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LARGE KINETIC ISOTOPE EFFECTS WITH UNSYMMETRICAL TRANSITION STATES

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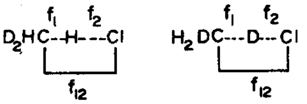
Abstract—The results of a series of calculations for a wide, unrestricted variation in the force constants for the making and breaking bonds and their interaction constant are presented for the abstraction reactions of CH_2D_2 with Cl atoms. A wide range of asymmetrical force constants leads to a high kinetic isotope effect as has been pointed out by others for a more restricted range of consideration. These results pointedly contradict the assumed connection between a high kinetic isotope effect and a symmetrical transition state. It is found by examining the atomic displacements of the normal modes that the motion of the H or D atom in the real stretch of the transition state will often have little influence on the isotope effect because the mode can be dominated by end group motions. It is further found that a 3-center model multiplied by a constant factor to account for the contributions of the other vibrations is capable of very satisfactorily reproducing the more rigorous 6-center calculations.

A number of years ago Westheimer proposed that the magnitude of a primary kinetic deuterium isotope effect was dependent on the "symmetry of the transition state".[1] In particular, he suggested that a necessary criterion for a large kinetic isotope effect in a hydrogen or deuterium abstraction reaction was near equality in the force constants associated with the breaking and forming bonds in the transition state, f_1 and f_2 respectively. It was felt that only under these conditions would the real stretching frequency associated with the hydrogen or deuterium be mass independent—a necessary requirement for a common zero point energy for these vibrations and consequently a high isotope effect.[1]

At about this same period of time an investigation, conducted in part by one of us, on the kinetic isotope effect in the chlorination of dideuteromethane gave data which seemed to support Westheimer's hypothesis.[2] The high kinetic isotope effect observed (14.4 at 250 K) was assumed to be a necessary consequence of a rather symmetrical transition state. This conclusion was based on a comparison of the experimental isotope effect with that calculated (10.4 at 250 K) for a transition state obtained from a semi-empirical potential energy reaction surface. The transition states used in these calculations (see below) had values for f_1, f_2 and f_{12} of 0.711, 1.050 and 1.470 mdynes/A respectively, where f_1 and f_2 are the stretching force constants and f_{12} is the interaction constant.



In the succeeding years it has been a rather common acceptance by many workers in the field to equate large kinetic deuterium isotope effect to similar "symmetries" and, in addition, to suggest that the magnitude of the isotope effect can lend information on the shape of a reaction surface.[3,4] This acceptance has been made in spite of data presented by several authors which suggested that large isotope effects may be rather insensitive to transition state asymmetry.[4–8]

In a recent *ab initio* determination of the reaction surface for the chlorination of methane, a very unsymmetrical transition state was obtained (f_1, f_2 and f_{12} = −0.480, 2.054 and 1.676 mdynes/A, respectively).[9] In spite of the lack of symmetry, the calculated isotope effect (11.6 at 250 K) was also in qualitative agreement with the experimental value, supporting those who questioned the Westheimer postulate and confirming that the magnitude of the isotope effect need not lend information on the shape of a reaction surface.

In the present paper, we are reporting the results of an investigation on the sensitivity to transition state symmetry of the calculated kinetic isotope effect in the chlorination of dideuteromethane.[10]

This model reaction has the advantage of a common reactant so that the isotope effect may be calculated from a consideration of the transition state alone. The trends in isotope effect are not appreciably sensitive to geometry and therefore the parameters obtained from the *ab initio* surface were used in all calculations (Table 1).[9] The dependence of the calculated isotope effect was then determined for a wide variety of f_1, f_2 and f_{12} values. Because of the increased sensitivity of the calculated isotope effect to variations in f_1, f_2 and f_{12} at lower temperatures, all calculations were at 250 K.

For the two reactions

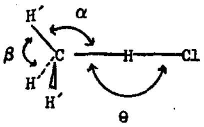
$$CH_2D_2 + Cl\cdot \begin{array}{l} \xrightarrow{k_H} CHD_2\cdot + HCl \\ \xrightarrow[k_D]{} CDH_2\cdot + DCl \end{array}$$

the isotope effect is given by[2]

$$\frac{k_H}{k_D} = \left(\frac{M_H^{\neq}}{M_D^{\neq}}\right)^{3/2} \frac{(I_x^{\neq} I_y^{\neq} I_z^{\neq})_H{}^{1/2}}{(I_x^{\neq} I_y^{\neq} I_z^{\neq})_D{}^{1/2}} \prod_j^{3n-7} \frac{1-e^{-u_j^{\neq}(D)}}{1-e^{-u_j^{\neq}(H)}}.$$

