Secondary Deuterium Kinetic Isotope Effects in the Rotations of Alkenes and Allyl Radicals: Theory and Experiment

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Abstract: Secondary deuterium kinetic isotope effects (KIEs) associated with restricted rotation about the C−C bonds of ethylene, propene, and allyl radical substituted by H or D were calculated. Geometries and force constants of ground states and transition states were obtained by *ab initio* MCSCF calculations with the 6-31G* and/or 6-311G** basis sets. The KIEs were then calculated from the partition functions for the Bigeleisen equation. The "rotational" KIEs are predicted to be larger than typical secondary KIEs. For simple alkenes, predicted k_H/k_D values range from 1.32−1.46 at 25 °C to 1.15−1.25 at 275 °C. Predicted values are compared with existing experimental results. As a test of our prediction that high-temperature alkene isomerizations should display large KIEs, samples of *cis*-stilbene and α,α′-dideuterio-*cis*-stilbene were pyrolyzed; the measured KIE was a remarkable $k_H/k_{D2} = 1.47 \pm 0.13$ (σ_n) at 287 °C.

Introduction

Secondary deuterium kinetic isotope effects which were interpreted as arising mainly from rotational motions of isotopic substituents have been observed in a number of reactions. Examples are product-determining KIEs in the formation of methylenecyclopropanes from partially deuterated trimethylenemethane biradicals[1] and large rate effects on the {1,3} sigmatropic shifts of vinylcyclopropanes,[2] cyclopropylallene,[3] and vinylcyclobutanes[4] upon deuteration of *exo*-methylene groups. In a few cases, the experiments were accompanied by semiempirical quantum mechanical calculations.

Caldwell *et al.* observed $k_H/k_D = 2.0$ at 25 °C in the thermal isomerization of the transient *trans*-2-deuterio-1-phenylcyclohexene (Figure 1);[5] MNDO calculations on a model trisubstituted alkene predicted an isotope effect of $k_H/k_D = 1.85$. Large secondary KIEs were observed[6] experimentally ($k_H/k_{D2} = 1.4$ and $k_H/k_{D12} = 1.5$ at 25 °C) by Courtney *et al.* and calculated[7] by Negri and Orlandi using a QCFF/PI method ($k_H/k_{D2} = 1.4 - 1.7$ and $k_H/k_{D12} = 1.2-1.7$ depending on the nature of the assumed transition state) for the photochemical isomerization of *trans*-stilbenes. Product-determining rotational KIEs ($k_H/k_{D4} = 1.15-1.20$ at 220 °C) were encountered in cycloadditions of allene performed by Dolbier and Dai[8] and investigated theoretically by Halevi and Wolfsberg using an AM1/CI method ($k_H/k_{D4} = 1.17$ at 220 °C).[9]

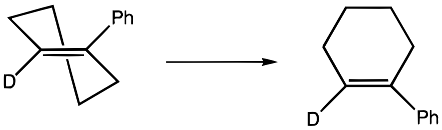

Figure 1. The Caldwell *et al.* reaction for which $k_H/k_D = 2.$[5]

Recently, Perrin *et al.* measured deuterium KIEs upon C−N rotation in a series of substituted formamides.[10] Their experiments were stimulated in part by the surprisingly large magnitude of the experimental and theoretical KIEs reported by Caldwell *et al.*[5] The amide KIEs were smaller (at least within a given temperature range) than those seen in alkenes; this supported Perrin's hypothesis that either Caldwell's *trans*-cycloalkene might be a nonrepresentative case or that the alkene experiments might be in error. We carried out *ab initio* theoretical studies of rotation of formamides[11] and obtained results in good agreement with experiments.

In order to better compare the amide and alkene rotational isotope effects, it is desirable to study KIEs of alkene rotation theoretically using *ab initio* methods. As pointed out by Perrin *et al.*,[10] amides remain closed-shell species throughout C−N bond rotation, and these KIEs are therefore well-represented by restricted Hartree−Fock methods. However, such calculations inadequately describe singlet biradicals, such as the 1,2-biradicals encountered in thermal *cis*−*trans* isomerizations of alkenes. In this work, we have employed MCSCF *ab initio* methods[12] to calculate the geometries and force constants of open-shell species encountered in alkene and allyl radical bond rotation. MCSCF calculations have been previously reported

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(1) (a) Crawford, R. J.; Cameron, D. M. Tokunaga, H. *Can. J. Chem.* **1974**, *52*, 4025. (b) Gajewski, J. J.; Chou, S. K. *J. Am. Chem. Soc.* **1977**, *99*, 5696.

