Scripta*, (*a*) 1975, **8**, 27; (*b*) 1977, **10**, 82.

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

[5] D. J. McLennan, *J.C.S. Perkin II*, 1977, 1753.

[6] A. Grout, D. J. McLennan, and I. H. Spackman, *J.C.S. Chem. Comm.*, 1977, 775; *J.C.S. Perkin II*, 1977, 1758.

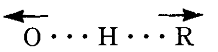
[7] L. B. Sims, A. Fry, L. T. Netherton, J. C. Wilson, K. D. Reppond, and S. W. Crook, *J. Amer. Chem. Soc.*, 1972, **94**, 1364;

and heavy atom motion in the reaction co-ordinate is restricted so as merely to preserve the centre of mass, *i.e.* (B)—(D), non-unit KIEs are calculated. This result should finally lay to rest the idea commonly held by organic chemists that force constant changes at a reacting atom, due to bond making or breaking, or to rehybridization, are necessary before KIEs accrue. Analysis of these particular KIEs terms of equation (2) reveals that the temperature-independent factor $\nu_{L}^{\ddagger}{}_{(35)}/\nu_{L}^{\ddagger}{}_{(37)}$ (TIF) is primarily responsible for the patterns, and

$$k_{35}/k_{37} = [\nu_{L}^{\ddagger}{}_{(35)}/\nu_{L}^{\ddagger}{}_{(37)}]\ (VP\cdot EXC\cdot ZPE) \quad (2)$$

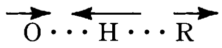
that the temperature-dependent factor (TDF) is more independent of TS structure. When $n_4 = 1.0$ we are dealing with simple proton transfer processes, as in *E*1cB elimination, and we may thus observe the kinetic effect of chlorine mass without the complications that geometric, bonding, and reaction co-ordinate coupling changes can bring.

Thus, let us first consider the [1 910] ⟶ [9 110] series. The KIE passes through a shallow but distinct minimum as the degree of proton transfer increases. The structure at which the minimum occurs corresponds to the maximum in $k_H/k_D$,[1] which is also apparent in Saunders' results.[3] At the point where the proton is half transferred in force constant terms (close to [3 710]), it is motionless in the real, symmetrical TS stretching mode (I). Isotopic hydrogen substitution thus has no effect



(I)

on the *ZPE* of (I), and the contribution to $k_H/k_D$ of the TDF (which comprises frequencies of real modes in IS and TS) is maximized since the isotopic dependence of the initial state *ZPE* dominates completely. On the other hand the unstable reaction co-ordinate mode (II),



(II)

peculiar to the TS, whose imaginary frequencies generate the TIF, is an asymmetric stretch, and the frequencies $\nu_{L}^{\ddagger}{}_{(H)}/\nu_{L}^{\ddagger}{}_{(D)}$ are generated by making the off-diagonal coupling force constant $f_{OH,HR}$ greater than or equal to $(f_{OH}f_{HR})^{\frac{1}{2}}$. These frequencies are maximal for $f_{OH} = f_{HR}$, and so proton motion is also maximal in the relative sense in the reaction co-ordinate mode, as is the isotopic sensitivity, *i.e.* the TIF. Thus since *both* the TDF and the TIF have maximal values for a symmetrical TS structure, their product ($k_H/k_D$) is also at a maximum. We call this the principle of *complementarity*.

Now let us consider the group R, first in the case where no bonding changes are occurring therein. It follows from the above that for a symmetrical TS in force constant terms, the heavy group R will have maximal relative motion in real modes such as (I) (which we call anti-reaction co-ordinate modes), and minimal relative motion in the unstable reaction co-ordinate vibration. The effect of isotopic substitution in R will then lead to a maximum in the isotopic dependence of real TS frequencies, which will largely be cancelled by the IS isotope dependence, leaving TDF small, and a minimum in the isotopic dependence of the decomposition frequencies, leaving TIF also small. Thus the isotopic substitution of a heavy non-reacting atom in the fragment R will, by the complementarity principle, give rise to a *minimal* isotope effect if the proton is half transferred.

