JOURNAL OF THE TENNESSEE ACADEMY OF SCIENCE
VOLUME 64, NUMBER 4, OCTOBER 1989

HYDROGEN KINETIC ISOTOPE EFFECT FOR HYDROGEN-TRANSFER IN *cis*-1,3–PENTADIENE — A MODEL CALCULATION

CHIEN-FON SHIH,[a] BORIS FRANZUS,[b] AND THOMAS T.-S. HUANG
Department of Chemistry
East Tennessee State University
Johnson City, Tennessee 37614

ABSTRACT

Based on transition-state theory, model calculations on the hydrogen kinetic isotope effect (KIE) have demonstrated that the {1,5} sigmatropic hydrogen migration in *cis*-1,3–pentadiene cannot be by linear transfer; alternatively, the H-shift can be better described as proceeding via an out-of-plane bent transition state. For a bent transition state, the H-kinetic isotope effect could be temperature dependent, as has been described by Roth and Konig. However, Kwart's statement that for the transfer of a cyclic isotopic atom, linear transfer is frequently associated with temperature dependent KIE is not accurate. A variety of theoretical considerations are discussed in the report.

INTRODUCTION

Kwart noted[1a] that in the Arrhenius expression

$$k/k' = (A_H/A_D)e^{-\Delta E_a/RT}$$

where $\Delta E_a = E_a(H) - E_a(D)$, if $0.75 \leq A_H/A_D \leq 1.2$ and $\Delta E_a \neq 0$ (i.e., k/k' is temperature dependent) then the transition state should be linear. If, on the other hand, $\Delta E_a \approx 0$, then $k/k' = A_H/A_D$ and is temperature independent, and here the transition state should be nonlinear. Recently, McLennan and Gill[1b] expressed their doubts from a theoretical point of view concerning Kwart's statements and concluded that the proposed criterion of the transition state appeared to be without foundation. In this paper, the {1,5} sigmatropic shift of hydrogen(*) in 1,3–pentadiene is considered (Panel 1 (a)). When delineating the bond angles considered, one must look at the transition state for two angles (α and β) in the migration step (Panel 1 (b)).

In a transition state where $\beta = 0$, one would envision the type of orbital interaction in the non-bonding molecule orbital shown in Panel 1 (c). The problem with this type of configuration lies in the realization that this type of reaction has absolutely no driving force regardless of the value of α. In no way can one rationalize a {1,5} hydrogen migration merely as a whim of the system. Indeed, this is in direct opposition to the orbital symmetry approach, which does involve an appropriate driving force (Panel 1 (d)). Naturally, orbital symmetry is best accomplished by an angle of 90° for β.

These are the two conflicting pictures. One theoretical picture of the transition state requires that it be linear[1,2] ($\beta = 0°$, $\alpha = 180°$); the other orbital symmetry model requires that it be nonlinear with $\beta = 90°$, preferably. Experimental results showed[3] that there was a large temperature dependence ($\Delta E_a = 1.4$ Kcal/mol and $A_H/A_D = 1.15$) over a considerable temperature range. Using the traditionally accepted truism, Kwart pointed out that these results demanded a linear H-transfer transition state. Recent energetic considerations,[4] however, demonstrated that a nonlinear bent transition state is preferred. In this paper, exact model calculations on the hydrogen KIE have been made using the systems considered by Kwart and treating them in terms of both nonlinear and linear hydrogen transfer.

DESCRIPTIONS OF CALCULATIONS AND METHODS

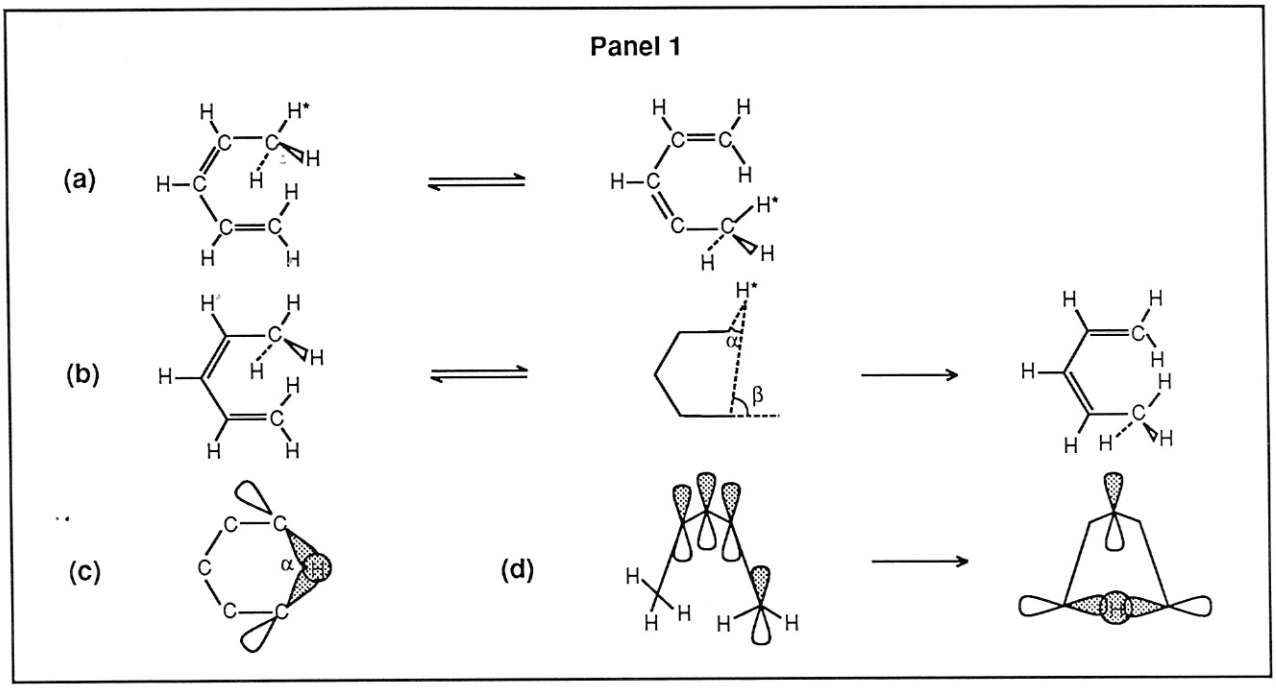
All numerical calculations were made on an IBM 4341-VM computer.

