Model Calculations of Hydrogen–Deuterium Isotope Effects for *E*2 and *E*1cB Dehydrochlorinations of 1,1-Diaryl-2,2-dichlorethanes

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A 14-atom transition-state model is employed as the basis for computations of primary β-deuterium and secondary α-deuterium isotope effects for the dehydrochlorination of the substrates $\mathrm{Ar_2CH{\cdot}CHCl_2}$ by alkoxide bases. The structure of the transition state is systematically altered by varying the bond orders of $\mathrm{O \cdots H}$, $\mathrm{H \cdots C_\beta}$, $\mathrm{C_\beta \overset{\cdots}{-} C_\beta}$ and $\mathrm{C_\alpha \cdots Cl}$, with a progressive change in the angular geometry about $\mathrm{C_\alpha}$ and $\mathrm{C_\beta}$ from tetrahedral to trigonal and proportional to the degree of $\mathrm{C_\alpha \overset{\cdots}{-} C_\beta}$ double bond character. These changes are translated into force constant changes by means of empirical relations involving bond orders, bond angles, and the associated force constants. The results of changing the way in which the imaginary reaction co-ordinate vibration is formulated are also investigated. Best agreement between experimental values of primary $k_\mathrm{H}/k_\mathrm{D}$ isotope effects and computed isotope effects is obtained when proton transfer is allowed to dominate the reaction co-ordinate motion, with the reacting heavy atoms remaining relatively motionless.

COMPUTER simulations have confirmed that kinetic isotope effects are a function of changes in bonding at the isotopic atom in the transition state, subject to modification by the choice of reaction co-ordinate vibration.[1-3] Comparison of calculated isotope effects with experimentally determined values, especially when employing labelling at several successive positions,[4] affords a critical test of a model of transition structure and its assumed response, in terms of bonding changes, to alterations in substituent and environmental parameters.

Bimolecular β-elimination (*E*2) reactions in solution have been extensively investigated experimentally by means of deuterium isotope effect measurements, supplemented by a small number of heavy atom isotope effect measurements, mostly involving $^{14}\mathrm{N}/^{15}\mathrm{N}$ leaving group isotope effects.[5-8] Several approaches to theoretical calculations of both deuterium and heavy atom isotope effects have been put forward in recent years.[9-11] However, only in the work of Saunders [9,10] is the existence of a spectrum of *E*2 transition states [12,13] recognized, with isotope effects being calculated with respect to variations in transition state structure. Saunders has investigated the model reactions of $^-\mathrm{OH}$ with $\mathrm{EtSMe_2^+}$ (β-deuterium and sulphur-34 isotope effects) [9] and those of $^-\mathrm{OH}$ with EtX, with $\mathrm{X = SMe_2^+, NMe_3^+}$, Cl, or Br (primary β-deuterium, secondary α- and β-deuterium, primary α- and β-carbon-13, and leaving group effects).[10] Valuable guidelines as to the relationship of isotope effects to transition state structure are contained in these papers, but no comparison of calculated isotope effects with experimental values was attempted, since no isotope effects have been measured for reactions of EtX with $^-\mathrm{OH}$ in $\mathrm{H_2O}$ (although some reports pertain to alcoholic [7b,14] and other [15] media). Furthermore, ethyl

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bromide yields only 1% olefin when treated with EtO^- in EtOH [16] and so isotope effect measurements for $E2$ reactions of it, and ethyl chloride, would not be a practical proposition.

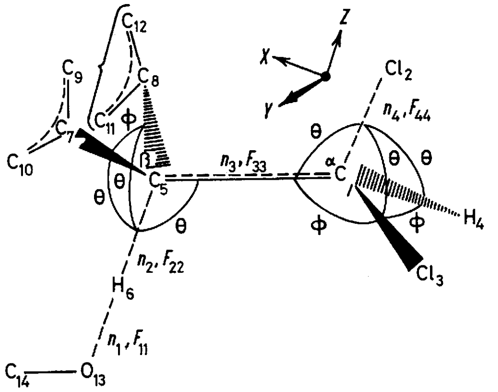
Primary deuterium isotope effects for the $E2$ dehydrochlorination of 1,1-diaryl-2,2-dichloroethanes by MeO^- in MeOH [17] and Bu^tO^- in Bu^tOH [17,18] [equation (1)] have been measured and discussed in terms of the

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

variable transition state theory. It was desirable to perform isotope effect calculations, using models based on this system, in order to evaluate and interpret the experimental isotope effect trends by comparison with the calculated trends. This paper reports the results for primary β- and secondary α-deuterium isotope effects; a subsequent paper describes the heavy atom isotope effects.

CALCULATIONS

Geometric Model.—The general transition state model is shown in the Figure. The Stern–Wolfsberg cut-off procedure [1a,c] was applied to the alkoxide base, in which all atoms except the oxygen and the α-carbon atom were omitted. Extension of the cut-off procedure for aromatic systems [3,19] requires retention of only the phenyl C-1 and the two adjacent *ortho*-carbon atoms as an appropriate cut-off model of the aryl ring system (see Figure). The model contains a pseudo-plane of symmetry (a true plane of symmetry would require identity of atoms 3 and 4) containing atoms 1, 2, 5, 6, 13, and 14; the aryl carbon atoms lie in the planes defined by atoms 7, 5, and 6, and 8, 5, and 6, respectively. This corresponds to antisymmetric rotation of the rings away from coplanarity; in the reactant a rotation of 60° is implied, in accordance with comparable departures from coplanarity determined experimentally for structures of related molecules.[20]