For unsymmetrical reactant-like or product-like proton transfer TSs, it may be shown easily that TDF and TIF complement each other so as to cause $k_H/k_D$ to decrease, thus producing the familiar Westheimer maximum.[8] But as proton motion becomes relatively more pronounced in the anti-reaction co-ordinate modes and less pronounced in the reaction co-ordinate mode, it follows that the motions of R are affected in the opposite sense, as are the isotopic dependences of frequencies. Hence TDF and TIF will be larger for unsymmetrical TSs as far as isotopic substitution in R is concerned.

Thus the minimum in the [1 910] ⟶ [9 110] series can be logically understood. Now let us partially sever the $C_\alpha \cdots Cl$ bond in the fragment R at the TS. The same basic considerations will apply, even though more off-diagonal force constants are generally needed to generate a realistic reaction co-ordinate,[1] but so long as the bond order of the partial $C_\alpha \cdots Cl$ bond remains constant, motions of the entire group, and thus the isotopic sensitivity of frequencies, are coupled to proton motions and thus to the degree of proton transfer. It must be emphasized that the off-diagonal force constants are important in determining both the real and imaginary frequencies, as formulae for frequencies of linear proton transfer transition states readily show.[9] Thus on setting $n_4$ to a transition state value less than that in the initial state, a primary heavy atom KIE accrues, but by the principle of complementarity it is responsive to the degree of transfer of the light proton, and it should therefore pass through a minimum at the point where $k_H/k_D$ is maximal. Other results in Table 1 show that this is indeed the case, and in Table 2 we show how TDF and TIF largely complement each other in a typical row so as to produce a minimum in $k_{35}/k_{37}$.

The complementarity principle is described in detail since it is simple, has hitherto escaped explicit consideration, and will dominate discussion of other KIEs. The trend in $k_{35}/k_{37}$ is not large, but its persistence emphasizes the necessity for measuring more than a single isotope effect when probing TS structure.[10]

It is now appropriate to show that the complementarity principle in the present context arises out of the Redlich–Teller product rule, which for any TS involving light and heavy atoms (1) and (2) may be expressed by equation (3), where $MMI^{\ddagger}$ is the mass-moment-of-inertia term for the TS, $m_1$ and $m_2$ are the respective

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

[9] H. S. Johnston, ' Gas Phase Reaction Rate Theory,' Ronald Press, New York, 1966, p. 339.

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

masses of the light and heavy isotopes, and the frequencies $\nu_i^{\ddagger}$ are real TS frequencies. In going across a row in Table 1, IS structures, and therefore IS values of

$$\left(\frac{\nu_1{}^{\ddagger}{}_L}{\nu_2{}^{\ddagger}{}_L}\right) \prod_i^{3N-7} \left[\frac{\nu_i{}^{\ddagger}(1)}{\nu_i{}^{\ddagger}(2)}\right] = \left(\frac{m_2}{m_1}\right)^{\frac{3}{2}} \times MMI^{\ddagger} \quad (3)$$

*MMI*, *VP*, *EXC*, and *ZPE*, are unaltered. TS structures are altered by changing the position of a proton of insignificant mass.

Thus *MMI*, and hence the right hand side of equation (3) should be almost constant along such a series of TS structures. It then follows that, for instance, an increase in the isotopic sensitivity of the reaction co-ordinate vibrational mode $(\nu_1{}^{\ddagger}{}_L/\nu_2{}^{\ddagger}{}_L)$ will be compensated by a decrease in the isotopic sensitivity of real TS modes, $\prod_i^{3N-7} [\nu_i{}^{\ddagger}(1)/\nu_i{}^{\ddagger}(2)]$. As the latter term becomes minimal, the influence of the isotopic sensitivity of the (constant) IS real vibrational modes will dominate the *VP*, *EXC*, and *ZPE* terms that comprise the TDF, so that the latter will be maximal, and so will complement the maximal value of TIF.