Based on transition state theory, one of the normal modes of vibration in the activated complex is the motion along the reaction coordinate. That is, one frequency must have a zero or imaginary value corresponding to a flat or curved potential barrier, respectively. The method of calculation used in this report is primarily based on the method described by Buddenbaum and Yankwich.[5] They developed a general method for forcing a model transition state of arbitrary complexity to have a preselected imaginary (or zero) frequency corresponding to a preselected vibration motion, or the reaction coordinate. In this report we followed their procedure and only used the simple cases for our calculations.

---

[a]Present address: Department of Chemistry, University of North Carolina, Chapel Hill, NC 27514.

[b]Deceased August 3, 1985.



Schachtschneider's program[6] was used to calculate the vibrational frequencies of both reactants and transition states. The reaction coordinate in the transition state is such that the vibrational motion in that coordinate has associated with it a zero or imaginary frequency. In this report, all barriers are assumed to be flat. Let us denote this reaction coordinate by the column matrix $\mathbf{A}_1$; then according to Wilson's GF matrix formulation,[7]

$$\mathbf{GFA}_1 = 0$$
$$\mathbf{FA}_1 = 0$$

for a given structure. The solution of this equation will thus yield the restriction on the force field of the transition state for the given reaction coordinate. Three types of reaction coordinates are employed:

a. One-element reaction coordinate. A simple bond-cleavage process makes the force constant zero for the bond broken, i.e., $F_{nn} = 0$ corresponding to one non-zero element in $\mathbf{A}_1$, namely a_n.

b. Two-element reaction coordinate. When two non-zero elements are involved in the reaction coordinate, say a_n and a_m, the solution for the equation

$$\begin{pmatrix} F_{nn} & F_{nm} \\ F_{nm} & F_{mm} \end{pmatrix} \begin{pmatrix} a_n \\ a_m \end{pmatrix} = 0$$

requires that

$$F_{nm} = \pm(F_{nn}F_{mm})^{0.5}$$

c. Three-element reaction coordinate. Let a_n, a_m, and a_ℓ be the three chosen non-zero elements in the reaction coordinate; then the force constant restrictions are

$$F_{nm} = \frac{a_n^2 F_{nn} + a_m^2 F_{mm} - a_\ell^2 F_{\ell\ell}}{-2a_n a_m}$$
$$F_{n\ell} = \frac{a_n^2 F_{nn} + a_\ell^2 F_{\ell\ell} - a_m^2 F_{mm}}{-2a_n a_\ell}$$
$$F_{m\ell} = \frac{a_m^2 F_{mm} + a_\ell^2 F_{\ell\ell} - a_n^2 F_{nn}}{-2a_m a_\ell}$$

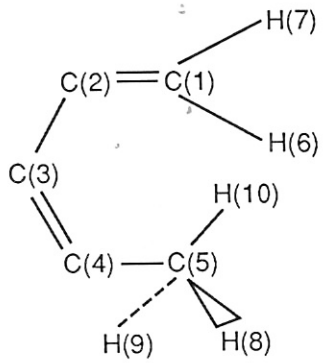
The elements of the reaction coordinate are positive when two motions move symmetrically and negative when they move asymmetrically.

RESULTS AND DISCUSSION

The structure of *cis*-1,3–pentadiene used in the calculations is summarized in Table 1. While the structure of the transition state will depend on the magnitudes of angles α and β, an example is given in Table 2, where α is kept at 115° with various β angles. For all proposed molecular structures a simple procedure has been developed in this laboratory to define a non-redundant set of internal coordinates. Table 3 and Table 4 show the definitions of the internal coordinates and their respective force constants for the reactant (*cis*-1,3–pentadiene) and those for the transition state used in this report (atom numbers are defined in Tables 1 and 2).