Tetrahedral geometry at the α- and β-carbon atoms (C-1 and C-5, respectively) and standard bond lengths,[21] r^0, for all bonds were assumed for the reactant. In the transition state model, bond lengths, r, for reacting bonds 1—4 (whose bond orders n_{1-4} were different from those in the reactant) were adjusted by the program by a revised [19] version of Pauling's expression [22] [equation (2)]. The angles at the α-

$$r = r^0 - 0.30 \ln n \qquad (2)$$

and β-carbon atoms were adjusted in the transition state model so as to simulate a change toward trigonal geometry ($109.5° > \theta > 90.0°$), consistent with the expected hybridization changes. This was accomplished by changing θ in proportion to the degree of double bond formation (see Table 1); since the $C_\alpha \cdots Cl$ bond was never more than half ruptured, the geometry change induced at C_β was never very large, which is consistent with experimental studies which suggest that the hybridization of C_β at the transition state is close to sp^3, even when it is distinctly carbanionic.[17] Bond lengths and angles pertaining to other bonds remained constant. Primary deuterium isotope effects were largely insensitive to tetrahedral *vs.* trigonal geometry (and the associated force constant changes), as has been found by Saunders,[10] but secondary k_H/k_D was crucially affected. The base was not included in the reactant model,[10] consistent with the assumption of independent reactant species inherent in the statistical thermodynamic treatment of isotope effects.[2] The geometry of each model was most conveniently specified in terms of bond lengths and bond angles, which the program converted into Cartesian coordinates of the atoms; the relevant bond distances and angles are summarized in Table 1.

Force Constants and the Variable Transition State.—Initial state stretching force constants (F_{ii}^0) for each reacting bond 1—4 were modified for transition state models according to equation (3), where n_i is the order of the bond in questions.[23] The transition state stretching force

$$F_{ii} = n_i F_{ii}^0 \qquad (3)$$

constants for the non-reacting C(1)–H(4), C(1)–Cl(3), and C(5)–C_{Ar} bonds were increased from values appropriate to sp^3-hybridized carbon towards those appropriate for sp^2-hybridized carbon as n_4 was decreased from 1.0 to 0.5. This force constant change mimics the approach of C_α and C_β towards trigonal geometry.

Angle bending force constants pertaining to bonds involving atoms undergoing covalency change were governed by the relationship in equation (4). Here, n_i and

$$F_\alpha = g_\alpha n_i n_j F_\alpha^0 \qquad (4)$$

n_j are the bond orders of the bonds involved in the bending mode. This is a modification [19] of a procedure suggested by Johnston.[23] The term g_α is an angle factor, defined by equation (5), in which α is the bond angle. The factor g_α

$$g_\alpha = 1.39 + 1.17 \cos \alpha \qquad (5)$$

has a value of unity when $\alpha = 109.47°$ and decreases as α increases. In this way we simulate the loosening of bending frequencies as the hybridization of both C_α and C_β changes from sp^3 towards sp^2 as n_4 decreases, but in a way which is different from that used by Saunders.[10]

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Torsional and out-of-plane bending force constants were maintained at their reactant values for all models. The additional torsion in the transition state involving the C–O $\cdots$ H $\cdots$ C $\overset{\cdots}{-}$ C moiety was arbitrarily assigned a reduced force constant whose value was found to have little effect on k_H/k_D. The bending force constant associated with the pair of linear bending vibrations for the O $\cdots$ H $\cdots$ C_β moiety was varied by equation (4), where the force constant $F^0{}_{LIBE} = g_{180}F^0{}_{180}$ was assigned a value similar to that employed by Saunders;[10] inadvertent omission of the variation in the linear bending force constants in preliminary calculations appeared to have little effect on the trend in computed isotope effects.

TABLE 1

Structural parameters[a] and force constants[b]

Co-ordinate[c] No. (i)	Motion	Atoms involved[d]	Reactant[e] r_i^0	Reactant[e] F_{ii}^0	Transition state[f] $(r_i^0 - r_i)/0.30$	Transition state[f] F_{ii}
1	$C_\alpha \cdots Cl$ stretch	1, 2	1.760	320	$\ln n_4$	$320n_4$
2	$C_\beta \overset{\cdots}{-} C_\alpha$ stretch	1, 5	1.537	450	$\ln n_3$	$450n_3$
3	$C_\beta \cdots H$ stretch	5, 6	1.094	500	$\ln n_2$	$500n_2$
4	$H \cdots O$ stretch	6, 13	(0.958)	(780)	$\ln n_1$	$70n_1$
5	C_α–Cl stretch	1, 3	1.760	320	0.0	$333—13n_4$
6	C_α–H stretch	1, 4	1.094	500	0.0	$520—20n_4$
7	C_β–C_{Ar} stretch	5,7; 5, 8	1.507	500	0.0	$520—20n_4$
8	$C_{Ar} \overset{\cdots}{-} C_{Ar}$ stretch	7, 9; 7, 10; 8, 11; 8, 12	1.394	700	0.0	700
9	C–O stretch	13, 14	(1.430)	(530)	0.0	530
			Angle (°)		Angle (°)[g]	
10	Cl–$C_\alpha \cdots$ Cl bend	3, 1, 2	109.5	55	$\theta = 90 + 19.5n_4$	$53n_4g_\theta$
11	H–$C_\alpha \cdots$ Cl bend	4, 1, 2	109.5	60	θ	$60n_4g_\theta$
12	$C_\beta \overset{\cdots}{-} C_\alpha \cdots$ Cl bend	5, 1, 2	109.5	100	θ	$100n_3n_4g_\theta$
13	$C_\alpha \overset{\cdots}{-} C_\beta \cdots$ H bend	1, 5, 6	109.5	65	θ	$65n_2n_3g_\theta$
14	C_{Ar}–$C_\beta \cdots$ H bend	7, 5, 6; 8, 5, 6	109.5	65	θ	$65n_2g_\theta$
15	Cl–C_α–H bend	3, 1, 4	109.5	60	$\theta = \cos^{-1} [1 - (3/2 \sin^2\theta]$	$60g_\theta$
16	Cl–$C_\alpha \overset{\cdots}{-} C_\beta$ bend	3, 1, 5	109.5	100	ϕ	$100n_3g_\phi$
17	H–$C_\alpha \overset{\cdots}{-} C_\beta$ bend	4, 1, 5	109.5	65	ϕ	$65n_3g_\phi$
18	C_{Ar}–C_β–C_{Ar} bend	7, 5, 8	109.5	100	ϕ	$100g_\phi$
19	C_{Ar}–$C_\beta \overset{\cdots}{-} C_\alpha$ bend	7, 5, 1; 8, 5, 1	109.5	100	ϕ	$100n_3g_\phi$
20	$C_{Ar} \overset{\cdots}{-} C_{Ar}$–$C_\beta$ bend	9, 7, 5; 10, 7, 5; 11, 8, 5; 12, 8, 5	120	100	120	100
21	C_{Ar}–C_{Ar}–C_{Ar} bend	9, 7, 10; 11, 8, 12	120	100	120	100
22	C–O $\cdots$ H bend	14, 13, 6	(109.5)	(60)	109.5	$60n_1$
23	Out-of-plane bend[h] at C-7 and C-8	9, 7, 10, 5; 7 11, 8, 12, 5	0.0	20	0.0	20
24	Linear bending[i] pair about H-6	5, 6, 13	(180)	(33)	180	$33n_1n_2$
25	Torsions about[j] C–C bonds		See text	7.2	See text	7.2
26	Torsion about O $\cdots$ H $\cdots$ C_β		See text		See text	