TABLE 2

Contributions to chlorine isotope effects

| Transition state | *VP* | *EXC* | *ZPE* | *VP·EXC·ZPE* | $\nu^{\ddagger}{}_{L(35)}/\nu^{\ddagger}{}_{L(37)}$ | $k_{35}/k_{37}$ [a] |
|---|---|---|---|---|---|---|
| [199] | 1.003 097 | 0.997 024 | 1.000 546 | 1.000 657<br>(65.73%) [b] | 1.000 343<br>(34.27%) [b] | 1.001 00 |
| [379] | 1.003 104 | 0.997 173 | 1.000 414 | 1.000 682<br>(97.15%) [b] | 1.000 020<br>(2.85%) [b] | 1.000 70 |
| [559] | 1.003 022 | 0.997 292 | 1.000 348 | 1.000 654<br>(94.74%) [b] | 1.000 036<br>(5.26%) [b] | 1.000 69 |
| [739] | 1.002 792 | 0.997 410 | 1.000 390 | 1.000 585<br>(63.93%) [b] | 1.000 330<br>(36.07%) [b] | 1.000 91 |
| [919] | 1.002 232 | 0.997 341 | 1.001 110 | 1.000 676<br>(35.94%) [b] | 1.001 205<br>(64.06%) [b] | 1.001 88 |

[a] Not corrected for tunnelling. Reaction co-ordinate (A). [b] Percentage contribution of this term to the total isotope effect.

We now return to other aspects of results in Table 1. Reaction co-ordinate (E) may be intuitively rejected in that anomalously large chlorine KIEs are obtained even in the $n_4 = 1.0$ series. Use of it also generates low $k_H/k_D$ values.[1] Thus a further source of uncertainty is revealed. While it is not an absolute necessity,[1] it may be more appropriate to construct variable reaction co-ordinates so that, for instance, TSs with barely broken $C_{\alpha} \cdots Cl$ bonds would have a reaction co-ordinate designed to minimize heavy atom motion and *vice-versa*. However, this would introduce a further dimension of arbitrariness into the model, and in the absence of accurate potential energy surfaces for such reactions we feel safer using a constant reaction co-ordinate model within each set.

Secondary chlorine KIEs for loss of $^{35}Cl$ from $Ar_2CH\cdot CH^{35}Cl_2$ *vs.* loss of $^{35}Cl$ from $Ar_2CH\cdot CH^{35}Cl^{37}Cl$ have been calculated. Excluding reaction co-ordinate (E) results, they are negligibly small, being no greater than 1.000 1. As demanded by the complementarity principle, they pass through a minimum as the degree of proton transfer increases at constant $n_4$, but the minimum is even shallower. The point of these calculations was to check the veracity of the assumption [6] that primary intermolecular and intramolecular chlorine KIEs are about equal, since the two are interrelated *via* the secondary KIE as shown in equation (4). The trends

$$k_{35}/k_{37}\ (\text{intra.}) = [k_{35}/k_{37}(\text{inter.})]/[k_{35}/k_{37}\ (\text{sec.})] \quad (4)$$

shown in Table 1 are without exception evident in the intramolecular KIEs.

$C_{\alpha}$ *Isotope Effects.*—Carbon-14 KIEs, $k_{12}/k_{14}$ for $C_{\alpha}$, are presented in Table 3. No direct comparison with experimental results is possible at the moment, and only a few scattered literature examples of carbon KIEs in *E*2 reactions are available.[11] Some general conclusions can be drawn, however.

Our $k_{12}/k_{14}$ values expressed as percentages are roughly twice as large as Saunders' calculated values of $k_{12}/k_{13}$,[3] but are lower than almost any that have been evaluated experimentally.[11] The KIEs decrease slightly with increasing $C_{\alpha} \cdots Cl$ bond rupture at a constant degree of proton transfer. Barrier curvature has little effect. An increase in the degree of proton transfer at constant $n_4$ has a variable effect on $k_{12}/k_{14}$ but for reaction co-ordinate (A), in which a little heavy atom motion is permitted, a low maximum in the KIE is seen. This would be comprehensible if the bonding changes at $C_{\alpha}$ were viewed as $S_N2$ displacement of chloride by $C_{\beta}$,[7,12] but this maximum arises solely as a result of the tunnelling correction.