where $M^{\neq}$ = mass of activated complex; $I^{\neq}$ = principal

Table 1. Force constants and geometry of transition states

Constant		Value^a	Structure
k_{CH}	(f_1)	variable	
k_{HCl}	(f_2)	variable	
k_{CHCl}	(f_{12})	variable	
$k_{CH'}$		7.761	
k_θ		0.192×10^{-11}	
k_α		0.754×10^{-11}	
k_β		0.235×10^{-11}	
θ_0		180°	
α_0		99.65°	
β_0		117.25°	
R_{CH}		1.513	
$R_{CH'}$		1.097	
R_{HCl}		1.423	

^{a} Stretching constants in mdyne/Å, bending constants in erg/rad^2, distance in angstroms, angles in degrees.

moments of inertia; $u_j = h\nu_j/kT$; ν_j = real vibrational frequencies of the activated complex.

The Teller–Redlich Product Rule enables further simplification of the isotope effect:[3]

$$\frac{k_H}{k_D} = \frac{\nu^*(H)}{\nu^*(D)} \prod_j^{3n-7} \frac{U_j(H)\,(e^{U_j(D)} - e^{-U_j(D)})}{U_j(D)\,(e^{U_j(H)} - e^{-U_j(H)})}$$

where $U_j = (0.71941625/T)\nu_j\,(\mathrm{cm}^{-1})$; ν^* = imaginary frequency associated with the activated complex; ν_j = real vibrational frequencies of the activated complex. Thus, in the absence of tunnelling, the deuterium isotope effect is reduced to an analysis of the real and imaginary vibrational frequencies associated with each isotopic activated complex. These frequencies were obtained from the standard GF matrix calculation using a variety of f_1, f_2 and f_{12} constants along with the geometry and the other force constants obtained from an *ab initio* surface.[9]

All GF calculations were checked to see that they agree with the Teller–Redlich product rule. That is,

$$\frac{(I_x^* I_y^* I_z^*)_H^{1/2}}{(I_x^* I_y^* I_z^*)_D^{1/2}} = \frac{\nu^*(H)}{\nu^*(D)} \prod_j^{3n-7} \frac{\nu_j(H)}{\nu_j(D)} = 1.17617.$$

Since a normal single bond has a force constant of about 5 mdyne/A,[11] conservation of bond order[12] suggested a maximum value of 5 mdyne/A for either f_1 or f_2. Table 2 shows the expected isotope effects under the most extreme of circumstances.

It is obvious that the interaction constant (f_{12}) can almost negate the effect of asymmetry on the magnitude of the kinetic isotope effect. Since some loss of bond order was expected in the activated complex, maximum values of f_1 and f_2 were arbitrarily restricted to 2 mdyne/A in the more detailed study that follows. This limitation covers the range of force constants found in the previous studies on this reaction.[2,9]

To preserve the imaginary frequency, the values of f_1, f_2 and f_{12} were adjusted to insure that the determinant of the F-matrix containing these constants was negative.

Table 2. Calculated isotope effects for asymmetric activated complexes

f_1*	f_2*	f_{12}*	k_H/k_D
~ 5	~ 0	~ 0	1.098
~ 5	~ 0	5	12.210
~ 0	5	~ 0	1.040
~ 0	5	5	11.601

* Force constants in mdyne/A, all force constants are positive.

$$\det \begin{vmatrix} f_1 & f_{12} \\ f_{12} & f_2 \end{vmatrix} < 0.$$

When $(f_1 f_2 - f_{12}^2) \geq 0$, the imaginary frequency is annihilated. Whenever either f_1 or f_2 is negative, the magnitude of f_{12} is no longer critical.

Twenty calculations are presented from among three hundred which were performed to represent a reasonably broad spectrum of deuterium isotope effects. Table 3 shows the effect of positive values of f_1, f_2 and f_{12}, whereas Table 4 shows the effect of negative values for f_1 and positive values for f_2 and f_{12}. There is no implied relationship between f_1, f_2, and f_{12} other than the requirement of a negative determinant. It should be noted that Tables 3 and 4 have included an isotope effect (k_H/k_D)(3-ctr). This value which is obtained from a three center approximation[11] and which is always in close agreement with the complete GF calculation is obtained as follows.