[a] See ref. 21. [b] Taken from a variety of sources including: (*a*) ref. 29; (*b*) G. Herzberg, 'Molecular Spectra and Molecular Structure, Part II. Infrared and Raman Spectra of Polyatomic Molecules,' Van Nostrand, Princeton, 1945; (*c*) J. H. Schachtschneider and R. G. Snyder, *Spectrochim. Acta*, 1963, **19**, 117; (*d*) a general survey of *J. Mol. Spectroscopy* and *Spectrochim. Acta*, 1960—1973. [c] Solid lines represent bonds remaining intact, dotted lines are reacting bonds. [d] See Figure for numbering. [e] Bond distances in Å (see footnote *g*); stretching force constants in Nm^{-1}; bending force constants in 10^{-20} N m rad^{-2}; 10^2 N m^{-1} = 1 mdyn $Å^{-1}$; 10^{-18} N m rad^{-2} = 1 mdyn Å rad^{-2}. Values in parentheses are for co-ordinates not present in the reactant model, but are accepted values for the type of co-ordinate involved. [f] Bond distances adjusted according to equation (2); force constants adjusted as in text, equations (3)—(5). [g] See Figure. Angle ϕ is related to θ as given, which assures a local 'C_{3v}'-type symmetry about bonds 2 and 4 at all times. [h] Angle between plane of aryl ring and bond joining it to C-5. A value of 0.0 implies coplanarity. [i] The two bending frequencies of the O $\cdots$ H $\cdots$ C_β linear submolecule will not necessarily be doubly degenerate as in CO_2, for example, since the environment experienced by the groups upon bending in any two perpendicular planes will be different in the present case. [j] The torsional force constant usually quoted for ethane [see ref. (d) in footnote *b*] of 2.4 Nm rad^{-2} must be used for all three of the equivalent torsional co-ordinates which can be defined, owing to the local C_{3v} symmetry of each CH_3 group, giving an effective value of 7.2. In general, if symmetry demands that *m* torsional co-ordinates be defined, the appropriate force constant for each in 7.2/*m*.

We have reduced the number of variables by assuming that $n_1 + n_2 = 1.0$ (constant total bonding of the proton) and $n_3 + n_4 = 2.0$ (constant total bonding of C_α).[23] Furthermore, n_4 is restricted to the range 1.0—0.50. If proportional distribution of charge is assumed and delocalization is ignored, the partial negative charges on oxygen, C_β, and Cl in the transition state will be $1 - n_1$, $n_4 - n_2$, and $1 - n_4$, respectively, so that all transition states are 'central' ($n_2 = n_4$), or have β-carbanionic character ($n_4 > n_2$).[12]

The independent parameters of the model are thus the bond orders, n_{1-4}, of the reacting bonds; the geometrical parameters (bond lengths and angles) and force constants associated with these bonds are determined by the empirical relations given in the text and in equations (2)—(5). Details of this bond-order approach to calculating kinetic isotope effects and justification for the empirical relations are given elsewhere.[19]

The present models and input are thus similar in some respects to those used by Saunders[9,10] and significantly different in others. Saunders does not alter the length of reacting bonds, nor appropriate bond angles, in designing transition state models, and merely allows the appropriate force constants to vary (in some cases) so as to mimic bonding and hybridization changes. We allow both the appropriate bond lengths and angles to change as hybridization at C_α and C_β changes. Most important, we allow the stretching force constant of the $\mathrm{C}_\alpha\overset{\cdots}{-}\mathrm{C}_\beta$ bond to vary as the bond order (degree of double bond development) changes with variation in n_2 and n_4. Saunders' model uses a constant value for this force constant over all values of n_2 and n_4, corresponding to *ca.* 50% π-bond formation (n_3 *ca.* 1.5).[10a] This is unrealistic if both n_2 and n_4 are greater than 0.5, since the π-bond cannot be formed to a greater extent than electrons and orbitals are freed by the departure of the proton and leaving group. However, this condition is relaxed by Saunders in a more recent paper.[10b]

Force constants are shown in Table 1.

