

# Ground States of Molecules. 51.<sup>1</sup>

## MNDO (Modified Neglect of Diatomic Overlap)

### Calculations of Kinetic Isotope Effects

S. Bruce Brown,<sup>2a</sup> Michael J. S. Dewar,\* George P. Ford,<sup>2b</sup> Donna J. Nelson,<sup>2a</sup> and Henry S. Rzepa<sup>2b</sup>

Contribution from the Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712. Received April 3, 1978

**Abstract:** Transition states for hydrogen abstraction by methyl and trifluoromethyl radicals from ethane and methane were located using the MNDO semiempirical SCF-MO method. Although the energies of activation were badly overestimated, the kinetic deuterium isotope effects, derived from the calculated normal vibrational frequencies of the reactants and transition states, agreed well with other model calculations and with experiment at high temperatures. At lower temperatures, the experimental values were higher than the calculated ones, due to proton tunnelling, neglected in our calculations. Calculated and observed isotope effects are compared for several other reactions.

The main purpose of the work reported in this series of papers has been the development of a practical procedure for studying the course of chemical reactions, this being an area inaccessible to direct experimental study and of obvious major importance. While our two latest methods, MINDO/3<sup>3</sup> and MNDO,<sup>4</sup> have given encouraging results,<sup>5</sup> there are obvious uncertainties attached to the extrapolation of such empirical procedures into areas where experimental data are lacking, e.g., to the nonequilibrium segments of potential surfaces separating the minima corresponding to stable molecules. Any experimental tests of the ability of MINDO/3 and MNDO to reproduce these would therefore be of great value.

One obvious check is provided by the calculation of molecular vibration frequencies, these being a measure of the curvatures of potential surfaces around the corresponding minima. Detailed calculations for a wide variety of molecules have indeed shown that vibration frequencies are quite well reproduced by MINDO/3<sup>6</sup> and MNDO,<sup>7</sup> the agreement being usually within  $\pm 10\%$ . The calculated geometries and vibration frequencies of molecules are indeed good enough for their thermodynamic properties (entropies, specific heats) to be calculated with surprising accuracy.<sup>8</sup>

According to the transition-state approximation, there are three further properties of the intermediate segments of potential surfaces that can be measured, i.e., the enthalpies and entropies of transition states, and the changes in rate brought about by isotopic substitution, i.e., kinetic isotope effects. The latter arise from differential changes in the entropies and vibrational energies of the reactants and corresponding transition states, due to isotopic shifts in the vibrational frequencies. Previous work has shown<sup>5</sup> that enthalpies of activation are mostly reproduced by MINDO/3 and MNDO with an accuracy equal to that for heats of formation of stable species, and calculated entropies<sup>8</sup> of activation seem to agree at least as well with experiment. Since MINDO/3 has been shown<sup>9</sup> to reproduce isotopic frequency shifts very well, it seemed likely that the same would prove true of kinetic isotope effects. One example of such success has already been reported,<sup>10</sup> here we present the results of a detailed study of kinetic isotope effects for some hydrogen (deuterium) abstraction reactions for which experimental data are available, together with calculated values for some other systems.

#### Theoretical Procedure

The calculations were carried out using the published MNDO method.<sup>4</sup> Equilibrium and transition state geometries for the reactions of CH<sub>3</sub> or CF<sub>3</sub> with ethane and methane respectively were located, with full optimization of *all* geomet-

rical variables, using standard procedures which have been described in detail elsewhere.<sup>5</sup> Open-shell species were calculated using a spin-unrestricted version (UMNDO<sup>11</sup>) of MNDO. The force constant matrices for all stationary points located in the potential surface were obtained by standard methods.<sup>7,12</sup> These were shown to have one, and only one, negative eigenvalue for structures corresponding to transition states<sup>13</sup> and no negative eigenvalues for structures corresponding to stable molecules. Vibrational frequencies of both normal and isotopically substituted molecules were calculated from the force constant matrices in the usual manner.<sup>14</sup> In the rigid-rotor-harmonic-oscillator approximation and neglecting tunnelling effects, the kinetic isotope effect for a bimolecular reaction has been shown to be given by eq 1-4.<sup>15</sup>

$$\frac{k_1 s_2^A s_2^B s_1^C}{k_2 s_1^A s_1^B s_2^C} = \text{HRR} = \frac{\nu^{\ddagger 1}}{\nu^{\ddagger 2}} (\text{VP})(\text{EXC})(\text{ZPE}) \quad (1)$$

$$\text{VP} = \frac{\prod_i^{3n-6 A} \frac{u_{2i}}{u_{1i}} \prod_i^{3n-6 B} \frac{u_{2i}}{u_{1i}}}{\prod_i^{3n-7 C} \frac{u_{2i}}{u_{1i}}} \quad (2)$$

$$\text{EXC} = \frac{\prod_i^{3n-6 A} \frac{1 - e^{-u_{1i}}}{1 - e^{-u_{2i}}} \prod_i^{3n-6 B} \frac{1 - e^{-u_{1i}}}{1 - e^{-u_{2i}}}}{\prod_i^{3n-7 C} \frac{1 - e^{-u_{1i}}}{1 - e^{-u_{2i}}}} \quad (3)$$