The stretching frequencies for the linear system

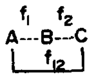


Table 3. Calculated isotope effects for the chlorination of dideuteromethane 250 K—positive force constants

f_1	0.0005	0.001	0.35	0.001	0.5	0.002	0.6	0.001	0.001	1.1	mdyne/A
f_2	2.0	2.0	2.5	1.5	1.5	2.5	1.5	0.5	0.5	1.0	mdyne/A
f_{12}	0.1	0.5	1.0	0.5	0.9	1.2	1.0	0.3	0.5	1.2	mdyne/A
k_H/k_D(FG)	2.85	4.25	4.73	5.90	7.96	8.23	9.14	11.12	12.01	12.27	
k_H/k_D(3-ctr)	2.86	4.25	4.74	5.88	7.99	8.21	9.16	11.14	12.09	12.41	

Teller-Redlich Products = 1.17617

Table 4. Calculated isotope effects for the chlorination of dideuteromethane 250 K—negative f_1, positive f_2, f_{12}

f_1	-0.001	-0.5	-1.0	-1.5	-2.0	-0.5	-2.0	-2.0	-0.5	-0.5	mdyne/A
f_2	2.5	2.5	2.0	2.0	2.0	2.5	2.5	2.0	1.5	0.5	mdyne/A
f_{12}	0.3	0.3	0.1	0.1	0.1	1.2	0.9	0.9	0.9	0.9	mdyne/A
k_H/k_D(FG)	2.77	3.55	4.98	6.74	8.29	9.73	10.31	11.04	11.25	12.06	
k_H/k_D(3-ctr)	2.78	3.52	4.90	6.68	8.41	9.91	10.72	11.43	11.46	12.21	

Teller-Redlich Products = 1.17617

are evaluated using the following relationship:[11]

$$\text{eqn (1)} \quad \lambda_{\text{real}} = (-b + (b^2 - 4c)^{1/2}/2)$$

$$\text{eqn (2)} \lambda_{\text{imag}} = (-b - (b^2 - 4c)^{1/2}/2)$$

where

$$b = \frac{2}{M_B}(f_{12}) - \left(\frac{1}{M_A} + \frac{1}{M_B}\right)(f_1) - \left(\frac{1}{M_B} + \frac{1}{M_C}\right)(f_2)$$

$$c = \left(\frac{1}{M_A M_B} + \frac{1}{M_A M_C} + \frac{1}{M_B M_C}\right)(f_1 f_2 - f_{12}^2)$$

M = masses of A, B or C in amu
f = force constants (mdyne/A).

Vibrational frequencies, expressed in wave numbers (cm^{-1}), are evaluated using the following expression:

$$\nu_{(\text{cm}^{-1})} = 1302.832(\lambda)^{1/2}.$$

If one incorporates the appropriate atomic weights associated with the activated complex model, the formulas required for the three-center approximation condense to the following:

Hydrogen abstraction (D_2HC-H-Cl)

$$\text{eqn (3)} \quad \nu_{\text{real, imag}(\text{cm}^{-1})} = 1302.832(-b \pm (b^2 - 4C)^{1/2}/2)^{1/2}$$

$$b = 1.985\, f_{12} - 1.051\, f_1 - 1.021\, f_2$$

$$c = 0.0883\,(f_1 f_2 - f_{12}^2)$$

Deuterium abstraction (H_2DC-D-Cl)

$$\text{eqn (4)} \quad \nu_{\text{real, imag}(\text{cm}^{-1})} = 1302.832\,(-b' \pm (b'^2 - 4c')^{1/2}/2)^{1/2}$$

$$b' = 0.993\, f_{12} - 0.559\, f_1 - 0.525\, f_2$$

$$c' = 0.0470\,(f_1 f_2 - f_{12}^2)$$

note that $b \cong 2b'$, $c \cong 2c'$ and $\nu\nu^* = 1302.832\,(c)^{1/2}$

ν = 3 cntr real frequency

ν^* = 3 cntr imaginary frequency.

In the full GF treatment, the only off diagonal force constant considered was f_{12}. For this reason, all frequencies with the exception of the real and imaginary stretching frequencies may be considered constant with changes in f_1, f_2 and f_{12}.