The Reaction Co-ordinate.—Saunders has discussed the problem of formulating a reaction co-ordinate vibrational mode such that curvature is negative at the barrier and decomposition frequencies are imaginary.[9,10] We employ his method and description. Force constants for coupling of the stretching modes of the reacting bonds in the transition states were obtained from equations (6)—(8). The

$$F_{12} = a_{12}(F_{11}F_{22})^{\frac{1}{2}} \qquad (6)$$

$$F_{23} = a_{23}(F_{22}F_{33})^{\frac{1}{2}} \qquad (7)$$

$$F_{34} = a_{34}(F_{33}F_{44})^{\frac{1}{2}} \qquad (8)$$

relationship amongst the constants a_{ij} is given by equation (9), in which D may be zero (flat barrier) or negative

$$1 - a_{12}^2 - a_{23}^2 - a_{34}^2 - a_{12}^2a_{34}^2 = D \qquad (9)$$

(curved barrier). The relative magnitudes of the constants a_{ij} define the relative motion of the atoms involved in the decomposition vibrational mode; in other words, they are functions of the eigenvectors corresponding to the motions of the pertinent atoms. We have investigated five models for the reaction co-ordinate mode, all of which involve a curved barrier, as follows.

(A) The parameters for this co-ordinate are: $a_{12} = 1.05$, $a_{23} = a_{34} = 0.329\,598$, $D = -0.20$. The lighter proton moves much more than do the heavy atoms.

(B) In this reaction co-ordinate, $a_{12} = 1.1$, $a_{23} = a_{34} = 0.0$, and $D = -0.21$. The barrier curvature is the same as for (A), but the decomposition vibration involves only proton transfer. The heavy atoms move only to preserve the centre of mass in this mode, even though their bonds are modified on proceeding from initial to transition state.

(C) For this reaction co-ordinate, $a_{12} = 1.05$, $a_{23} = a_{34} = 0.0$, and $D = 0.102\,5$. Again only proton motion is involved, but the barrier is flatter than in (B).

(D) Again we employ $a_{23} = a_{34} = 0.0$, with a_{12} calculated from the empirical formula of More O'Ferrall and Kouba.[24] Now D is dependent on the degree of proton transfer at the barrier, as shown in Table 2.

(E) For this reaction co-ordinate, we allow the heavy atoms to move more relative to the proton motion than in the other models, by employing $a_{12} = 0.90$, $a_{23} = a_{34} = 0.572\,478$, and $D = -0.20$. Curvature is thus the same as for (A) and (B).

Tunnel Corrections.—Since several criteria commonly accepted for tunnelling were satisfied in the experimental study,[17,18] the computed rate constants were accordingly corrected. Both the Wigner[25] and simple Bell[26] corrections were employed. The latter is shown in equation (10), in which $u_\mathrm{L}^\ddagger = h\nu_\mathrm{L}^\ddagger/kT$, $\nu_\mathrm{L}^\ddagger$ being the imaginary

$$k_\mathrm{H}/k_\mathrm{D}(\mathrm{corr.}) = k_\mathrm{H}/k_\mathrm{D}(\mathrm{uncorr.})\\ [u_\mathrm{L}^\ddagger{}_{(\mathrm{H})}\sin|u_\mathrm{L}^\ddagger{}_{(\mathrm{D})}/2|]/[u_\mathrm{L}^\ddagger{}_{(\mathrm{D})}\sin|u_\mathrm{L}^\ddagger{}_{(\mathrm{H})}/2|] \qquad (10)$$

frequency of decomposition. In all cases where the correction was significant, the Bell expression was the larger and hence was used for all the results quoted here. It too is possibly an underestimate, but the more realistic expression recently employed by Bell and co-workers[27] cannot be used here as the barrier height is unknown. Calculations based on our computed values of $\nu_\mathrm{L}^\ddagger$ and barrier heights in the 15—20 kcal mol^{-1} range[10b] show that equation (10) is satisfactory, however.

TABLE 2

Parameters used for reaction co-ordinate (D)[a]

n_1[b]	a_{12}	D
0.9	1.008 1	−0.016
0.7	1.044 1	−0.090 1
0.5	1.062 5	−0.129
0.3	1.044 1	−0.090 1
0.1	1.008 1	−0.016

[a] See ref. 24. [b] $n_2 = 1 - n_1$. [c] $a_{12} = [1 + (n_1n_2)^2]$.

Computations.—The program employed was a modified version of a program for vibrational frequency calculations.[28] The input of atomic masses, force constants, and geometries allows calculation of vibrational frequencies through a procedure involving mass-weighted Cartesian co-ordinates, and only a single co-ordinate transformation (from mass-weighted Cartesian to normal co-ordinates in the potential energy matrix) is required. The advantage of the present method over the more widely used Wilson FG matrix procedure[29] is that less computer time and memory are required, thus making calculations for large molecules economically feasible. The resulting frequencies and moments of inertia which are printed out for inspection are then substituted into the primary equation[1,2] (11) for the isotope effect. Application of the Teller–Redlich product rule[30] to equation (11) produces the Bigeleisen–Wolfsberg

$$k_\mathrm{H}/k_\mathrm{D} = MMI{\cdot}EXC{\cdot}ZPE \qquad (11)$$

expression,[31] equation (12), which permits evaluation of the

$$k_\mathrm{H}/k_\mathrm{D} = [\nu_\mathrm{L}^\ddagger{}_{(\mathrm{H})}/\nu_\mathrm{L}^\ddagger{}_{(\mathrm{D})}](VP{\cdot}EXC{\cdot}ZPE) \qquad (12)$$

temperature independent factor $\nu_\mathrm{L}^\ddagger{}_{(\mathrm{H})}/\nu_\mathrm{L}^\ddagger{}_{(\mathrm{D})}$.