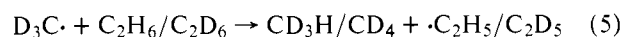
ZPE =

$$\frac{\exp\left[\sum_i^{3n-6 A} (u_{1i} - u_{2i})/2\right] \exp\left[\sum_i^{3n-6 B} (u_{1i} - u_{2i})/2\right]}{\exp\left[\sum_i^{3n-7 C} (u_{1i} - u_{2i})/2\right]} \quad (4)$$

Superscripts A, B, and C refer to the reactants A and B and the transition state C, subscripts 1 and 2 refer to light and heavy isotopes, *s* are symmetry numbers,  $\nu^{\ddagger}$  refers to the frequency of the imaginary mode of the transition state, and  $u_i = h\nu_i/kT$ .

#### Results and Discussion

Our first calculations referred to the reactions of methyl radical with ethane or perdeuterioethane (eq 5), and of trifluoromethyl radical with methane or perdeuteriomethane (eq 6), processes which have been studied in detail over a wide



range of temperatures by numerous investigators.<sup>16,17</sup> Figure 1 shows the geometries calculated for the reactants and transition states. It will be seen that while methyl radical is predicted to be planar and trifluoromethyl pyramidal, apparently

**Table I.** Observed and Calculated Deuterium Kinetic Isotope Effects for the Hydrogen Abstraction Reactions of Methyl and Trifluoromethyl Radicals

reaction	temp, K	obsd	MNDO	ref
$CD_3\cdot + C_2H_6/C_2D_6$	563	3.86	2.97	<i>a</i>
	604	3.56	2.76	
	611	3.65	2.73	
	666	3.12	2.52	
	760	2.79	2.26	
	$\infty$		1.35	
$CF_3\cdot + CH_4/CD_4$	325	18.5	5.63	<i>b</i>
	422	7.59	3.93	
	588	3.56	2.73	
	710	2.69	2.32	
	1015	2.09	1.84	
	1710	1.57	1.53	
	1880	1.54	1.49	
$\infty$		1.35		

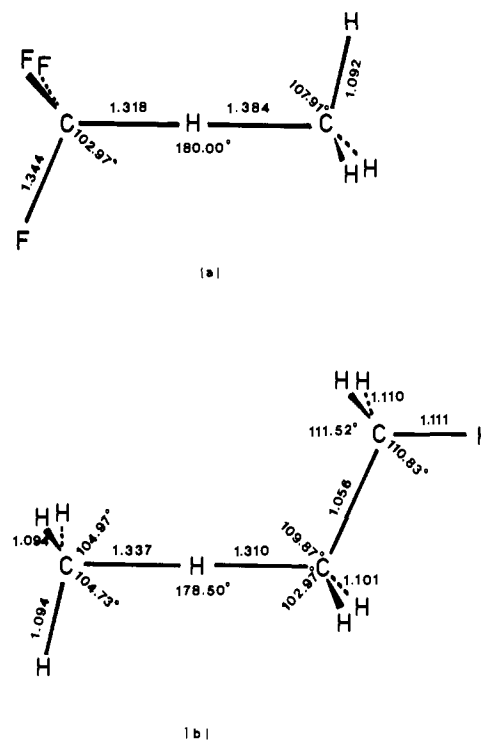
*a* J. R. McNesby, *J. Phys. Chem.*, **64**, 1671 (1960). *b* Data<sup>17</sup> for the reactions of  $CHD_3$  and  $CH_2D_2$  with  $\cdot CF_3$ .

in agreement with experiment,<sup>18,19</sup> both are pyramidal in the corresponding transition states.