TABLE 3

Carbon isotope effects ($k_{12}/k_{14}$) for $C_{\alpha}$ isotopic substitution at 25 °C

Reaction co-ordinate (A)

| | | | | |
|---|---|---|---|---|
| [1 910]<br>1.021 0 | [3 710]<br>1.029 0 | [5 510]<br>1.023 2 | [7 310]<br>1.015 2 | [9 110]<br>1.012 9 |
| [199]<br>1.017 2 | [379]<br>1.025 3 | [559]<br>1.019 6 | [739]<br>1.011 6 | [919]<br>1.009 4 |
| | [377]<br>1.020 0 | [557]<br>1.014 6 | [737]<br>1.006 7 | [917]<br>1.004 8 |
| | | [555]<br>1.012 7 | [735]<br>1.005 2 | [915]<br>1.003 5 |

Saunders, however, reports an *increase* in $C_{\alpha}$ KIE as $C_{\alpha} \cdots X$ rupture increases at a constant degree of proton

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[11] W. H. Saunders and A. F. Cockerill, 'Elimination Mechanisms,' Wiley–Interscience, New York, 1973, p. 88.

[12] H. Yamataka and H. Ando, *Tetrahedron Letters*, 1975, 1059.

transfer. This is not a tunnel-related effect.[3] We may attribute part of the discrepancy to the fact that we have varied the bond angles around $C_\alpha$ and $C_\beta$ so as to mimic hybridization changes, whereas Saunders has not done so. Whether or not this procedure is followed is of little consequence as far as $k_H/k_D$ and $k_{35}/k_{37}$ are concerned. The most important factor, however, seems to be the variability of $n_3$, the $C_\beta \overset{\cdot\,\cdot}{-} C_\alpha$ bond order. When Saunders employs varying $n_3$ values that are compatible with $n_2$ and $n_4$, trends closer in nature to those observed here are obtained.[3b]

Again series [1 910] ⟶ [9 110] is illustrative. In the absence of the tunnel correction, the $C_\alpha$ KIEs pass through a minimum centred at [3 710]. The corresponding trend in the TIF term is similar to that already described for the primary chlorine isotope effects, except that a maximum is reached at [7 310]. The maximum and minimum coincide with maximal and minimal relative motion of $C_\beta$ relative to $C_\alpha$ in the reaction co-ordinate, as found by inspection of the appropriate eigenvectors. The operation of the complementarity principle again carries over into the $n_4 < 1.0$ series for uncorrected isotope effects.

Inverse isotope effects are predicted for several transition state models in reaction co-ordinates (B)—(D), in which heavy atom motion is almost non-existent. These will be discussed along with inverse $C_\beta$ isotope effects in the following section.

$C_\beta$ *Isotope Effects*.—Results for reaction co-ordinate (A) alone are displayed in Table 4. Inverse carbon KIEs abound for all other reaction co-ordinates save (E).

TABLE 4

Carbon isotope effects ($k_{12}/k_{14}$) for $C_\beta$ isotopic substitution [a]

| | | | | |
|---|---|---|---|---|
| [1 910] | [3 710] | [5 510] | [7 310] | [9 110] |
| 1.007 3 | 1.020 1 | 1.053 4 | 1.069 4 | 1.065 8 |
| [199] | [379] | [559] | [739] | [919] |
| 0.998 6 | 1.010 9 | 1.043 9 | 1.060 4 | 1.057 5 |
| | [377] | [557] | [737] | [917] |
| | 0.994 0 | 1.026 4 | 1.044 4 | 1.043 0 |
| | | [555] | [735] | [915] |
| | | 1.010 9 | 1.031 1 | 1.031 1 |

[a] Reaction co-ordinate (A), corrected for tunnelling, at 25 °C. Bond angles systematically varied

The results roughly accord with those of Saunders[3] when the degree of proton transfer at constant $n_4$ is considered. The $C_\beta$ KIE increases monotonically with the extent of proton transfer. However, when the bond order of the remote $C_\alpha \cdots Cl$ bond is decreased at a constant degree of proton transfer (reading down the column), we predict a decrease in the KIE, whereas Saunders calculates essentially no change. The difference can again be partly ascribed to the different treatments accorded to $n_3$; in our model this is coupled with $n_4$ and so remote bonding changes do affect the bonding situation at $C_\beta$ even though $n_1$ and $n_2$ are held constant. Saunders later allowed $n_3$ to be coupled,[3b] but a fair comparison of our results with his is not possible since he permitted $n_2$ and $n_4$ to increase in concert as well.