We note that an earlier set of calculations, employing the same bond order approach (but utilizing the Wilson FG procedure[29]) predicted that carbon isotope effects in $S_\mathrm{N}2$ reactions ($\mathrm{N}^- + \mathrm{R_3CX} \longrightarrow \mathrm{NCR_3} + \mathrm{X}^-$) should pass through a maximum as the balance between bond making and breaking in the transition state is systematically varied.[3] Experimental verification of this prediction, originally made by Fry,[4] has recently been claimed.[32]

Transition State Code.—A shorthand notation for the various transition states will be used. With reference to

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the Figure, a transition state with $n_1 = 0.1$, $n_2 = 0.9$, $n_4 = 0.9$ will be coded [199]. This would be a very reactant-like transition state with no carbonionic charge on C_β. The transition state [917] will have an almost completely transferred proton, a $C_\alpha \cdots Cl$ bond that is 30% broken (or 70% intact) and a formal charge on C_β of $0.3e$.

TABLE 3

Computed primary hydrogen isotope effects and imaginary decomposition frequencies [a]

Reaction co-ordinate (A)				
[1 910]	[3 710]	[5 510]	[7 310]	[9 110]
3 020	10.211	11.236	5.342	2.436
2.762	8.120	8.841	4.635	2.240
(2.995)	(6.817)	(7.399)	(5.059)	(2.431)
284.97i	859.43i	864.53i	454.81i	149.09i
[199]	[379]	[559]	[739]	[919]
2.906	10.004	11.081	5.295	2.430
2.668	7.960	8.726	4.598	2.235
(2.880)	(6.608)	(7.259)	(5.013)	(2.425)
288.95i	865.89i	867.49i	454.92i	148.90i
	[377]	[557]	[737]	[917]
	9.559	10.728	5.191	2.417
	7.621	8.467	4.517	2.224
	(6.199)	(6.973)	(4.913)	(2.412)
	876.37i	871.64i	455.62i	148.93i
		[555]	[735]	[915]
		10.337	5.077	2.403
		8.183	4.428	2.212
		(6.687)	(4.804)	(2.398)
		874.07i	456.08i	149.43i
Reaction co-ordinate (B)				
[1 910]	[3 710]	[5 510]	[7 310]	[9 110]
3.218	13.829	15.892	6.202	2.553
2.927	10.457	11.761	5.312	2.338
(3.195)	(7.796)	(8.507)	(5.796)	(2.548)
267.62i	936.77i	957.93i	474.38i	144.77i
[199]	[379]	[559]	[739]	[919]
3.080	13.401	15.587	6.144	2.547
2.814	10.164	11.553	5.267	2.334
(3.058)	(7.555)	(8.335)	(5.758)	(2.542)
263.12i	936.78i	958.53i	476.30i	145.16i
	[377]	[557]	[737]	[917]
	12.551	14.951	6.022	2.535
	9.580	11.124	5.173	2.323
	(7.075)	(7.981)	(5.614)	(2.529)
	936.80i	960.02i	481.39i	146.37i
		[555]	[735]	[915]
		14.314	5.893	2.521
		10.689	5.073	2.312
		(7.625)	(5.483)	(2.516)
		961.74i	487.81i	148.26i
Reaction co-ordinate (C)				
[1 910]	[3 710]	[5 510]	[7 310]	[9110]
2.912	9.329	10.272	5.076	2.410
2.670	7.685	8.388	4.433	2.217
(2.906)	(7.577)	(8.296)	(4.986)	(2.408)
167.73i	641.53i	641.09i	282.72i	93.45i
[199]	[379]	[559]	[739]	[919]
2.786	9.041	10.070	5.027	2.405
2.566	7.471	8.239	4.395	2.213
(2.781)	(7.342)	(8.129)	(4.937)	(2.403)
167.95i	641.58i	641.84i	283.68i	93.61i
	[377]	[557]	[737]	[917]
	8.470	9.655	4.926	2.393
	7.043	7.931	4.316	2.203
	(6.877)	(7.785)	(4.836)	(2.391)
	641.71i	643.73i	286.44i	94.14i
		[555]	[735]	[915]
		9.237	4.821	2.380
		7.619	4.233	2.192
		(7.437)	(4.730)	(2.378)
		645.99i	290.29i	95.02i
Reaction co-ordinate (D)				
[1 910]	[3 710]	[5 510]	[7 310]	[9 110]
2.690	8.985	11.249	4.965	2.291
2.482	7.448	9.035	4.345	2.115
(2.689)	(7.533)	(8.376)	(4.894)	(2.291)
56.33i	598.77i	730.66i	259.26i	33.56i
[199]	[379]	[559]	[739]	[919]
2.573	8.707	11.027	4.917	2.286
2.384	7.240	8.873	4.307	2.111
(2.573)	(7.300)	(8.207)	(4.846)	(2.286)
56.35i	598.82i	731.37i	260.08i	33.58i
Reaction co-ordinate (E)				
[1 910]	[3 710]	[5 510]	[7 310]	[9 110]
2.568	5.113	5.163	3.542	2.109
2.381	4.443	4.490	3.183	1.961
(2.529)	(4.505)	(4.698)	(3.472)	(2.105)
357.43i	640.96i	579.27i	359.53i	151.13i
[199]	[379]	[559]	[739]	[919]
2.485	5.041	5.112	3.515	2.104
2.311	4.384	4.450	3.161	1.956
(2.443)	(4.403)	(4.637)	(3.446)	(2.100)
365.52i	651.39i	582.81i	357.71i	152.16i
	[377]	[557]	[737]	[917]
	4.870	4.983	3.450	2.092
	3.946	4.349	3.108	1.947
	(4.198)	(4.506)	(3.385)	(2.089)
	664.45i	583.93i	352.20i	150.13i
		[555]	[735]	[915]
		4.829	3.376	2.079
		4.228	2.049	1.935
		(4.367)	(3.316)	(2.076)
		578.09i	344.04i	147.59i

[a] Below each transition state code appear, in order, k_H/k_D at 25 °C, k_H/k_D at 50 °C (both corrected for tunnelling), k_H/k_D at 25 °C, uncorrected for tunnelling (in parentheses), and the value of $\nu_L{}^{\ddagger}{}_{(H)}$ in cm^{-1}.