The observed activation energies varied somewhat with temperature, being ca 11 kcal/mol.<sup>16,17</sup> Our calculated values (32.7 kcal/mol for eq 5; 27.2 kcal/mol for eq 6) are therefore much too large.<sup>20</sup> One of the few systematic errors in MNDO in its present form is a tendency to underestimate the strengths of two-electron three-center bonds, which has manifested itself in calculations for nonclassical carbonium ions<sup>4b</sup> and boron hydrides.<sup>4c</sup> Apparently a similar error holds for the three-electron three-center bonds present in these transition states.

This is one respect in which MNDO is less satisfactory than the earlier MINDO/3 procedure which has been found to give good results for "nonclassical" carbonium ions.<sup>23</sup>

Table I compares the calculated deuterium kinetic isotope effects with those obtained over a wide range of temperatures. The agreement is excellent at high temperatures but the calculated values become progressively too small as the temperature decreases. Similar discrepancies have been reported by Johnston<sup>17</sup> for the  $CF_3-CH_4$  system, for calculations based on an assumed force field<sup>24</sup> for the transition state. Johnston considered a variety of simple models, ranging from a system based on just three point masses to a treatment in terms of nine atomic masses. The results from all of these were similar over a wide range of temperature and also similar to the results obtained in the present study. This agreement suggests that the isotope effect is mainly determined by the nature of the bonds attached directly to the migrating hydrogen atom. Johnston assigned equal lengths (1.318 Å) to both these bonds, identical with our value for the bond to trifluoromethyl and slightly shorter than ours for the bond to methyl. Since our procedure leads directly to a complete Cartesian force constant matrix, no meaningful comparison with the valence force field assumed by Johnston<sup>17</sup> is possible. The frequencies of the normal vibrations associated with hydrogen transfer calculated here are somewhat higher than those obtained by Johnston (cf. Table II). However, we expect our values to be overestimated somewhat in view of the known tendency<sup>7</sup> of the MNDO method to overestimate CH vibration frequencies. Nevertheless our value (1.345) for the ratio  $\nu_H^\ddagger/\nu_D^\ddagger$ , equal to the high-temperature limit for the predicted isotope effect, is close to those estimated by Johnston, which ranged from 1.403 for the simplest to 1.391 for the more complete model. The errors associated with the calculated kinetic isotope effects at lower temperatures are undoubtedly due, as Johnston pointed out, to hydrogen tunnelling, which was neglected in both sets of



**Figure 1.** Calculated (MNDO) transition-state geometries for the reactions (a)  $CH_4 + CF_3$  and (b)  $CH_3CH_3 + CH_3$ .

calculations and which plays an increasingly important role at lower temperatures. Johnston showed that the discrepancies could be satisfactorily explained on this basis. Since, as Figure 2 indicates, Johnston's force field leads to results very similar to those given by MNDO, his conclusions apply equally to the MNDO ones.

It would of course be possible to calculate the potential surface in sufficient detail for the tunnelling corrections to be evaluated directly. This, however, would destroy the simplicity of our approach which in its present form may be applied routinely to any reaction for which the transition state has been located. The calculation of the necessary vibrational frequencies is straightforward, requiring only the output geometry from the MNDO program. In those cases where the tunnelling factor is relatively small, it can be evaluated approximately by one of several alternative procedures which we will discuss presently. Here of course the correction is too large to be estimated in this way.

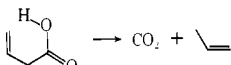
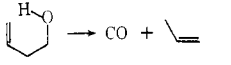
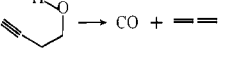
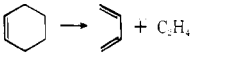
Thus in spite of the unusually large errors in the activation energies calculated for these reactions, the MNDO predictions of isotope effects seem to be in good agreement with experiment. This is interesting, because it suggests that comparisons of calculated and observed kinetic isotope effects may allow a distinction between different possible mechanisms for a reaction in cases where the calculated activation energies do not differ sufficiently for such a distinction to be made. A further point of interest is the good agreement between the MNDO isotope effects and those measured at high temperatures, where tunnelling should be unimportant. Apparently no errors have arisen from our treatment of the relevant species as rigid rotators. This is a fortunate conclusion since serious problems arise in the treatment of species with internal rotation, and since most reactions involve reactants and/or transition states that fall in this category. It should also be possible to use MINDO/3 in place of MNDO for such calculations since the vibration frequencies given by MINDO/3 agree with experiment as well as do those from MNDO. This could be useful in the isolated cases (e.g., carbocations)<sup>23</sup> where MINDO/3 is superior to the present version of MNDO.