One important difference requires detailed examination however. Saunders typically computes minimal (and inverse) $C_\beta$ KIEs when $n_1 = 0.3$, $n_2 = 0.7$ (about the position for the $k_H/k_D$ maximum) across a proton transfer series at constant $n_4$, although in several of his models the inverse KIE is rendered normal by the tunnel correction.[3] This trend persists whether or not $n_3$ is held constant.[3a,b] We do not observe this in any of our calculations, and $k_{12}/k_{14}$ increases steadily as the extent of proton transfer increases.

We first surmized that the behavioural difference might result from the fact that bond angles about $C_\alpha$ and $C_\beta$ are systematically varied in our calculations but not in Saunders' set, but calculations based on an all-tetrahedral geometry for both IS and TS (Table 5) show that this is not so. In Table 5 we have selected the [1 910] ⟶ [9 110] proton transfer series as an example so that $n_3$ is constant and equal to 1.00.

TABLE 5

Carbon isotope effects ($k_{12}/k_{14}$) for $C_\beta$ isotopic substitution in an all-tetrahedral DDD proton-transfer model [a]

| | [1 910] | [3 710] | [5 510] | [7 310] | [9 110] |
|---|---|---|---|---|---|
| $k_{12}/k_{14}$ | 0.996 4 | 0.999 2 | 1.019 7 | 1.046 0 | 1.057 4 |
| TIF | 1.001 07 | 1.000 45 | 1.004 15 | 1.004 98 | 1.001 13 |
| TDF | 0.995 32 | 0.998 79 | 1.015 47 | 1.040 85 | 1.056 19 |

[a] Reaction co-ordinate (D), 25 °C, no tunnel correction.

We now believe that the difference is a consequence of the differing masses of the atoms bonded to $C_\beta$. We employ two partial phenyl groups (six carbon atoms in all), a hydrogen atom, and a $CHCl_2$ group, whereas in Saunders' model, $C_\beta$ is bonded to three hydrogen atoms and a $CH_2Cl$ group, and so is a lighter model overall. To confirm this view we have performed $C_\beta$ KIE calculations on a lighter proton-transfer model [equation (5)], employing all-tetrahedral geometry. Results are displayed in Table 6, wherein a TS code of [73] for instance refers to a TS having $n_1 = 0.7$, $n_2 = 0.3$. The Saunders minimum is now evident at [37]. What then is the molecular nature of this difference in behaviour between the heavy (DDD) and light ($CH_3$) models?

$$C{-}C_\beta H_2{-}H + O{-}C \longrightarrow C{-}C_\beta H_2 \overset{n_2}{\cdots} H \overset{n_1}{\cdots} O{-}C \qquad (5)$$

In Tables 5 and 6 we show the respective TIF and TDF terms that comprise the KIE. In the DDD case, TIF passes through a minimum, whereas TDF steadily increases. The latter therefore dominates the KIE trend. In the $CH_3$ case the TIF term (now larger than with DDD) also passes through a minimum, but now dominates the KIE as the TDF, again increasing, does not reflect the different KIE trend. Since the TIF is the

TABLE 6

Carbon isotope effects ($k_{12}/k_{14}$) for $C_\beta$ isotopic substitution in an all-tetrahedral $C{-}CH_3$ proton-transfer model [a]

| | [19] | [37] | [55] | [73] | [91] |
|---|---|---|---|---|---|
| $k_{12}/k_{14}$ | 1.011 4 | 0.995 8 | 1.018 8 | 1.068 4 | 1.087 3 |
| TIF | 1.018 77 | 1.000 82 | 1.008 26 | 1.027 09 | 1.023 62 |
| TDF | 0.992 75 | 0.995 03 | 1.010 43 | 1.040 21 | 1.062 19 |