The bond order of the $C_\beta \overset{\cdots}{-} C_\alpha$ bond is not included in the code but can be obtained from $n_3 = 2 -$ (one tenth of the final digit). For transition states in which the C_α–Cl bond is allowed to remain intact, *i.e.* those appropriate to *E*1cB elimination where the first-formed product is a carbanion intermediate, a four-figure code of the type [1910] signifies that $n_4 = 1.0$.

RESULTS AND DISCUSSION

Primary Hydrogen Isotope Effects.—Isotope effects (k_H/k_D) for temperatures 25 and 50 °C, corrected for tunnelling *via* equation (10), are shown in Table 3. This is arranged in sections according to which of reaction co-ordinates (A)—(E) had been used. Each section is further arranged so that reading across rows from left to right corresponds to an increase in the degree of proton transfer with the amount of $C_\alpha \cdots Cl$ rupture being kept constant. Reading down the columns (where appropriate) corresponds to an increase in the latter, with the degree of proton transfer being kept constant.

Before the choice of reaction co-ordinate is discussed, some facets of these results are worthy of comment. First, systematic variation of the degree of proton transfer at constant n_4 produces the theoretically [24,27,33]

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[33] F. H. Westheimer, *Chem. Rev.*, 1961, **61**, 265; J. Bigeleisen, *Pure Appl. Chem.*, 1964, **8**, 217; A. O. Cohen and R. A. Marcus, *J. Phys. Chem.*, 1968, **72**, 4249; R. P. Bell, *Discuss. Faraday Soc.*, 1965, **39**, 16; *Chem. Soc. Rev.*, 1974, **3**, 513; W. J. Albery, *Trans. Faraday Soc.*, 1967, **63**, 200; D. J. McLennan, *J. Chem. Educ.*, 1976, **53**, 348.

and experimentally[34] respectable k_H/k_D maximum at about 'half transfer,' no matter which n_4 set is considered. This is also the case for Saunders' calculations,[9,10] and is not solely a tunnelling-related phenomenon as the uncorrected isotope effects exhibit the trend. However, as expected, the tunnel correction increases with k_H/k_D (uncorrected), which in turn increases with increasing $\nu_L^\ddagger$. Secondly, the isotope effects are controlled largely by the zero-point energy change attendant upon isotopic substitution, as shown by typical results for the $n_4 = 0.9$ set in reaction co-ordinate (A) in Table 4.

TABLE 4

Origin of primary k_H/k_D isotope effects[a]

Transition state	*EXC*	*MMI*	*VP*	*ZPE*	$\nu_L^\ddagger{}_{(H)}/\nu_L^\ddagger{}_{(D)}$
[199]	0.986 8	1.007 3	0.951 1	2.897 5	1.059 1
[379]	0.994 0	1.006 8	0.766 0	6.602 4	1.314 4
[559]	0.988 7	1.006 3	0.761 0	7.295 5	1.322 4
[739]	0.962 2	1.005 8	0.869 7	5.180 0	1.156 4
[919]	0.888 3	1.004 7	0.956 9	2.717 5	1.049 9

[a] Reaction co-ordinate (A), 25 °C.

Sample calculations based on tetrahedral C_α and reaction co-ordinates (A) and (E) (results not shown) gave isotope effects almost identical with those in Table 3. Geometric considerations of this type are therefore unimportant. In fact the changes in hybridization at C_α and C_β are partly taken into account by variation of stretching force constants involving bonds between these atoms and non-reacting atoms when tetrahedral geometry is maintained.

The most important fact that can be gleaned from the results is that the degree of proton transfer producing a given value of k_H/k_D is not, within the framework of a given reaction co-ordinate formulation, dependent on the degrees of $C_\gamma \cdots Cl$ breaking and $C_\beta \overset{\cdots}{-} C_\alpha$ formation. The maximum occurs for the same degree of proton transfer (a little less than 50% in bond order terms) whatever the reaction co-ordinate. It is thus clear that k_H/k_D does reflect the degree of proton transfer in *E*2 reaction series, with the reservation that other evidence is required before a low isotope effect can be attributed to a less or a more than 'half transferred' proton. This conclusion also emerges from Saunders' results,[9,10] even though the models are different. The small change in k_H/k_D that one may note on reading down columns in Table 3 will not generally be significant in the experimental context.

Thus, experimental observations to the effect that k_H/k_D is essentially invariant when changes in molecular or environmental variables are effected do not necessarily mean that transition state structure remains constant.[35] When lower than maximal isotope effects are obtained, transition states as disparate at [199] and [915] could be involved, whilst maximal isotope effects may be obtained, however much the $C_\alpha \cdots X$ bond is broken. In addition, the suggestion that isotope effect variation from 7.6 to 9.0, as the base inducing elimination from $PhCH_2{\cdot}CH_2Br$ in dimethylformamide is changed from PhO^- to $p\text{-}NO_2{\cdot}C_6H_4{\cdot}O^-$, is indicative of an almost constant degree of proton transfer[36] is not supported by the present results. The proton could be less than 30% transferred to PhO^- and 50% transferred to the weaker base.

A recent claim that isotope effect maxima in *E*2 eliminations arising from changes in transition state structure have not been observed has been made.[37a] Investigations to this end generally employ variation in a β-bound benzene ring substituent[37b] or solvent.[34c] Without committing ourselves as to the veracity of this claim we find the paucity of k_H/k_D maxima not really surprising. Because of the weak dependence of k_H/k_D on n_4, an isotope effect maximum can only be *guaranteed* if changes in substituent or solvent are such that only n_1 (and therefore n_2) suffers change along a reaction series. But, as is shown in the preceding paper, this is unlikely, and it is most probable that base, substituent, or solvent changes will occasion shifts in transition state structure which correspond to diagonal movements across Table 3, rather than neat progressions across rows or down columns. In this way a maximum can conceivably be avoided even though the proton may pass through the half-transferred situation. Furthermore, calculations to be published elsewhere show that relaxation of the restriction $n_1 + n_2 = 1.00$ leads to larger values of k_H/k_D, when $n_1 + n_2 < 1.00$ (looser transition states), and again a maximum could be avoided.