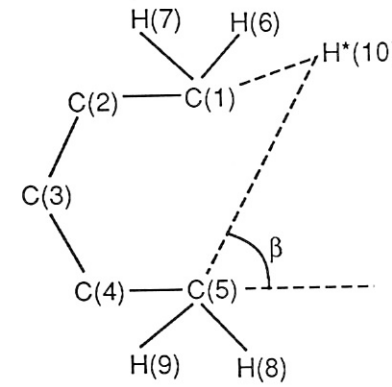
For simplicity, the first group of our calculations was made using only *one* isotopic atom substituted in the reactant molecule such that the reactions would proceed as indicated in Panel 2 (a) and (b). However, this is the simplest case one can use to see the kinetic isotope

Table 1. Structure of *cis*-1,3–pentadiene



Atom number	Cartesian coordinates (Å) x	y	z
1	2.0790	1.2840	0
2	0.7415	1.2840	0
3	0	0	0
4	0.6685	–1.158	0
5	2.1700	–1.158	0
6	2.6470	0.339	0
7	2.6470	2.230	0
8	2.5410	–1.683	0.908
9	2.5410	–1.683	–0.908
10	2.5410	–0.110	0

Table 2. The Structure of the Transition State with Different Angles β, at Angle α = 115°



Atom number	Cartesian coordinates (Å) x	y	z	Angle β
1	2.0850	1.2040	0	
2	0.6950	1.2040	0	
3	0	0	0	
4	0.6950	–1.2040	0	
5	2.0850	–1.2040	0	
6	2.4542	1.8983	0.7863	
7	2.4542	1.8983	–0.7863	
8	2.4542	–1.8983	0.7863	
9	2.4542	–1.8983	–0.7863	
10	2.85655	0	0	(0°)
10	2.75318	0	0.38578	(30°)
10	2.63057	0	0.54557	(45°)
10	2.47078	0	0.66818	(60°)
10	2.28469	0	0.74526	(75°)
10	2.08500	0	0.77155	(90°)

effect sensitivity of each internal coordinate involved in the reaction coordinate.

a. Results for one-element reaction coordinate. If one plots $\ln(k/k')$ vs. $1/T$ for the one-element reaction coordinate undergoing hydrogen transfer, two groups of lines with different magnitudes of slope (I and II) are obtained as shown in Figure 1. Group I includes the plots of the atoms (1–10) stretch and (5–10) stretch; they are identical, as expected from symmetry of the molecules. Group II gives the plots of all others, i.e., the (1–10–5) bend, the (6–1–10) bend, the (6–1–2) bend, and the (6–1–4) torsional bend. As the temperature increases, $\ln(k/k')$ approaches zero from the negative side for all one-element reaction coordinates; this is regarded as an "inverse" isotope effect. The effect of changing angle β is negligible.

b. Results for two-element reaction coordinate. Two-element reaction coordinates are divided into two types, symmetric and asymmetric motions. The results are similar to those of the one-element reaction coordinate except for the occurrence of crossovers, i.e., the isotope effect reverses its direction as temperature varies (see Figure 2). All crossovers occur in the group with asymmetric motions, and as angle β increases, the crossover appears at lower temperatures.

c. Results for three-element reaction coordinate. Three three-element reaction coordinates were employed; they are designated below:

I. atoms (1–10) stretch + (5–10) stretch + (1–5–10) bend

II. atoms (1–10) stretch + (5–10) stretch + (6–1–10–5) torsion

III. atoms (1–10) stretch + (5–10) stretch + (6–1–10) bend

Figure 3 shows the results for I, II, and III, for which

Table 3. The Nonredundant Internal Coordinates Defined in the Calculation and the Diagonal Force Fields of Reactant (*cis*-1,3–pentadiene)

Internal coordinate number	Code[a]	Atom number involved				Force constant (mdyne/Å)
1	1	6	1			5.1
2	1	7	1			5.1
3	1	1	2			9.9
4	1	2	3			5.0
5	1	3	4			9.9
6	1	4	5			5.0
7	1	5	8			4.8
8	1	5	9			4.8
9	1	5	10			4.8
10	2	6	1	7		0.3
11	2	6	1	2		0.5
12	2	1	2	3		0.6
13	2	2	3	4		0.6
14	2	3	4	5		0.6
15	2	4	5	8		0.5
16	2	4	5	9		0.5
17	2	8	5	9		0.46
18	2	8	5	10		0.46
19	2	9	5	10		0.46
20	3	7	1	2	6	0.2
21	4	7	1	2	3	0.2
22	4	1	2	3	4	0.2
23	4	2	3	4	5	0.2
24	4	3	4	5	10	0.2

[a]code: 1 = stretch; 2 = bend; 3 = out-of-plane wag; 4 = torsional.