[a] Reaction co-ordinate (D), 25 °C, no tunnel correction.

ratio of the isotopic reduced (effective) masses for the reaction co-ordinate, it will be relatively larger the lighter are the atoms bonded to $C_\beta$ as long as these atoms are involved to some extent in the reaction co-ordinate motion. We can again use the product rule or the complementarity principle to rationalize the KIE behaviour. In comparing a typical heavy and light (in the chemical, not the isotopic sense) TS in terms of equation (3), it is clear that $MMI^\ddagger$ for the TS increases as the model becomes heavier ($MMI^\ddagger \leqslant 1$) so that the left hand side of equation (3) must also increase. It is seen from Tables 5 and 6 that the TIF decreases as the model becomes heavier, so the isotopic sensitivity of real frequencies, $\prod_i^{3N-7} \nu_i^\ddagger(1)/\nu_i^\ddagger(2)$ must increase on going to the heavier model. It can then be easily shown that, for a real IS frequency decreasing on proceeding to the TS (and by equal amounts for light and heavy models) the $ZPE$ term for the heavy model will exceed that for the light model. The TDF term is thus larger for the heavy model, and as TIF is smaller, the former dominates the KIE trend and no minimum is seen. The converse applies for the light model and the minimum in the larger TIF term is passed on to the KIE.

Tables 5 and 6 reveal that the normal order, TDF (heavy) > TDF (light), is reversed when the proton has almost completely departed from $C_\beta$, *i.e.* in [9 110] and [91]. In this case the real symmetrical stretch in the TS ($O \cdots H \cdots C_\beta$) will have such a low frequency as to lose almost all its isotopic sensitivity as far as $C_\beta$ is concerned. It is then possible that the (non-reacting) $H{-}C_\beta$ bonds in the light model will have sufficient isotopic sensitivity to outweigh the contributions of the lower frequency modes involving the non-reacting $C{-}C_\beta$ bonds of the heavier model.

The conclusion is then that values of and trends in $C_\beta$ KIEs in proton transfer and $E2$ reactions are crucially dependent on the overall masses of atoms and groups bonded to $C_\beta$. The only relevant experimental data have been provided by Saunders and his co-workers;[13] they find that for eliminations of $PhCH_2{\cdot}CH_2X$ induced by $^-OH$ in $H_2O{-}Me_2SO$, $k_{12}/k_{13}$ increases for $X = SMe_2^+$ as the water content of the solvent increases (a base-weakening effect), whereas for $X = NMe_3^+$ $k_{12}/k_{13}$ could possibly pass through a minimum before increasing. The solvent change is predicted to induce greater degrees of proton transfer,[2,14] together with little change in the degree of $C_\alpha \cdots X$ rupture if the TSs are basically carbanion-like.[2] We predict an increase in the $C_\beta$ KIE in such circumstances, in essential agreement with experiment. The $PhCH_2{\cdot}CH_2{\cdot}SMe_2^+$ results at least are therefore consistent with ' heavy-residue ' behaviour.

The anomalous inverse $C_\alpha$ and $C_\beta$ KIEs for reaction co-ordinates (B)—(D) are now considered. These arise from inverse TDF terms, since TIF must always be greater than unity, being a classical term. Examination of the appropriate reaction co-ordinate eigenvectors for selected representative examples reveals that for (B)—(D), reaction co-ordinate motion involves movement of $C_\beta$ *away* from $C_\alpha$, which is opposite to the motion required to produce an olefinic product. These reaction co-ordinate formulations are thus invalid, and the influence of off-diagonal force constants on the TDF is again illustrated. This matter has recently been stressed by Buddenbaum and Shiner in another context.[15] The cautionary point is emphasized by the fact that the spurious reaction co-ordinate models nonetheless yield apparently normal hydrogen[1] and chlorine KIEs.