The contribution of these constant frequencies can be factored out of the expression for the kinetic isotope effect. The ratio of the partition functions for the constant frequencies in this model is

$$\text{All const freq} \prod_j \frac{U_{j(H)}(e^{U_{j(D)}} - e^{-U_{j(D)}})}{U_{j(D)}(e^{U_{j(H)}} - e^{-U_{j(H)}})} \cong 8.7765.$$

The three-centered approximation for the kinetic isotope effect may then be reduced to

$$\frac{k_H}{k_D} = \frac{\nu_H^*}{\nu_D^*}\frac{Q_H}{Q_D} 8.7765$$

where $Q = U(e^U - e^{-U})^{-1}$; $U = (0.71941625/T)\nu_{\text{cm}^{-1}}$; ν^* = imaginary frequency; ν = real frequency. Since $(\nu_H \nu_H^* / \nu_D \nu_D^*)$ is constant, further reduction leads to the expression:

$$\text{eqn (5)} \quad k_H/k_D = 12.0296\left[\frac{e^{U_{(D)}} - e^{-U_{(D)}}}{e^{U_{(H)}} - e^{-U_{(H)}}}\right].$$

The term in the brackets is ~1 for $\nu_H \cong \nu_D$ (this condition generally occurs when the magnitude of ν_H and ν_D are low) and decreases as ν_H and ν_D increases. The difference between ν_H and ν_D increases as ν_H increases. A maximum isotope effect is, therefore, obtained when the real stretching frequency, ν_H, is low. λ_H from eqn (1) is given by

$$\lambda_H = -b + \frac{(b^2 - 4c)^{1/2}}{2}$$

$$b \cong 2f_{12} - f_1 - f_2$$

$$c = 0.0880\,(f_1 f_2 - f_{12}^2).$$

By inspection, it can be seen that for a system of positive force constants ($f_{12}^2 > f_1 f_2$) the minimum value of λ_H and therefore ν_H, is associated with very small positive values of b and very small negative values of c. Assuming both b and c approach zero, a maximum isotope effect is obtained when $f_1 \cong f_2$ and f_{12} is infinitesimally larger than f_1 and f_2. With combinations of mixed sign values of f_1 and f_2, it is found that the largest isotope effects are evaluated in the limit when the product f_1f_2 approaches zero and f_{12} is very small.

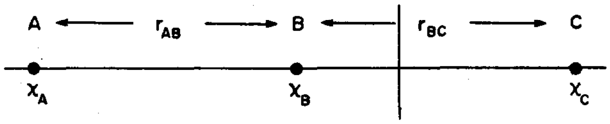
One way of presenting the range of isotope effects associated with various sign combinations of f_1 and f_2 is to plot calculated isotope effects on a two dimensional plane holding the value of f_{12} constant, Figs. 1–3.

The role of the interaction constant (f_{12}) is clearly evident in the preceeding figures. Increased values of f_{12} offset force constant asymmetry with respect to f_1 and f_2 and increase calculated isotope effects. This is also apparent in recent data reported by Mellander.[13] When both f_1 and f_2 are positive, a maximum isotope effect is calculated, as Westheimer predicted,[1] when the transition state is symmetric. However, a variety of non-symmetric transition states can lead to isotope effects that are nearly as large in magnitude. Since Westheimer proposed that these large isotope effects should require: one, a real stretching frequency with a symmetric vibrational mode; and two, little or no motion of the central isotope (H or D), these aspects were examined in more detail.

Nuclear displacements

The nuclear displacements were evaluated with the aid of the normalized displacement eigen-vectors extracted from the GF matrix and by a modification of the method described by Wiberg for the frequency analysis of a three center linear system.[11] These latter results, which are substantially in agreement with the former, have been omitted for brevity. They could be used, however, by anyone not wishing to analyze a system by a complete GF treatment.

The GF treatment was applied as follows. A three particle vibrational system is placed on an χ axis with the molecular center of mass at the origin.



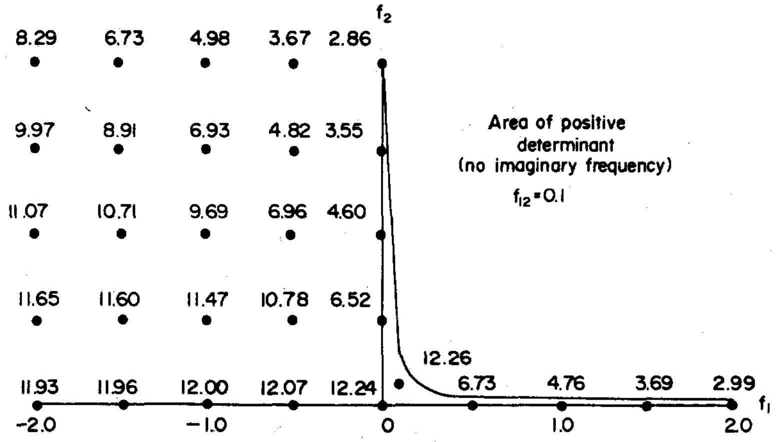


Fig. 1. The calculated isotope effect k_H/k_D is displayed above the filled circle in a grid corresponding to the values of f_1 and f_2 used in the calculation. The points in the grid are separated by 0.5 mdynes/A and start from the point (0.0, 0.0) at the intersection of the axes. The C–H stretching constant is f_1 and the H–Cl stretching constant is f_2. The value of the interaction constant f_{12} is 0.1 mdyne/A.