Table 4. The Nonredundant Internal Coordinates Defined in the Calculation and the Diagonal Force Fields of the Transition State

Internal coordinate number	Code[a]	Atom number involved				Force constant (mdyne/Å)
1	1	1	2			7.62
2	1	2	3			7.62
3	1	4	5			7.62
4	1	1	10			5.1
5	1	5	10			5.1
6	1	1	6			5.1
7	1	1	7			5.1
8	1	5	8			5.1
9	1	5	9			5.1
10	2	1	2	3		0.4
11	2	3	4	5		0.4
12	2	1	10	5		0.4
13	2	6	1	10		0.3
14	2	7	1	10		0.3
15	2	6	1	2		0.5
16	2	7	1	2		0.5
17	2	8	5	10		0.3
18	2	9	5	10		0.3
19	2	8	5	4		0.5
20	3	9	5	4		0.5
21	4	1	4	3	5	0.2
22	4	5	2	1	3	0.2
23	4	6	1	10	5	0.2
24	4	8	5	10	1	0.2

[a]code: 1 = stretch; 2 = bend; 3 = out-of-plane wag; 4 = torsional.

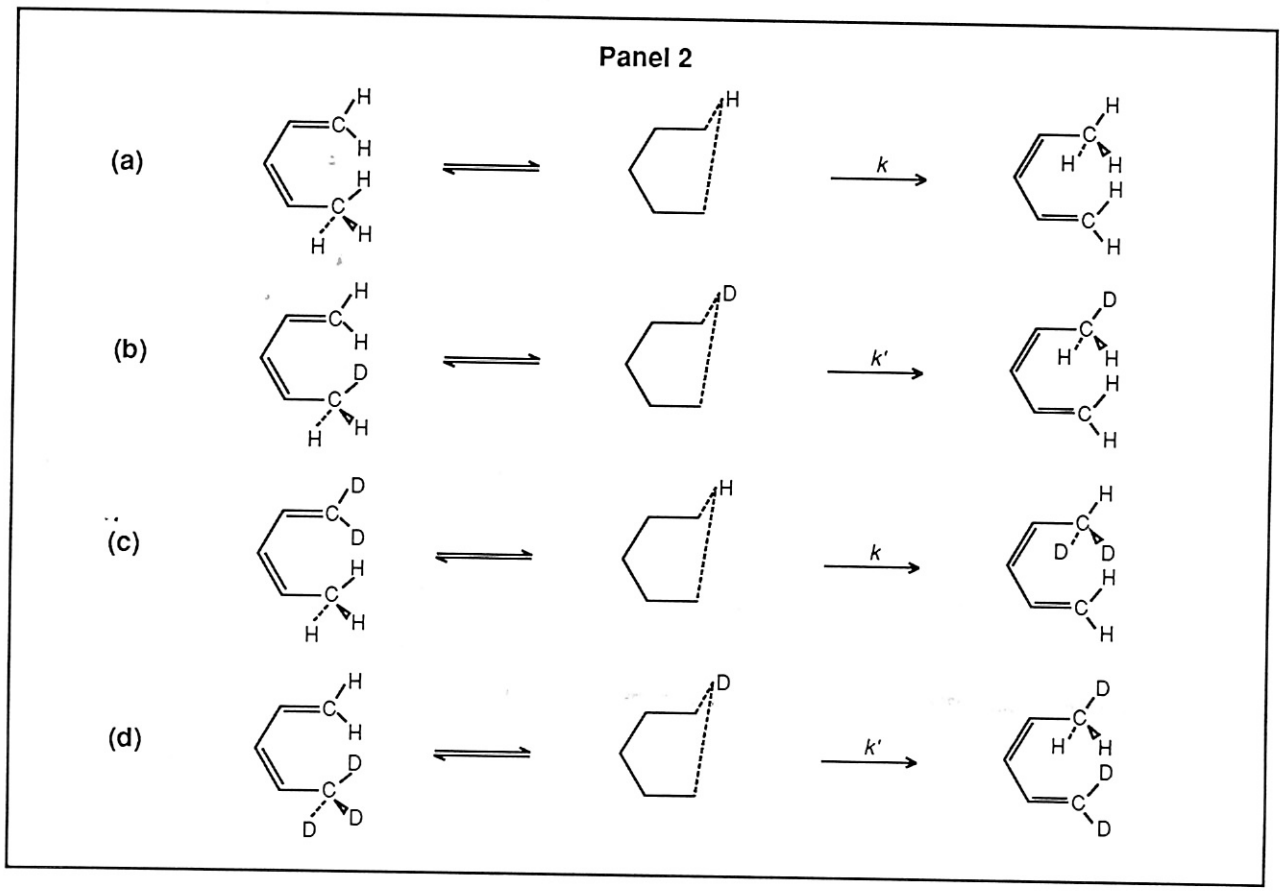
the relative participation of each element in the three-element reaction coordinate is 1 to -1, i.e., the eigenvectors (a_n, a_m, a_ℓ) are $(1, -1, 1)$. All $\ln(k/k')$ vs. $1/T$ surfaces are generally "inverse" type for the three-element reaction coordinate, and the ln(TDF) are all negative as the other two types of calculations. A crossover surface of $\ln(k/k')$ vs. $1/T$ is obtained only for III, due to a larger ln(TIF) value, which occurs only with the motion of the reaction coordinate, where TDF is the temperature dependent factor and TIF is the temperature independent factor, as defined by Yankwich and Buddenbam.[5] As angle β increases, a plateau is obtained at about 60° for III, which is exactly opposite for I and II.