**Table II.** Calculated (MNDO) Vibrational Frequencies Used to Obtain the Kinetic Isotope Effect Data in Table I<sup>a-c</sup>

	C <sub>2</sub> H <sub>6</sub>	C <sub>2</sub> D <sub>6</sub>		CD <sub>3</sub> ·H·C <sub>2</sub> H <sub>5</sub>	CD <sub>3</sub> ·D·C <sub>2</sub> D <sub>5</sub>	
<i>D</i> <sub>3d</sub> : a <sub>1g</sub>	3339	2392	C <sub>s</sub> : a'	3350	2491	
	1499	1336		3338	2422	
	1217	954		3256	2410	
	187	126		2728*	2402	
	a <sub>1u</sub>	3347		2402	2491	2391
	a <sub>2u</sub>	1479		1130	2413	2020*
	e <sub>g</sub>	3256		2402	1497	1349
		1440		1078	1459	1110
		1185		917	1441	1075
	e <sub>u</sub>	3276		2421	1385	1055
	1444	1049	1247	1048		
	907	653	1213	1015		
			1061	959		
			1042	933		
			979	737		
<i>C</i> <sub>3c</sub> : a <sub>1</sub>	CF <sub>3</sub> ·H·CH <sub>3</sub>	CF <sub>3</sub> ·D·CD <sub>3</sub>	a''	566	534	
	3391	2409		462	437	
	2411* <sup>d</sup>	1792 <sup>d</sup>		164	147	
	1400	1356		3317	2492	
	1339	1048		3262	2455	
	782	776		2492	2406	
	453	413		1437	1064	
	a <sub>2</sub>	31		22	1329	1054
	e	3382		2507	1180	977
		1629		1626	1044	915
		1413		1048	912	658
		1332		957	680	580
		651		558	313	260
		524		456	128	93
		142		132	22	21
<i>T</i> <sub>d</sub> : a <sub>1</sub>	CH <sub>4</sub>	CD <sub>4</sub>				
	3387	2396				
	e	1442				
	f <sub>2</sub>	3306	2440			
	1436	1090				

<sup>a</sup> Units, cm<sup>-1</sup>. <sup>b</sup> Since the reactants CH<sub>3</sub>· in eq 5 and CF<sub>3</sub>· in eq 6 are common to the reactions of both the heavy and light reactants their vibrational frequencies cancel in eq 1-4 and are not therefore required. <sup>c</sup> The vibrational frequencies corresponding to the imaginary modes of the various transition states are marked with an asterisk. <sup>d</sup> Values of 1995 and 1233 cm<sup>-1</sup> were obtained by Johnston<sup>17</sup> for these quantities using an empirical force field and a model of nine atomic masses.

**Table III.** Comparison of Calculated (MINDO/3 and MNDO) Kinetic Isotope Effects

reaction	temp, K	isotope	KIE(obsd)	KIE(calcd)
(A) 	650 550	H/D <sup>12</sup> C/ <sup>14</sup> C	2.7 <sup>a</sup> 1.035 <sup>c</sup>	2.1 <sup>b</sup> 1.031 <sup>b</sup>
(B) 	650	H/D	2.7 <sup>a,d</sup>	1.72 <sup>b</sup>
(C) 	650	H/D	2.7 <sup>a</sup>	1.67 <sup>b</sup>
(D) CH <sub>3</sub> NC → CH <sub>2</sub> CN	503 503	H/D <sup>12</sup> C/ <sup>13</sup> C	1.07 <sup>f</sup> 1.018 <sup>g</sup>	1.062 <sup>e</sup> 1.021 <sup>e</sup>
(E) 	493	H/D	1.173 <sup>h</sup>	1.220 <sup>b,i</sup>

<sup>a</sup> Reference 26. <sup>b</sup> MINDO/3 calculation. <sup>c</sup> Data for PhCH=CHC(Me)<sub>2</sub><sup>14</sup>CO<sub>2</sub>H: D. B. Bigley and J. C. Thurman, *J. Chem. Soc. B*, 941 (1967). <sup>d</sup> Data for CH<sub>2</sub>=CHCH<sub>2</sub>CHMeOH. <sup>e</sup> MNDO calculation. <sup>f</sup> Isotope effect at the high-pressure limit. Cf. F. W. Schneider and B. S. Rabinovitch, *J. Am. Chem. Soc.*, **85**, 2365 (1963). <sup>g</sup> Average high-pressure-limit isotope effect for label in C-Me and C-CN: J. F. Wettaw and L. B. Sims, *J. Phys. Chem.*, **72**, 3440 (1968). <sup>h</sup> Data for the retro-Diels-Alder reaction of dibenzobicyclo[2.2.2]octane: M. Taagepera and E. R. Thornton, *J. Am. Chem. Soc.*, **94**, 1168 (1972). Cf. ref 25. <sup>i</sup> *k*<sub>H</sub>/*k*<sub>D</sub> refers to 4,4,5,5-tetra-deuteriocyclohexene.