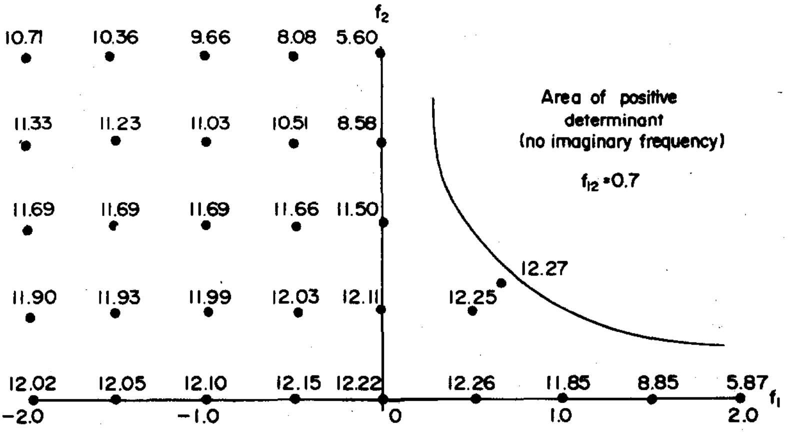


Fig. 2. The calculated isotope effect k_H/k_D is displayed above the same grid used in Fig. 2. The interaction constant f_{12} is now 0.7 mdyne/A.

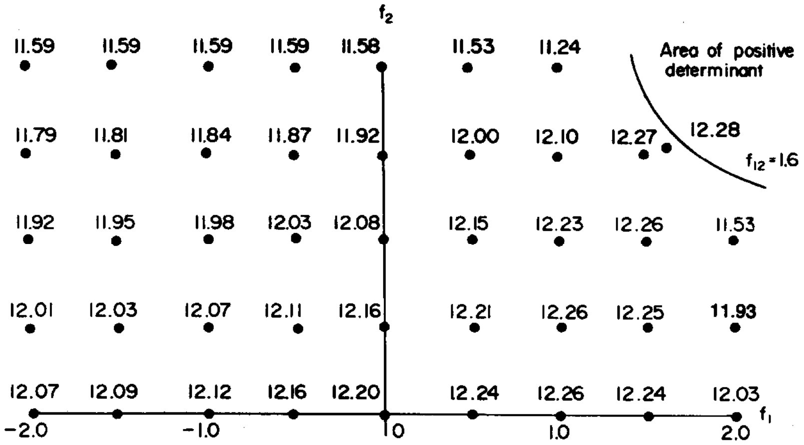


Fig. 3. The calculated isotope effect k_H/k_D is displayed above the same grid used in Fig. 2. The interaction constant f_{12} is now 1.6 mdyne/A.

where

$$\chi_B - \chi_A = r_{AB};\quad \chi_A = \chi_B - r_{AB};$$
$$\chi_C - \chi_B = r_{BC};\quad \chi_C = \chi_B + r_{BC}.$$

Since

$$\Sigma m_i r_i(\chi) = 0$$

then

$$M_C(\chi_C - 0) + M_B(\chi_B - 0) + M_A(\chi_A - 0) = 0$$

substituting values of χ_A, χ_B and χ_C from above gives

$$M_C(r_{BC} + \chi_B) + M_B(\chi_B) + M_A(\chi_B - r_{AB}) = 0.$$

Thus,

$$\chi_B = \frac{M_A r_{AB} - M_C r_{BC}}{M_A + M_B + M_C},$$

where χ_B represents the isotope (H or D) coordinates. It was assumed that molecular vibrational activity conserves the center of mass and that bond distortion is proportional to the coefficients e_1 and e_2 of the eigenvectors (extracted from the GF matrix treatment and associated with r_{AB} and r_{BC} respectively):

$$r'_{AB} = r_{AB} + e_1 r_{AB} U$$
$$r'_{BC} = r_{BC} + e_2 r_{BC} U. \qquad U = \text{unit of distortion}$$

The isotope coordinates after bond distortion is then

$$\chi'_B = \frac{M_A(r_{AB} + e_1 r_{AB} U) - M_C(r_{BC} + e_2 r_{BC} U)}{M_A + M_B + M_C}.$$

Thus the motion of the isotope during the real vibration is given by:

$$\Delta\chi_B = \chi_B - \chi'_B = -\left[\frac{M_A e_1 r_{AB} - M_C e_2 r_{BC}}{M_A + M_B + M_C}\right] U.$$