Choice of Reaction Co-ordinate.—The adjustable parameters a_{ij} in equations (6)—(8) control the respective relative extents of motion of the proton in relation to O and C_β, of C_β in relation to the proton and C_α, and of C_α in relation to C_β and Cl. Let us first examine reaction co-ordinate (E), in which proton and heavy atom motion is pronounced. Isotope effects no greater than 4.8 are predicted by this model and we may reject it as a basis for discussing experimental values[17,18] for the system in question, and in a more general sense.[6] It is probable that the tunnel correction has been underestimated, but a further factor of two or more seems unlikely.[27] Saunders has suggested[10] that a value of a_{34}/a_{23} near unity might be associated with a 'highly concerted

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[34] (*a*) R. P. Bell and D. M. Goodall, *Proc. Roy. Soc.*, 1966, **A294**, 273; (*b*) R. P. Bell and D. J. Barnes, *ibid.*, 1970, **A318**, 421; (*c*) A. F. Cockerill, *J. Chem. Soc.* (*B*), 1967, 964; (*d*) R. P. Bell and B. G. Cox, *ibid.*, 1970, 193; (*e*) D. W. Earls, J. R. Jones, and T. G. Rumney, *J.C.S. Faraday I*, 1972, 925; (*f*) D. J. McLennan and R. J. Wong, *J.C.S. Perkin II*, 1974, 526; (*g*) J. R. Keefe and N. H. Munderloh, *J.C.S. Chem. Comm.*, 1974, 17; (*h*) J. E. Dixon and T. C. Bruice, *J. Amer. Chem. Soc.*, 1970, **92**, 905; (*i*) W. A. Pryor and K. G. Kneipp, *ibid.*, 1971, **93**, 5584; (*j*) J. L. Longridge and F. A. Long, *ibid.*, 1967, **89**, 1292; (*k*) Y. Pocker and J. M. Exner, *ibid.*, 1968, **90**, 6764; (*l*) A. J. Kresge, D. S. Sagatys, and H. L. Chen, *ibid.*, 1968, **90**, 4174; (*m*) S. B. Hanna, C. Jermini, H. Loewenschuss, and H. Zollinger, *ibid.*, 1974, **96**, 7222; (*n*) F. G. Bordwell and W. J. Boyle, *ibid.*, 1975, **97**, 3447.

[35] C. A. Pollock and P. J. Smith, *Canad. J. Chem.*, 1971, **49**, 3856; A. F. Cockerill, S. Rottschaefer, and W. H. Saunders, *J. Amer. Chem. Soc.*, 1967, **89**, 901.

[36] S. Alunni, E. Baciocchi, and V. Mancini, *J.C.S. Perkin II*, 1974, 1866.

[37] L. F. Blackwell and J. L. Woodhead, *J.C.S. Perkin II*, 1975, (*a*) p. 234; (*b*) p. 1218.

reaction,' but this is not mechanistically significant, as can be seen from reaction co-ordinates (A) and (E). Both have the same barrier curvature, and the a_{12} parameter in each is similar. Yet unrealistically low isotope effects are calculated for the latter irrespective of the structure of the transition state.

In practical terms, and in the light of uncertainty as to the magnitude of the tunnelling correction, there is little to choose amongst the remaining four reaction co-ordinates. In three the heavy atoms are relatively motionless in the decomposition vibration and only in (A) are they permitted to move to any extent. The curvature of the barrier has some effect in that maximal isotope effects for reaction co-ordinate (B) are larger than any that have been observed experimentally.[18] This leaves (A), (C), and (D) as contenders, and although they differ quite markedly in nature, no real distinction can be made on the basis of the isotope effects alone.

Little would be gained at this stage from a definitive attempt to marry the experimental results [17,18] to a transition state structure within a reaction co-ordinate model. Other isotope effects are required.[4] But a tentative approach to this end could involve examination of the temperature dependence of isotope effects,[5a,d,f,10b] since the difference in activation energies, $(E_a)_D - (E_a)_H$, over the limited temperature range may be calculated. In Table 5 are shown calculations, for [557] as a typical transition state, of $(E_a)_D - (E_a)_H$ and the quotient of Arrhenius pre-exponential factors A_D/A_H, as a function of the reaction co-ordinate model. It is clear that only reaction co-ordinates (A) and (B) produce results that are anywhere near the commonly accepted criteria for tunnelling.[26] As far as the comparison with experimental values [17] is concerned the calculations again fail badly. Two assumptions may be at fault here. First, it is assumed that $\log k_H/k_D$ can be linearly extrapolated to $1/T = 0$ in order to obtain A_D/A_H. This is not the case.[11] Secondly, the Bell tunnel correction is derived for a one-dimensional barrier, and is thus not strictly applicable to $E2$ reactions. A more sophisticated version of this tunnel correction [27] is not appropriate here, and its application to model proton transfer calculations has been criticized elsewhere.[38]

TABLE 5

Calculated isotopic dependence of Arrhenius activation parameters [a] for various reaction co-ordinate models [b]

Reaction co-ordinate [a]	$(E_a)_D - (E_a)_H$/ kcal mol^{-1}	A_D/A_H
(A)	1.54	1.27
(A) *	1.10	1.09
(B)	2.13	2.43
(B) *	1.17	1.11
(C)	1.42	1.14
(C) *	1.25	1.06
(D) [d]	1.57	1.28
(D) * [d]	1.19	1.10
(E)	0.98	1.05
(E) *	0.86	1.04
Expt: $(p\text{-}ClC_6H_4)_2CH{\cdot}CHCl_2$ [e]	2.4	6.3
Expt: $Ph_2CH{\cdot}CHCl_2$ [e]	2.0	4.0

[a] Calculated assuming a linear relationship between $\log k_H/k_D$ and $1/T$ over the 298—323 K range. [b] For transition state [557]. [c] The asterisk signifies that no tunnel correction applies and the lack of an asterisk means that the basic Bell correction has been employed. [d] For [559]. [e] The minimum values as established by the experimental uncertainties.