When the eigenvector $\mathbf{A}_1$ is varied to reflect the degree of participation of the motion in the reaction coordinate other than the stretches, a plot of $\ln(k/k')$ vs. $1/T$ would be too complicated to show the effects. Since ln(TDF) changes only slightly, the variation of $\ln(k/k')$ vs. β at different eigenvectors $\mathbf{A}_1$ can be clearly demonstrated in Figure 4. Generally, larger TIF values are obtained when the β angle is larger than 60° for all eigenvectors of $\mathbf{A}_1$ and the magnitude of TIF increases as the participation of the third reaction coordinate increases until approximately $a_\ell = 0.8$.

The angle α of the transition state was changed from 115° to 160° for the three-element reaction coordinate with $a_n = 1$, $a_m = -1$, and $a_\ell = 0.8$ at $\beta =$ 75°. Figure 5 shows these results. The $\ln(k/k')$ vs. $1/T$ surface has been observed to proceed from "inverse" to "normal," then back to inverse. At approximately $\alpha =$ 130°, the isotope effect is almost temperature independent in this region. A bent transition state was correlated with the temperature independence, with the optimum angle α around 130° to 140°.

The results above demonstrate the following:

a. Values of ln(TDF) are generally negative, which can be attributed to the results from cyclic geometry. Positive $\ln(k/k')$ is the result of reaction coordinate ef-



fects, i.e., ln(TIF).

b. A plateau in the plot of $\ln(k/k')$ vs. $1/T$ is the result of geometry. The maximum isotope effect is generated at $\beta \sim 75°$ and $\alpha \sim 135°$. It is not true that a bent transition state is always correlated with a temperature-independent k_H/k_D. This conclusion is exactly the same as reported recently by Anhede and Bergman,[9] who made some model calculations on the intramolecular proton transfer in monoprotonated methylene diamine.

c. The participation of a third element in the reaction coordinate could generate the abnormal temperature dependence of the kinetic isotope effect. Furthermore, its participation shifts the overall magnitude of k/k'.

With the understanding of the sensitivity to different factors, it is then an easy task to make a sample calculation on the shift shown in Panel 2 (c) and (d), which was observed experimentally.[3] A calculation for k/k', using the three-element reaction coordinates, namely, atoms (1–10) stretch + (5–10) stretch + (6–1–10) bend with eigenvalues $a_n : a_m : a_\ell = 1 : -1 : 0.8$ and $\beta = 75°$, was made, and $\ln(k/k')$ vs. $1/T$ was plotted with angle α varying from 115° to 160° as shown in Figure 6. A variety of temperature dependencies of $\ln(k/k')$ is demonstrated in the figure, within the experimental temperature range. Since the original experimental result in k_H/k_D shows an inherently large uncertainty with the method used, the magnitude of the kinetic isotope effect is less important than the trend of temperature dependence. It is clear that at $\beta = 75°$ and α between 130° and 150° the calculated temperature dependence of $\ln(k/k')$ has the same trend as that of the experimental results. Furthermore, when comparing these results with the model calculations before, they indicate that more D-substituted reactants tend to switch the "temperature independence" to "temperature dependence" for the reaction. Additionally, it should be pointed out here that the magnitude of the kinetic isotope effects in this system is very sensitive to the values of the torsional force constants used. Generally the smaller the torsional force constants, the larger the kinetic isotope effect (0.001 to 0.2 dyne/cm^3 were tested in this investigation). Thus it is relatively a simple matter to match the magnitude of the experimental kinetic isotope effect by varying the size of the torsional force constants in the calculations after the trend of temperature dependence of the KIE is matched. It is clear that the temperature dependent effects for a bent transfer process shown in this report conflict with the conclusion assumed by Kwart,[1] which was often the