As a further check on these conclusions, we have calculated deuterium kinetic isotope effects for some additional reactions involving hydrogen abstraction, i.e., two retroene reactions (B and C in Table III) and a molecular rearrangement (D in Table III). The results are compared with experiment in Table II which also recapitulates data from earlier papers for a third retroene reaction (A)<sup>10</sup> and the archetypal Diels-Alder re-

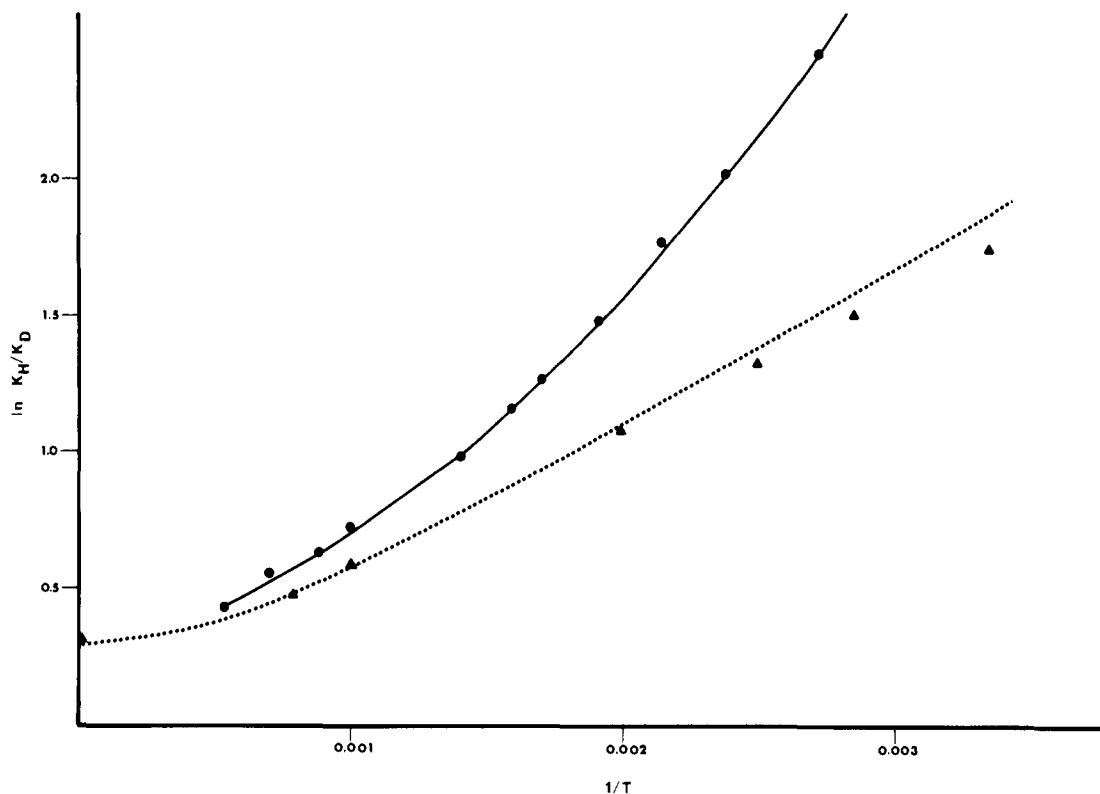
action<sup>25</sup> (E). The calculations were carried out using MINDO/3 except for reaction D where MNDO was used. In two cases (A and D) carbon secondary isotope effects have been reported so we have included calculated values for these as well. It will be seen that the agreement with experiment is very satisfactory.

In the case of reactions A-C, the deuterium isotope effects<sup>26</sup>

**Table IV.** Comparison between Calculated (MINDO/3) and Observed Activation Parameters for the Retroene Decompositions (A-C)<sup>a</sup> at 650 K