Primary Isotope Effects in the Absence of Tunnelling.—In Table 3 we show in parentheses primary hydrogen isotope effects at 25 °C, uncorrected for tunnelling, for the various models and structures. The reason for this is that the reactions of $Ar_2CH{\cdot}CHCl_2$ with EtO^-–EtOH [39] and with Bu^tOK–Bu^tOH [17] do not seem to be attended by significant tunnelling. Similarly the addition of dimethyl sulphoxide to MeO^-–MeOH media seems to cause a diminution in the tunnelling contribution.[17]

The comments relevant to the discussion of Table 3 apply here. Reaction co-ordinate (E) may be rejected, and reaction co-ordinate (A), which permits a little heavy atom motion, could be viewed as being only marginally satisfactory. The observed isotope effects fit well within the range established by the calculations. In particular, since the experimental evidence suggests that changes in base, solvent, and *para*-substituent shift the position of the proton in the transition state from one side to the other of the ' half-transferred ' position, but not by large amounts, it is gratifying to find that the experimental and calculated isotope effects are of the same magnitude as far as changes from, say, [379] to [739] are concerned.

Secondary Deuterium Isotope Effects.—Although no secondary isotope effects for $Ar_2CH{\cdot}CHCl_2$ *vs.* $Ar_2CH{\cdot}CDCl_2$ have been measured (and we have no immediate plans for doing so) we report some of the results of computations for various transition state structures and reaction co-ordinate models in Table 6. The temperature dependence between 25 and 50 °C is small, and only values for the former temperature are given. Inspection of terms in equations (11) and (12) reveals that the change in zero-point energy dominates, as it does

TABLE 6

Secondary α-deuterium isotope effects at 25 °C

Reaction co-ordinate (A)				
[1 910]	[3 710]	[5 510]	[7 310]	[9 110]
1.002 8	0.999 6	0.999 7	1.001 8	1.000 9
[199]	[379]	[559]	[739]	[919]
1.008 0	1.004 8	1.004 9	1.007 0	1.006 1
	[377]	[557]	[737]	[917]
	1.026 6	1.026 7	1.028 7	1.027 7
		[555]	[735]	[915]
		1.063 4	1.065 4	1.064 4
Reaction co-ordinate (E)				
[1 910]	[3 710]	[5 510]	[7 310]	[9 110]
1.010 7	1.003 6	1.005 0	1.006 6	1.002 1
[199]	[379]	[559]	[739]	[919]
1.016 0	1.008 6	1.010 2	1.011 7	1.007 2
	[377]	[557]	[737]	[917]
	1.030 2	1.032 1	1.033 3	1.028 7
		[555]	[735]	[915]
		1.069 1	1.069 9	1.065 4

[38] J. Banger, A. Jaffe, A.-C. Lin, and W. H. Saunders, *J. Amer. Chem. Soc.*, 1975, **97**, 7177.

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

with the primary isotope effects, and that the temperature independent factor $\nu_{L}{}^{\ddagger}{}_{(H)}(/\nu_{L}{}^{\ddagger}{}_{(D)}$ contributes no more than 6% of the total isotope effect.

The isotope effects increase significantly as the $C_{\alpha}\cdots Cl$ bond ruptures, from insignificant values for a nearly intact C_{α}–Cl bond, to a significant value of $k^{H}/k^{D} \simeq 1.06$ for a 50% ruptured $C_{\alpha}\cdots Cl$ bond. Calculations in which the tetrahedral geometry at C_{α} and C_{β} was maintained for all models (results not shown) produced no significant secondary deuterium isotope effects for any of the models; comparison with the values in Table 6 indicates that the isotope effect arises primarily from the changes in bending force constants as the geometry at C_{α} is altered so as to mimic the hybridization change from sp^3 towards sp^2. Our largest values for $n_4 = 0.5$ agree well with the value of $k^{H}/k^{D} \simeq 1.06$ for $n_4 = 0.5$ calculated by Saunders [10] for a different model. Our calculated isotope effects are of value in pointing out the requirement for force constant *and* geometric changes on going from initial to transition state in computations of secondary kinetic isotope effects. And since the geometric model is obviously appropriate for transition states having n_4 close to unity, the intuitive notions that secondary isotope effects should be small is reinforced.

Leaving Group Solvation.—It has been suggested that isotope effects for solution reactions may be influenced by the presence of solvent molecules in the transition state.[40] We have simulated this phenomenon by including three H–O fragments tetrahedrally bonded to the incipient chloride ion in the transition state,[19] with the $Cl\cdots H$ bonds having bond orders ranging from 0.015 to 0.04. The primary isotope effect due to the remote reacting hydrogen atom is, as expected, largely unaffected in all cases, especially the maximum value. Models in the $n_4 = 0.5$ series (greatest $C_{\alpha}\cdots Cl$ rupture) showed a reduction in the secondary α-deuterium isotope effect from *ca.* 1.065 to *ca.* 1.055. We conclude that solvational factors are relatively unimportant in the present situation where the $C_{\alpha}\cdots Cl$ bond is no more than half broken, but computations for Bu^{t}Cl solvolysis indicate that heavy atom isotope effects concerning the leaving group are largely controlled by the solvational bonds,[19] and we explore this effect further in a following paper.

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[7/195 *Received, 4th February,* 1977]

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[40] J. W. Hill and A. Fry, *J. Amer. Chem. Soc.*, 1962, **84**, 2763; T. H. Cromartie and C. G. Swain, *ibid.*, 1976, **98**, 545.