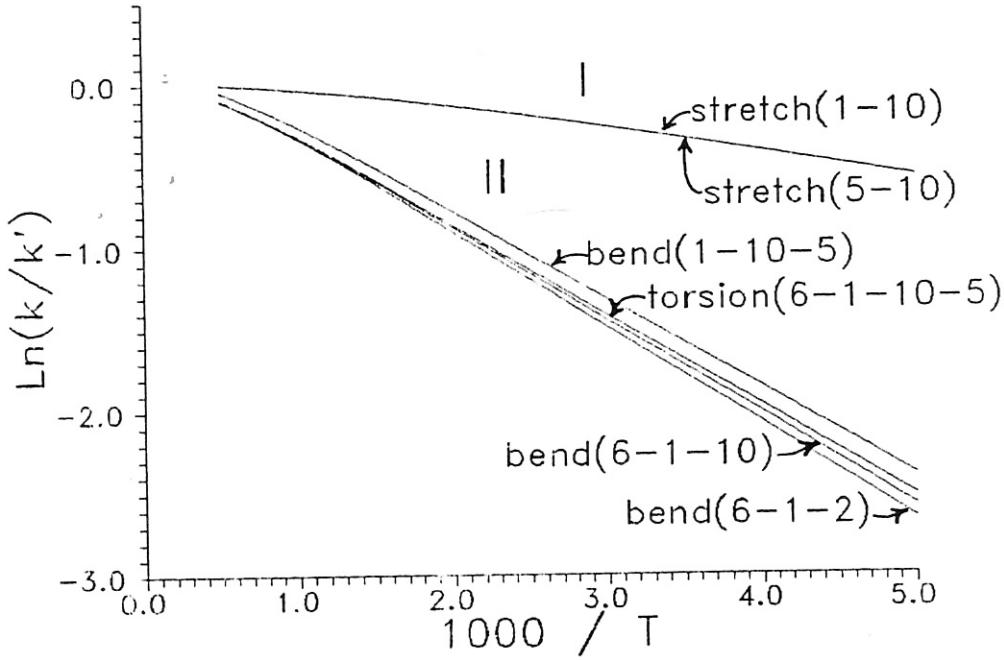


Figure 1. $\ln(k/k')$ vs. $1/T$ for one-element reaction coordinate at angle α = 115°, where β = 0° to 90°.

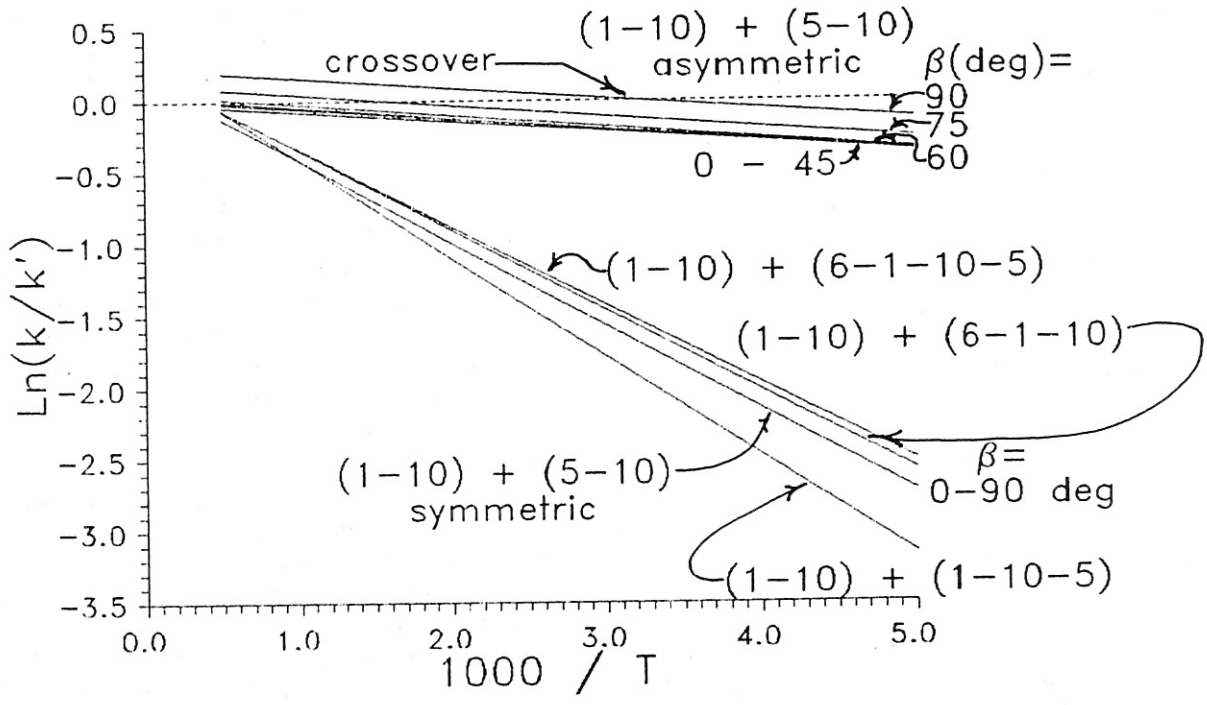


Figure 2. $\ln(k/k')$ vs. $1/T$ for two-element reaction coordinates at angle α = 115°, where β = 0° to 90°.