*Leaving Group Solvation.*—It has been suggested that partial hydrogen bonding by hydroxylic solvent molecules to an incipient anionic leaving group in a transition state may influence isotope effects.[16-18] The application of this perturbation to the present system has been briefly described,[1] and full details are now provided.

In simulating the effect of solvation, three H–O moieties are tetrahedrally arranged about the departing chlorine. The H–O distance is 0.957 Å and the $Cl \cdots H$ distance is adjusted by Pauling's rule. The H–O stretching mode is given the normal force constant[1] of 770 N $m^{-1}$, and the normal Cl–H force constant of 516 N $m^{-1}$ is multiplied by either 0.015 or 0.04, the assumed $Cl \cdots H$ bond orders. An $H \cdots Cl{-}C_\alpha$ bending force constant of $60 \times 10^{20}$ N m $rad^{-2}$ and a $Cl \cdots H{-}O$ linear bending force constant of $33 \times 10^{20}$ N m $rad^{-2}$ are employed, and are related to the actual transition state force constants, $F$, *via* equation (4), in

$$F = F^\circ(n_i n_j)^{\frac{1}{2}}\, g_\alpha \qquad (4)$$

which the terms are as described earlier.[1] The square root dependence of the bond order product was employed so as to give non-negligible values of $F$ for the very small values of $n_i$ used (0.015 or 0.04), with $n_j = 1.0$.

Calculations were performed only for TS [555] since such solvation should assume greatest importance for well broken $C_\alpha \cdots X$ bonds. Results are shown in Table 7 where results computed on the basis of no solv-

TABLE 7

Comparison of isotope effects for non-solvated (NS) and solvated (S) leaving groups [a]

| | NS | S($n_i = 0.015$) | S($n_i = 0.04$) |
|---|---|---|---|
| $\beta$-$k_H/k_D$ | 6.687 | 6.687 | 6.687 |
| $\alpha$-$k_{35}/k_{37}$ (inter.) | 1.003 94 | 1.003 06 | 1.001 85 |
| $\alpha$-$k_{35}/k_{37}$ (intra.) | 1.004 03 | 1.003 17 | 1.001 97 |
| $\alpha$-$k_{12}/k_{14}$ | 1.012 7 | 1.012 0 | 1.011 6 |
| $\beta$-$k_{12}/k_{14}$ | 1.010 9 | 1.010 8 | 1.010 8 |
| $\alpha$-$k_H/k_D$ (sec.) | 1.067 | 1.058 | 1.058 |

[a] At 25 °C, corrected for tunnelling except for $\beta$-$k_H/k_D$. Reaction co-ordinate (A); $n_i$ is $Cl \cdots H$ bond order.

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ation (NS) and solvation are compared. The results may be summarized by stating that only the primary intermolecular and intramolecular primary chlorine KIEs are sensibly affected by solvation. This result is also obtained for various models pertaining to $Bu^tCl$ solvolysis,[18] which is the reason why solvation effects have not been further explored here.

Solvation is thought to decrease the primary intermolecular chlorine KIE in the following ways. First, TIF(S) $<$ TIF(NS), which is presumably an effective mass effect. Secondly, since $MMI^{\ddagger}(\mathrm{NS}) < MMI^{\ddagger}(\mathrm{S})$, with $MMI^{\ddagger} \leqslant 1$, we have *via* equation (3) that the total isotopic sensitivity of transition state frequencies is, as discussed earlier in the $C_{\beta}$ section, greater for the heavier solvated model than for the lighter non-solvated model. That is, additional isotopically sensitive bonds are present in the former. However, their contribution is not counteracted by IS frequencies since the IS is the same for both solvated and non-solvated models, and hence TDF(S) $<$ TDF(NS). Thus on both grounds, KIE(S) $<$ KIE(NS).