	A		B		C	
	calcd	obsd	calcd	obsd	calcd	obsd
$\Delta H^\ddagger$ , kcal mol <sup>-1</sup>	46.3 <sup>b</sup>	39.3 ± 1.6 <sup>c</sup>	58.6 <sup>d</sup>	39.5 ± 1.3 <sup>e,f</sup>	63.4 <sup>g</sup>	38.2 ± 5.1 <sup>e,h</sup>
$\Delta S^\ddagger$ , cal mol <sup>-1</sup> K <sup>-1</sup>	-13.9	-10.2 ± 2.5 <sup>c</sup>	-9.0	-11.2 ± 1.9 <sup>e,f</sup>	-9.1	-11.3 ± 5.1 <sup>e,h</sup>
$\Delta H$ , kcal mol <sup>-1</sup> <sup>i</sup>	-6.8	-6.8 <sup>j</sup>	25.4	15.3 <sup>l</sup>	31.5	15.9 <sup>m</sup>
$\Delta S$ , cal mol <sup>-1</sup> K <sup>-1</sup> <sup>n</sup>	28.3	30.5 <sup>o</sup>	39.8	33.6 <sup>q</sup>	31.3	
$k_H/k_D$ (including tunnelling)	2.47 <sup>r</sup>	2.7 <sup>s</sup>	1.78 <sup>r</sup>	2.7 <sup>s,t</sup>	1.72 <sup>r</sup>	2.7 <sup>s</sup>
$\nu_H^\ddagger$ , cm <sup>-1</sup>	1395		808		654	
$\nu_D^\ddagger$ , cm <sup>-1</sup>	1118		676		542	
% H transfer <sup>u</sup>	54		58		61	

<sup>a</sup> Reaction designation corresponds to that of Table III. <sup>b</sup> Corrected for the zero-point energy and  $\Delta H_{\text{vib}}$  differences at 650 K: 46.3 = 51.4 - (2.7 + 2.4). <sup>c</sup> G. G. Smith and S. E. Blau, *J. Phys. Chem.*, **68**, 1231 (1964). <sup>d</sup> 58.6 = 62.3 - (2.4 + 1.3); cf. footnote b. <sup>e</sup> Activation parameter recalculated from a "least-squares" analysis of the published kinetic data according to the Eyring equation assuming a transmission coefficient of unity. Calculated error limits correspond to the 95% confidence limits of the Student t distribution. <sup>f</sup> Kinetic data from G. G. Smith and B. L. Yates, *J. Chem. Soc.*, 7242 (1965). <sup>g</sup> 63.4 = 65.9 - (1.9 + 0.6); cf. footnote b. <sup>h</sup> Kinetic data from A. Viola, J. H. MacMillan, R. J. Proverb, and B. L. Yates *J. Am. Chem. Soc.*, **93**, 6967 (1971). <sup>i</sup> Heat of reaction. <sup>j</sup> Estimated value from data in footnote k. See ref 10. <sup>k</sup> J. D. Cox and G. Pilcher "Thermochemistry of Organic and Organometallic Compounds", Academic Press, London, 1970. <sup>l</sup> Calculated from data in footnote k and an estimated value<sup>p</sup> of  $\Delta H_f(\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{OH})$ . <sup>m</sup> Estimated value from data in footnote k assuming  $\Delta H_f(\text{CH}\equiv\text{CCH}_2\text{CH}_2\text{OH}) \approx \Delta H_f(\text{CH}\equiv\text{CCH}_2\text{CH}_3) - \Delta H_f(n\text{-C}_4\text{H}_{10}) + \Delta H_f(n\text{-C}_4\text{H}_9\text{OH})$ . <sup>n</sup> Entropy of reaction. <sup>o</sup> Estimated value from footnote p. <sup>p</sup> S. W. Benson and H. E. O'Neal, "Kinetic Data on Gas Phase Unimolecular Reactions", National Standard Reference Data Series, National Bureau of Standards, Washington, D.C. <sup>q</sup> Calculated from data tabulated in ref 8 and an estimated value<sup>p</sup> of  $S^\circ(\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{OH})$ . <sup>r</sup> MINDO/3 value including a tunnelling correction calculated from eq 7. <sup>s</sup> Reference 26. <sup>t</sup> Data for  $\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{MeOH}$ . <sup>u</sup> Percentage transfer of hydrogen in transition state:  $100 \times d(\text{OH})/(d(\text{OH}) + d(\text{CH}))$ .

**Figure 2.** Kinetic isotope effects for the reaction  $\text{CF}_3 + \text{CH}_4/\text{CD}_4$ . Experimental values (●) and model calculations (▲) by Johnston et al.<sup>17</sup>; MINDO values (- -).

are only moderately well reproduced—a discrepancy which can only partially be attributed to tunnelling. According to Bell<sup>27</sup> the effect of tunnelling on a reaction is to enhance the specific rate constant by a factor  $\Gamma$  given by

$$\Gamma = (u^\ddagger/2)/\sin(u^\ddagger/2) \quad (7)$$

Although approximate, there is some justification<sup>28</sup> for Bell's formula provided that (as here)  $u^\ddagger < \pi$  and  $2\pi V^\ddagger/h\nu^\ddagger > 2$ , where  $V^\ddagger$  is the potential barrier hindering the reaction. We have accordingly calculated  $\Gamma(\text{H})/\Gamma(\text{D})$  and hence estimated "corrected" isotope effects (Table IV).