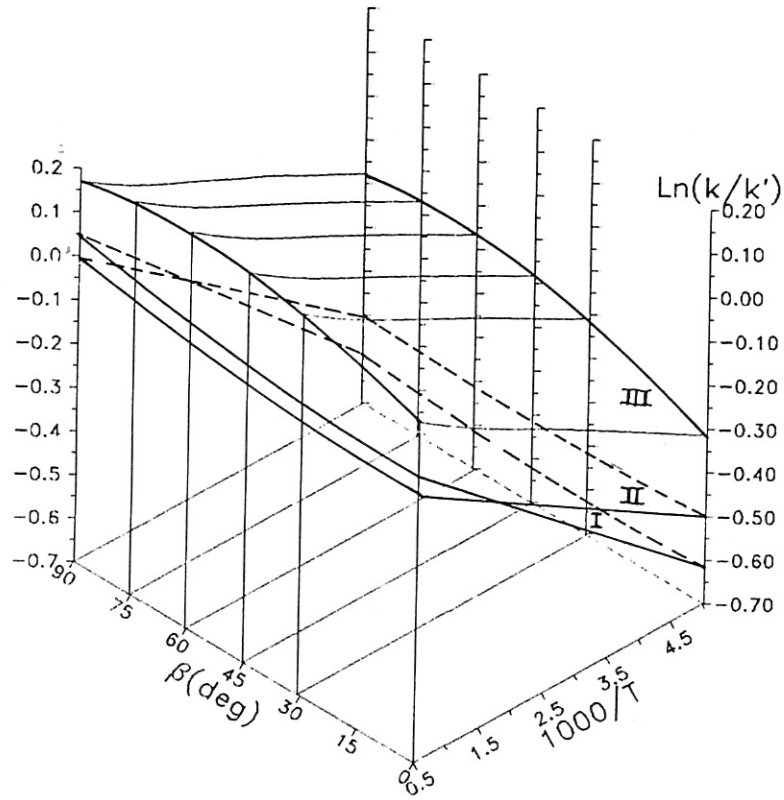


Figure 3. $\ln(k/k')$ vs. $1/T$ for three-element reaction coordinates at angle α = 115°, where β = 0° to 90°.

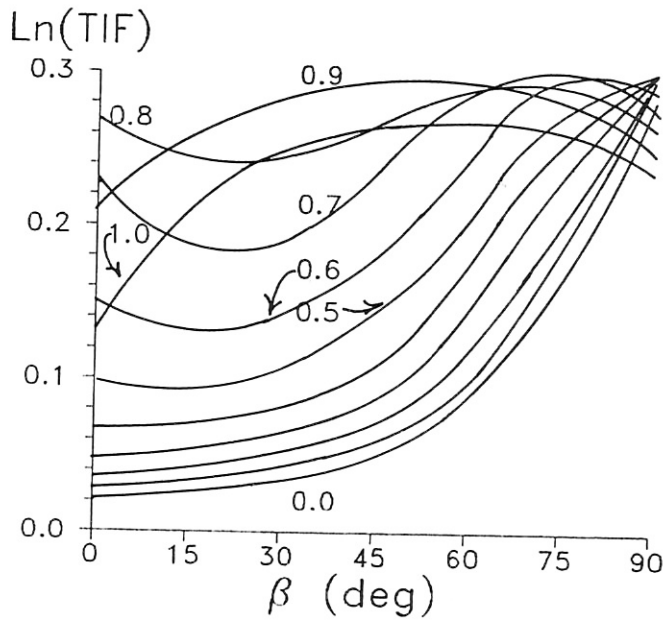


Figure 4. Temperature-independent factor (TIF) at different angles β and with different values of a_ℓ.

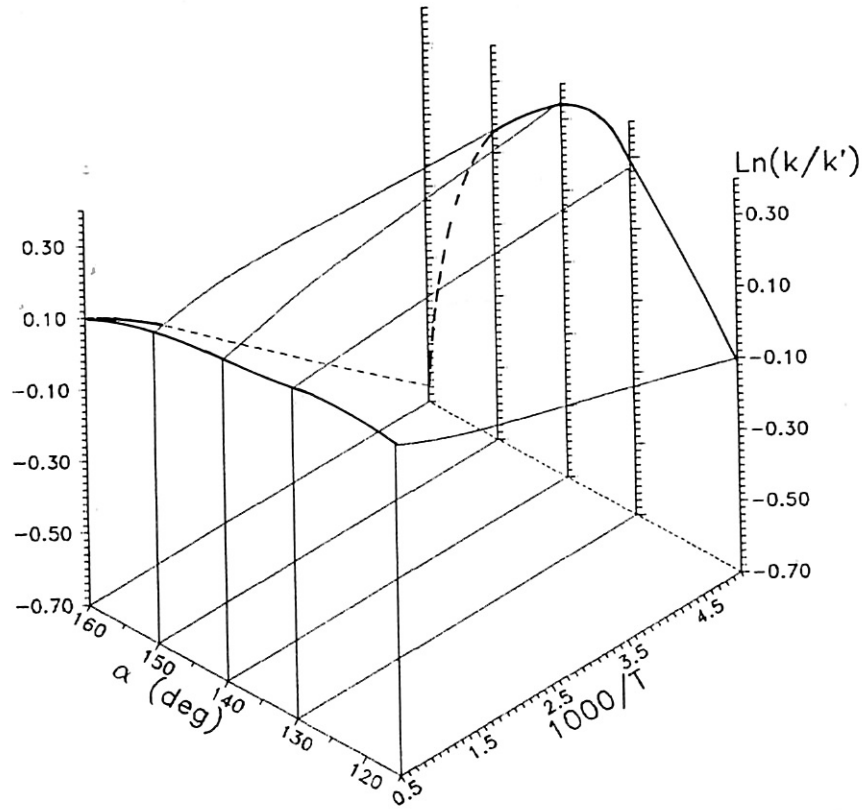


Figure 5. $\ln(k/k')$ vs. $1/T$ for the one D-substituted reaction with reaction coordinate (1–10) + (5–10) + (6–1–10), a_n = 1, a_m = −1, a_ℓ = 0.8, and at angle β = 75° and α = 115° to 160°.