By a similar method the following expressions are evaluated for the shift in the end group coordinates:

$$\Delta\chi_A = \left[\frac{e_1 r_{AB}(M_B + M_C) + e_2 r_{BC} M_C)}{M_A + M_B + M_C}\right] U$$

$$\Delta\chi_C = -\left[\frac{e_1 r_{AB} M_A + e_2 r_{BC}(M_A + M_B)}{M_A + M_B + M_C}\right] U.$$

The eigenvectors from the full GF treatment were truncated to representation over only r_{AB} and r_{BC} and renormalized in order to evaluate e_1 and e_2 in the above expressions. Further the displacements were normalized so that

$$(\Delta\chi_A)^2 + (\Delta\chi_B)^2 + (\Delta\chi_C)^2 = 1.$$

The results of 7 representative vibrations covering a span of isotope effects are shown in Fig. 4.

It is readily apparent from Fig. 4 why an unsymmetrical transition state with a proportionally large interaction constant (f_{12}) can give rise to a large isotope effect. When f_{12} is large, considerable motion of the heavy end groups takes place in the real vibrational mode, as in (e) and (f). Their mass then dominates the frequency of this vibrational mode and, contrary to Westheimer's postulate, it is rather immaterial whether the central isotope is displaced during the vibration. Only when the magnitude of f_{12} is small and end group displacement is also quite small, as in (a) and (b), does the motion and mass of the central isotope have an appreciable affect on the vibrational frequency and, therefore, only under these conditions can the isotope effect be reduced by transition state asymmetry, in accordance with the Westheimer postulate.[1]

This observation can also be accounted for by a more detailed examination of eqn (5) where if one assumes e^{-U_D} and e^{-U_H} are small, then $(k_H/k_D) \cong 12.0296\, e^{-U_D - U_H}$ and $\log(k_H/k_D) \cong 1.08025 + 0.00124975\ (\nu_D - \nu_H)$. Making the approximation that c in eqns (3) and (4) is negligible (over the range of f_1, f_2 and f_{12} considered, this approximation can effect the magnitude of the isotope effect by a maximum of ~10%), and since $b \cong 2b'$ in eqn (4), one obtains

eqn (6)
$$\log\frac{k_H}{k_D} \cong 1.08025 - 0.674428 \times \left[\frac{1}{M_D}(f_1 + f_2 - 2f_{12}) + \frac{f_1}{M_{CH_2D}} + \frac{f_2}{M_{Cl}}\right]^{1/2}.$$