Although the calculated enthalpy of activation for reaction A, the retroene decomposition of but-3-enoic acid, is slightly overestimated, the various reaction parameters,  $\Delta S^\ddagger$ ,  $\Delta S$ ,  $k_H/k_D$ , and  $k_{12}/k_{14}$ , are very satisfactorily reproduced.<sup>10</sup> The small calculated tunnelling correction brings the MINDO/3 value into substantially better agreement with experiment. On the other hand, the agreement between the calculated and experimental quantities in cases B and C is decidedly worse, probably because of the serious overestimation of the endothermicities of these two reactions. This error has two consequences: the calculated energies of activation are too large

and the structures of the transition states are correspondingly distorted to be more product-like. This is in accord with the Bell-Evans-Polanyi principle<sup>29</sup> (or Hammond postulate<sup>30</sup>) and is manifested in the calculated<sup>31</sup> degree of hydrogen transfer in the transition states (Table III). Thus in reaction A, which is calculated to be essentially concerted, the calculated value of  $k_H/k_D$  is at a maximum and in reasonable agreement with experiment. In reactions B and C, where the transition states are calculated to be too product-like,  $k_H/k_D$  is underestimated. This effect also leads to too small a curvature along the reaction coordinate and hence (cf. eq 7) the degree of tunnelling is also underestimated for reactions B and C.

It was suggested above that kinetic isotope effects may be calculated reliably from either MINDO/3 or MNDO even in cases where the activation enthalpies are not satisfactorily reproduced. This, however, is not true when the calculated transition state geometries are in error because vibration frequencies are sensitive to changes in molecular geometry. Consequently the accurate reproduction of kinetic isotope effects should be a powerful test of calculated transition state geometry, more so than the reproduction of entropies of activation since the latter do not explicitly include the normal vibration corresponding to the reaction coordinate.

Reactions D and E provide examples of secondary deuterium isotope effects which are not expected to be subject to the effects of tunnelling. The methyl isocyanide-acetonitrile rearrangement has previously been treated theoretically by Dewar and Kohn in the MINDO/2 approximation. The  $\pi$ -complex<sup>32</sup> transition state has been relocated using the MNDO method and very satisfactory agreement between the calculated and observed kinetic isotope effects obtained. For full details of the retro-Diels-Alder reaction (E) of cyclohexene the reader is referred to our recent publication on this subject.<sup>25</sup>

## Conclusions

The use of kinetic isotope effects in studies of reaction mechanisms is now a well-recognized and widely used technique. Its value has, however, been tempered by the lack of any satisfactory quantitative procedure for relating the measured effects to transition-state structures. It is often assumed that variations in isotope effects can be related to the degree of bond breaking or bond formation in the transition state. This, however, is a dubious assumption even in a qualitative sense, while attempts to use quantitative relationships between bond order and isotope effects are quite without foundation. The apparent ability of MINDO/3 and MNDO to provide such information should therefore be of major value, placing the interpretation of isotope effects on a quantitative basis. Secondary isotope effects should prove especially useful in this connection since here no complications arise as a result of tunnelling. Equally, however, our calculations may be of value in helping to assess the importance of tunnelling in reactions where hydrogen is transferred from one atom to another.

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**Supplementary Material Available:** Tables S1-S8 giving Cartesian coordinates and force constant matrices necessary for the calculation of the vibrational frequencies in Table II (20 pages). Ordering information is given on any current masthead page.