*Transition State Mapping.*—The ultimate aim of isotope effect calculations is to match a set of experimental isotope effects pertaining to as many atoms as possible with those predicted by a particular structural and vibrational TS model in order to ' solve ' the structure of the transition state.[10] In the present case this is an unattainable goal since there are many more approximations and arbitrary adjustments used in setting up the force fields than there are atoms whose isotope effects can be practically measured. However, it is a goal worth pursuing for the reason that understanding of the way in which isotope effects respond to variations in TS structure, within the framework of a given force field, is needed, even though absolute structural solutions may be doubtful at present.

To date we have measured primary β-hydrogen and intramolecular primary chlorine isotope effects, and this does not constitute a wide enough range for reasonably certain assignment of TS structures. Furthermore, the $k_H/k_D$ pattern in NaOMe–MeOH is complicated by what could be regarded as a substantial tunnel correction.[4,5] Our calculations based on the Bell tunnelling model do yield isotope effects within the experimentally observed range,[1] but the calculated temperature dependence does not accord with that observed. For this reason, matching experimental and theoretical $k_H/k_D$ values is at present impossible.

This leaves a comparison of experimental and theoretical chlorine isotope effects to be considered. All we can state at this stage is that the theoretical results with $1 \geqslant n_4 \geqslant 0.5$ span the range of values experimentally observed.[6] The experimental results were discussed on the basis of a less than half-broken $C_{\alpha} \cdots Cl$ bond, and this appears to be verified by the calculations. Moreover, the results are intelligible in terms of empirical $E2$ structural theories.[2,14]

Experimental isotope effects using $Bu^tOK$–$Bu^tOH$ as the medium do not appear to be complicated by tunnelling.[4,5] In Table 8, we compare experimental hydrogen and chlorine isotope effects with those based on the indicated TS models [reaction co-ordinate (A)]. The numerical agreement is impressive, but, for reasons given above, may yet be illusory. However, the shift in transition state structure from [377] to [288] as $C_{\beta}$ substituents become more powerful electron attractors is in accordance with empirical $E2$ TS structural rules,[2,16] and this must lend some credence to the agreement. It is noteworthy that the apparently successful matching of KIEs is achieved using the non-solvational model; it is unlikely in terms of our present solvational model that the addition of solvent would seriously affect KIE values when $n_4$ is in the 0.7—0.8 range.

TABLE 8

Experimental and calculated [a] isotope effects for dehydrochlorination of $(p\text{-}ClC_6H_4)_2CH{\cdot}CHCl_2$ and $Ph_2CH{\cdot}CHCl_2$ by $Bu^tOK$–$Bu^tOH$

| Isotopes | $T$/°C | Exptl. KIE | Calc. KIE [a] | TS [b] |
|---|---|---|---|---|
| | | (i) $(p\text{-}ClC_6H_4)_2CH{\cdot}CHCl_2$ | | |
| β-H,D | 30 | 4.9 | 4.49 [c] | [288] |
| α-$^{35}Cl$,$^{37}Cl$ | 30 | 1.001 40 | 1.001 60 [c] | [288] |
| | | (ii) $Ph_2CH{\cdot}CHCl_2$ | | |
| β-H,D | 30 | 6.1 | 6.19 [c] | [377] |
| β-H,D | 45 | 5.5 | 5.42 [c] | [377] |
| α-$^{35}Cl$,$^{37}Cl$ | 30 | 1.002 00 | 1.002 21 [c] | [377] |

[a] Calculated from transition state model in TS column. [b] No explicit calculations were performed for [288] but isotope effects can be interpolated. [c] Interpolated from results at 25 and 50 °C assuming a linear relationship between log(KIE) and $1/T$. Not corrected for tunnelling.

*Conclusion.*—In the final brief section of this paper, we have taken the first steps towards the ultimate aim of KIE model calculations—the understanding of TS structure, and the response of structure to changes in molecular and environmental variables. It is a little unfortunate that in this and the preceding theoretical paper [1] we have tended to emphasize differences between our calculated KIEs and those of Saunders.[3] What needs to be emphasized now is the fact that despite differences in the basic molecular systems, geometries, and force fields, most KIEs and KIE trends are remarkably similar in the two studies, which are therefore in no way competitive. The differences that have been noted thus serve as pointers as to where short-cuts in KIE calculations may or may not be permitted.

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