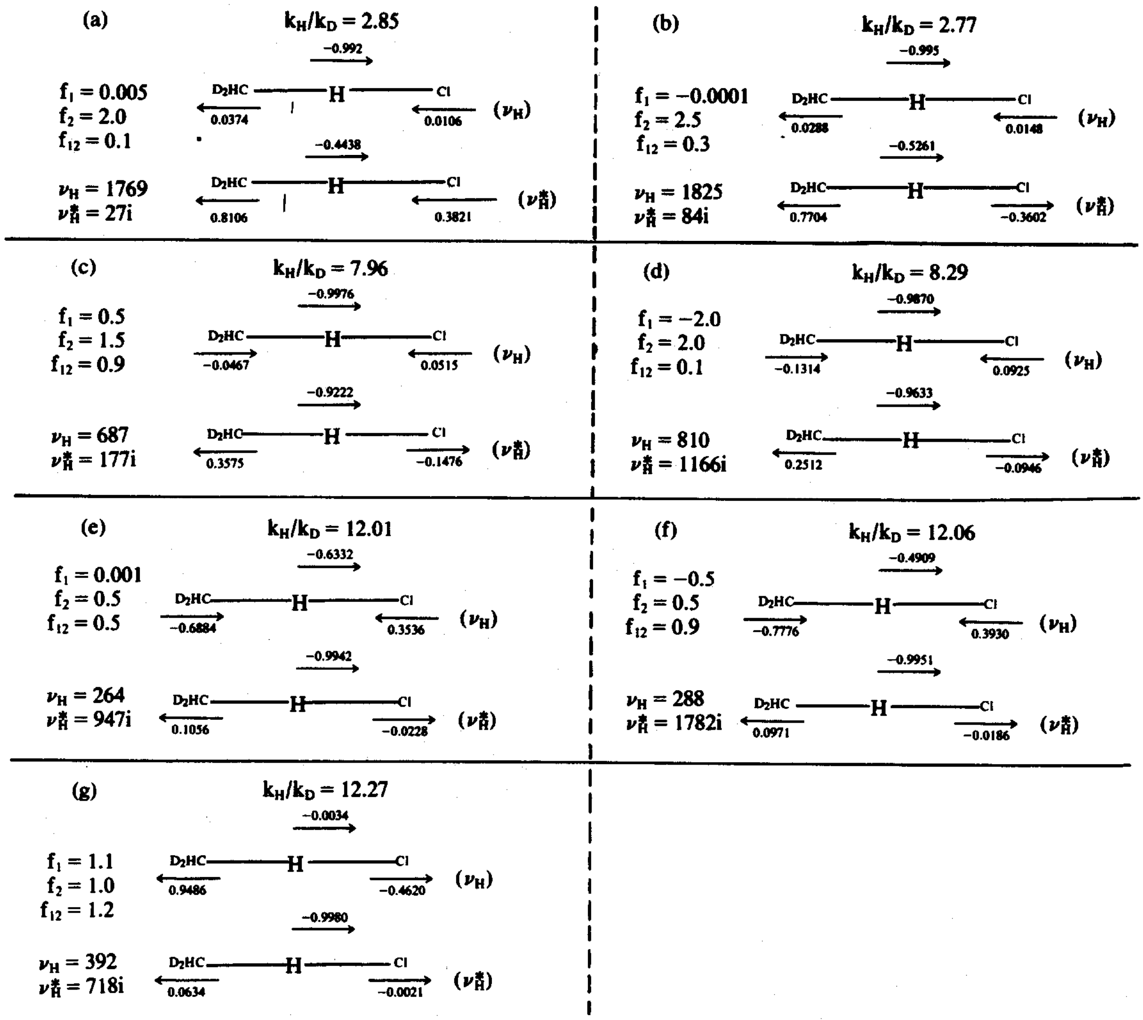


Fig. 4. Correlation of Isotope Effects and Nuclear Displacements. Frequencies are in cm^{-1}, arrows represent relative direction of motion while the magnitude of the adjacent number indicates that atom's relative displacement for that vibrational mode.

Since (f_1/M_{CH_2H}) and (f_2/M_{Cl}) are relatively small terms, it can be seen that at very low isotope effects (considerable imbalance between f_1 and f_2 and very low f_{12}), the isotope mass (M_D) dominates the expression in the square root term and k_H/k_D is reduced. However, as f_{12} increases the value of $(f_1 + f_2 - 2f_{12})$ approaches zero and the masses of the end groups become more important.

Vibrational symmetry

Consider the system $HD_2C\overset{r_1}{\text{———}}H\overset{r_2}{\text{———}}Cl$. A symmetric vibration results in r_1 and r_2 both being distorted positively (stretched) or negatively (compressed) and an antisymmetric vibration results in a stretch of one bond and a compression of the other. Figure 5 displays this graphically, a symmetric vibration corresponding to a line segment with positive slope and an antisymmetric vibration corresponding to a line segment with negative slope. It is frequently assumed that the real and imaginary stretches correspond to line segments that are at right angles to each other. However, as a result of the eigenvector correlation accomplished in this study, a considerably different point of view is generated. ϕ_V may be defined as the angle between the positive x-axis and the instantaneous displacement vector which represents the real symmetric stretch (see Fig. 5).

$$\phi_V = \tan^{-1}\left(\frac{r_1e_1}{r_2e_2}\right) = \tan^{-1}\left[1.0632\left(\frac{e_1}{e_2}\right)_V\right].$$

Likewise, for the imaginary frequency:

$$\phi_{V^*} = \tan^{-1}\left[1.0632\left(\frac{e_1}{e_2}\right)_V\right]$$

where $(e_1/e_2)_V$ represents the ratio of coefficients for r_{CH} and r_{HCl} in the eigenvector for the real mode. $(e_1/e_2)_{V^*}$ represents the same ratio for the imaginary mode. Table 5 provides an analysis of ϕ_V and ϕ_{V^*}. Only the abstraction data for hydrogen has been provided since deuterium abstraction has been found to follow a very similar pattern.