## References and Notes

- (1) For part 50 see, M. J. S. Dewar and M. L. McKee, *J. Am. Chem. Soc.*, **100**, 7499 (1978).
- (2) (a) Robert A. Welch Predoctoral Fellow; (b) Robert A. Welch Postdoctoral Fellow.
- (3) R. C. Bingham, M. J. S. Dewar, and D. H. Lo, *J. Am. Chem. Soc.*, **97**, 1285 (1975).
- (4) (a) M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, **99**, 4899 (1977); (b) *ibid.*, **99**, 4907 (1977); (c) M. J. S. Dewar and M. L. McKee, *ibid.*, **99**, 5231 (1977); (d) M. J. S. Dewar and H. S. Rzepa, *ibid.*, **100**, 58 (1978).
- (5) (a) M. J. S. Dewar, "Further Perspectives in Organic Chemistry, Ciba Foundation Symposium 53", Elsevier, Amsterdam, 1978, p 102; (b) *Faraday Discuss. Chem. Soc.*, **No. 62**, 197 (1977); (c) *Chem. Br.*, **11**, 97 (1975); (d) *Science*, **197**, 1037 (1975).
- (6) M. J. S. Dewar and G. P. Ford, *J. Am. Chem. Soc.*, **99**, 1685 (1977).
- (7) M. J. S. Dewar, G. P. Ford, M. L. McKee, H. S. Rzepa, W. Thiel, and Y. Yamaguchi, *J. Mol. Struct.*, **43**, 135 (1978).
- (8) M. J. S. Dewar and G. P. Ford, *J. Am. Chem. Soc.*, **99**, 7822 (1977).
- (9) M. J. S. Dewar and H. S. Rzepa, *J. Mol. Struct.*, **40**, 145 (1977).
- (10) M. J. S. Dewar and G. P. Ford, *J. Am. Chem. Soc.*, **99**, 8343 (1977).
- (11) M. J. S. Dewar, S. Olivella, and H. S. Rzepa, *Chem. Phys. Lett.*, **47**, 80 (1977).
- (12) J. W. McIver and A. Komornicki, *Chem. Phys. Lett.*, **10**, 303 (1971).
- (13) J. N. Murrell and K. J. Laidler, *Trans. Faraday Soc.*, **64**, 371 (1968).
- (14) E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, "Molecular Vibrations", McGraw-Hill, New York, N.Y., 1955.
- (15) C. J. Collins and N. S. Bowman, Eds., *ACS Monogr.*, **No. 167** (1970); A. Maccoll, *Annu. Rep. Prog. Chem., Sect. A*, **77** (1974); E. Bunzel and C. C. Lee, Eds., "Isotopes in Hydrogen Transfer Processes", Elsevier, Amsterdam, 1976.
- (16) P. D. Pacey and J. H. Purnell, *J. Chem. Soc., Faraday Trans. 1*, **68**, 1462 (1972).
- (17) T. E. Sharp and H. S. Johnston, *J. Chem. Phys.*, **37**, 1541 (1962); H. S. Johnston and E. Tschuikow-Roux, *ibid.*, **36**, 463 (1962).
- (18) D. E. Milligan and M. E. Jacox, *J. Chem. Phys.*, **47**, 5146 (1967).
- (19) D. E. Milligan, M. E. Jacox, and J. J. Comeford, *J. Chem. Phys.*, **44**, 4058 (1966).
- (20) Very similar results have been obtained<sup>21</sup> for the analogous reaction<sup>22</sup> ( $\text{CH}_4 + \text{CH}_3$ ) using various ab initio methods.
- (21) M. T. Rayez-Meaume, J. J. Dannenberg, and J. L. Whitten, *J. Am. Chem. Soc.*, **100**, 747 (1978).
- (22) The activation energy calculated for this reaction using MNDO (28.6 kcal mol<sup>-1</sup>) was almost identical to the STO 4-31G value (29.9 kcal mol<sup>-1</sup>), M. J. S. Dewar and D. J. Nelson, unpublished work.
- (23) M. J. S. Dewar and H. S. Rzepa, *J. Am. Chem. Soc.*, **99**, 7432 (1977); P. K. Bischof and M. J. S. Dewar, *ibid.*, **97**, 2278 (1975).
- (24) Cf. N. L. Arthur, K. F. Donchi, and J. A. McDonnell, *J. Chem. Soc., Faraday Trans. 1*, **71**, 2431 (1975).
- (25) M. J. S. Dewar, S. Olivella, and H. S. Rzepa, *J. Am. Chem. Soc.*, **100**, 5650 (1978).
- (26) H. Kwart and M. C. Latimore, *J. Am. Chem. Soc.*, **93**, 3770 (1971).
- (27) R. P. Bell, *Trans. Faraday Soc.*, **55**, 1 (1959).
- (28) H. S. Johnstone and D. Rapp, *J. Am. Chem. Soc.*, **83**, 1 (1961).
- (29) R. P. Bell, *Proc. R. Soc. London, Ser. A*, **154**, 414 (1936); M. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, **32**, 1333 (1936).
- (30) G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955).
- (31) The geometries have been published as part of a general review. See ref. 5b.
- (32) M. J. S. Dewar and M. C. Kohn, *J. Am. Chem. Soc.*, **94**, 2704 (1972).