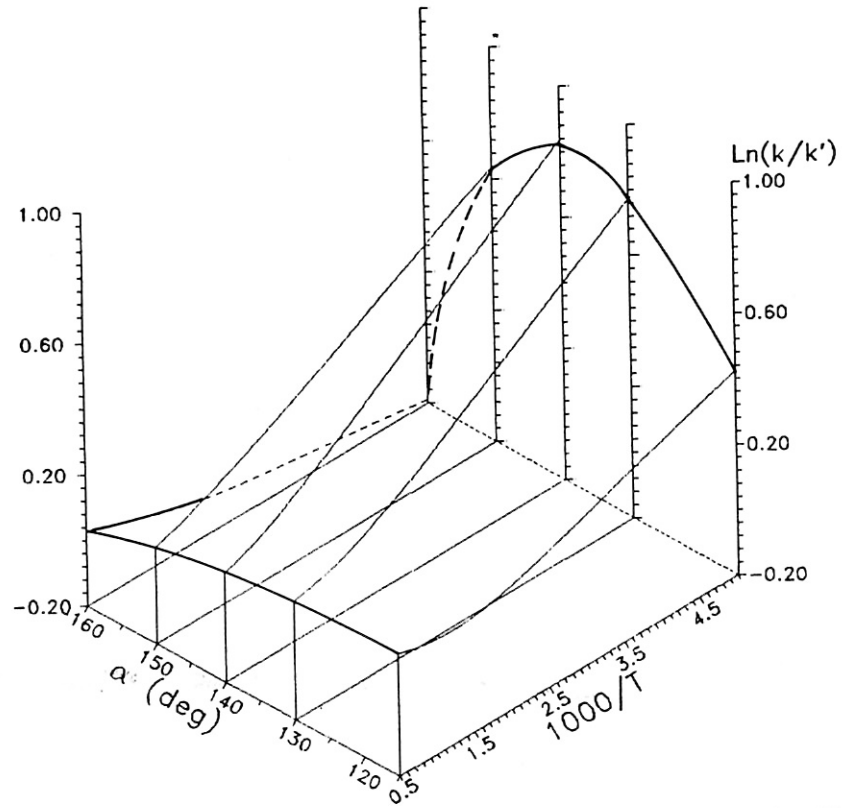


Figure 6. $\ln(k/k')$ vs. $1/T$ for the more D-substituted reaction with reaction coordinate (1–10) + (5–10) + (6–1–10), a_n = 1, a_m = −1, a_ℓ = 0.8, and at angle β = 75° and α = 115° to 160°.

generally accepted interpretation in mechanistic studies. It is better to describe the {1,5} sigmatropic hydrogen migration as proceeding via an out-of-plane bent transition state.

ACKNOWLEDGMENT

We are grateful for the services provided by the Computer Center personnel at East Tennessee State University.

LITERATURE CITED

1. a) Kwart, H.; Brechbiel, M.W.; Acheson, R.M.; Ward, D.C. *J. Am. Chem. Soc.* **1982**, *104*, 4671.
   b) McLennan, D.J.; Gill, P.M.W. *J. Am. Chem. Soc.* **1985**, *107*, 2971.
2. a) Kwart, H.; Nickle, J.H. *J. Am. Chem. Soc.* **1973**, *95*, 3394.
   b) Kwart, H.; Nickle, J.H. *J. Am. Chem. Soc.* **1976**, *98*, 2881.
   c) Kwart, H.; Stanulonis, J.J. *J. Am. Chem. Soc.* **1976**, *98*, 5249.
   d) Kwart, H.; George, T.J.; Louw, R.; Ultee, W. *J. Am. Chem. Soc.* **1978**, *100*, 3927.
   e) Kwart, H.; Benko, D.A.; Bromberg, M.E. *J. Am. Chem. Soc.* **1978**, *100*, 7093.
   f) Kwart, H.; Brechbiel, M.W. *J. Am. Chem. Soc.* **1981**, *103*, 4650.
3. Roth, W.R.; Konig, J. *Liebigs Ann. Chem.* **1966**, *699*, 24.
4. a) Hess, B.A., Jr.; Schaad, L.J. *J. Am. Chem. Soc.* **1983**, *105*, 7186.
   b) Rondan, Nelson G.; Houk, K.N. *Tetrahedron Lett.* **1985**, *25*, 2519.
   c) Hess, B.A., Jr.; Schaad, L.J.; Pancir, J.J. *J. Am. Chem. Soc.* **1985**, *107*, 149.
   d) Dormans, G.J.M.; Buck, H.M. *J. Am. Chem. Soc.* **1986**, *108*, 3253.
5. Buddenbam, W.; Yankwich, P.E. *J. Phys. Chem.* **1967**, *71*, 3136.
6. Schachtschneider, J.H.; Technical Report No. 261–2, 1962; Prog. No. 31450, Shell Development Co., Emeryville, CA.
7. Wilson, E.; Decius, J.; Cross, P. "Molecular Vibrations," McGraw-Hill Book Co., Inc.: New York, 1966, p. 63.
8. Herzberg, G. *Infrared and Raman Spectra,* Van Nostrand: Princeton, NJ, 1950, p. 171.
9. Anhede, B.; Bergman, N.A. *J. Am. Chem. Soc.* **1984**, *106*, 7634.