Of interest in Table 5 is the observation that a high kinetic isotope effect can be obtained even in situations where the real frequence is antisymmetric. Further, the common practice of depicting the real stretching mode perpendicular to the reaction coordinate (imaginary mode) may represent the exception more than the rule. It should be pointed out that this lack of perpendicularity is not

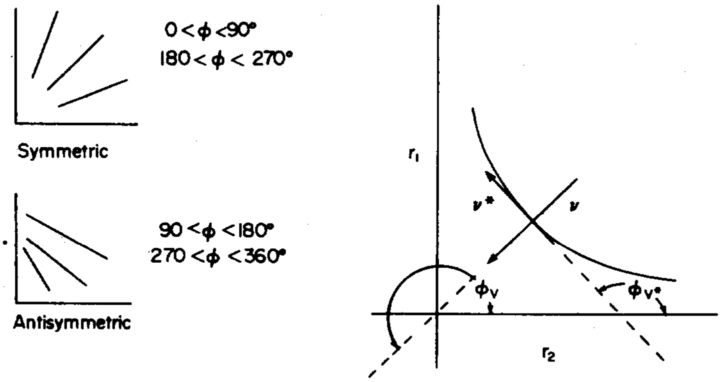


Fig. 5. Nuclear Displacements of the Transition State Modes. r_1 and r_2 are the C–H and H–Cl bond distances respectively. The curved path on the right represents the reaction pathway. The nuclear displacements of the real and imaginary normal modes of the transition state are denoted by ν and ν^*. The angles ϕ_V and ϕ_{V^*} between these vectors and the r_2 axis serve to differentiate the terms symmetric and antisymmetric. The difference between ϕ_V and ϕ_{V^*} is the angle between the nuclear displacements of the real and imaginary modes.

Table 5. Isotope effects and eigenvector analysis

	Real Stretch[b]		Imaginary Stretch[b]				
k_H/k_D	e_1	e_2	e_1	e_2	ϕ_V[a]	ϕ_{V*}	$\Delta\phi$
Date of Table 3 (Hydrogen Abstraction)							
2.86	0.6945	-0.7194	0.9986	-0.0522	134A	93	41
4.25	0.6675	-0.7335	0.9501	-0.3090	136A	107	29
4.73	0.6412	-0.7371	0.9189	-0.3938	137A	112	19
5.90	0.5983	-0.5921	0.9020	-0.4279	133A	114	12
7.96	0.6301	-0.7391	0.8408	-0.5411	138A	121	15
8.23	0.4710	-0.5902	0.7989	-0.5896	140A	125	15
9.14	0.5848	-0.7604	0.8060	-0.5912	141A	125	16
11.12	0.4566	-0.8826	0.7579	-0.6511	151A	129	22
12.01	-0.0516	-0.9811	0.7282	-0.6839	183S	131	52
12.27	0.6293	0.3222	0.7079	-0.7062	247S	133	114
Data of Table 4 (Hydrogen Abstraction)							
2.77	0.6899	-0.7235	0.9908	-0.1348	135A	97	38
3.55	0.6689	-0.7352	0.9371	-0.3219	136A	108	28
4.98	0.6218	-0.7374	0.8758	-0.4485	138A	116	22
6.74	0.4728	-0.6592	0.8169	-0.5465	143A	122	21
8.29	0.3881	-0.5206	0.7842	-0.5964	142A	126	16
9.73	0.3772	-0.6065	0.7668	-0.6294	147A	128	19
10.31	0.2921	-0.6101	0.7529	-0.6449	153A	129	24
11.04	0.2041	-0.6231	0.7437	-0.6590	161A	130	31
11.25	0.1416	-0.4188	0.7450	-0.6608	160A	130	30
12.06	-0.2804	-0.9191	0.7235	-0.6878	198S	132	66

[a] A = Antisymmetric; S = Symmetric.

[b] e_1 and e_2 are the normal mode eigenvector coefficients as defined in the text.

associated with a mass imbalance in the end groups. Calculations on models having identical mass end groups but with the force constants used in Table 5 led to similar deviations from perpendicularity.

In summary our data add to the argument[5–8] that the Westheimer model may be misleading in cases where large isotope effects are observed, and that the common assumption that transition state symmetry and large isotope effects are related should only be used with a great deal of caution. A wide variety of asymmetric transition states can also give large isotope effects providing that f_{12} is sufficiently large. This is because the end group motion dominates the real vibrational frequency and, therefore, the mass of the central hydrogen or deuterium has relatively little effect. This results in the zero point energies of this mode being the same for a hydrogen or deuterium abstraction—the condition necessary for a large kinetic isotope effect. This may be a frequently occurring case since it is reasonable to expect that the interaction constant associated with hydrogen between two atoms in an activated complex is fairly large.[4,13] In addition large isotope effects in reactions known to have asymmetric transition states may not necessarily be due to tunnelling.[14] Variations in the magnitude of the isotope effect in reactions with large interaction constants may in fact be due to tunnelling as suggested by Bell[14] or by bending zero point energy contributions as suggested by Willi and Wolfsberg.[6,8]

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