(2) (a) Chickos, J. *Abstracts of Papers, 187th Meeting of the American Chemical Society, St. Louis, MO*; American Chemical Society: Washington, DC, 1984; ORGN 228. (b) Gajewski, J. J.; Squicciarini, M. P. *J. Am. Chem. Soc.* **1989**, *111*, 6717. (c) Baldwin, J. E.; Villarica, K. A. *Tetrahedron Lett.* **1994**, *35*, 7905.

(3) Olson, L. P.; Gajewski, J. J. *Tetrahedron Lett.* **1993**, *34*, 2895.

(4) Gajewski, J. J.; Paul, G. C. *J. Org. Chem.* **1991**, *56*, 1986.

(5) Caldwell, R. A.; Misawa, H.; Healy, E. F.; Dewar, M. J. S. *J. Am. Chem. Soc.* **1987**, *109*, 6869.

(6) Courtney, S. H.; Balk, M. W.; Philips, L. A.; Webb, S. P.; Yang, D.; Levy, D. H.; Fleming, G. R. *J. Chem. Phys.* **1988**, *89*, 6697.

(7) Negri, F.; Orlandi, G. *J. Phys. Chem.* **1991**, *95*, 748.

(8) (a) Dai, S. H.; Dolbier, W. R., Jr. *J. Am. Chem. Soc.* **1970**, *92*, 1774. (b) Dai, S. H.; Dolbier, W. R., Jr. *J. Am. Chem. Soc.* **1972**, *94*, 3946.

(9) Halevi, E. A.; Wolfsberg, M. *J. Chem. Soc., Perkin Trans. 2* **1993**, 1493.

(10) Perrin, C. L.; Thoburn, J. D.; Kresge, A. J. *J. Am. Chem. Soc.* **1992**, *114*, 8800.

(11) Olson, L. P.; Li, Y.; Houk, K. N.; Kresge, A. J.; Schaad, L. J. *J. Am. Chem. Soc.* **1995**, *117*, 2992.

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for both ethylene and allyl radical. Yamaguchi *et al.* calculated the geometries and frequencies of planar and perpendicular ethylene, using a 2-electron, 2-orbital ($2e^-/2o$) active space and a double-ζ basis set.[13] Also, 3-electron, 3-orbital ($3e^-/3o$) MCSCF calculations of planar allyl radical have been done, including frequency calculations,[14a,b] and the barrier to $-CH_2$ rotation in allyl radical has been calculated using UHF, MP4, and CISD calculations with a variety of basis sets.[14c,d] Frequency calculations of twisted allyl radical appear only to have been done using UHF methods, however, and no zero-point energy correction was applied to the rotational barrier. It appears that no KIE calculations using MCSCF *ab initio* geometries and force constants have been previously reported for ethylene or allyl radical thermal isomerizations.

As a complement to our theoretical studies, we have studied the rate of alkene isomerization experimentally. *cis*-Stilbene has been shown to isomerize to the *trans* isomer in a first-order, unimolecular fashion in the gas phase.[15] We have measured the KIE upon gas-phase thermal isomerization of *cis*-stilbene and α,α'-dideuterio-*cis*-stilbene. This was done in order to test theoretical predictions concerning the magnitude and nature of alkene rotational KIEs.

Computational Methods

Ab initio calculations were performed using GAMESS[16a] or Gaussian 94.[16b] UHF Natural Orbital Analysis[17] indicated a [$2e^-/2o$] active space for ethylene and propene and a [$3e^-/3o$] active space for allyl radical. In allyl radical, orbitals ψ_{10} and ψ_{11} were reordered in the ground state species, so that ψ_{10} (a π orbital) was included and ψ_{11} (a σ orbital) was excluded from the active space; if these reorderings were not done, the calculations failed to reach self-consistency. No orbital reordering was necessary for twisted allyl radical. When necessary, force constant matrix contaminants resulting from molecular translation and rotation were removed by use of internal rather than Cartesian coordinates for frequency calculations. The CASSCF geometries and force constants were used as input to QUIVER,[18] which calculates the partition functions for the Bigeleisen equation.[19] In one test case, isotope effects were calculated from free energies of activation calculated in Gaussian 94.[16b]

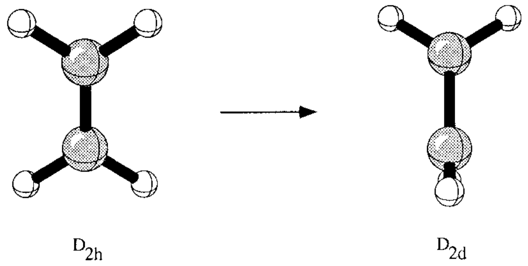

Figure 2. CASSCF/6-311G** [2e/2o] structures of ethylene: ground state (left); transition state (right).

Structures of Ground States and Transition States

Ethylene calculations were carried out in D_{2h} (ground state) and D_{2d} (transition state) symmetry (Figure 2; Tables 1 and 2), using the 6-31G* and 6-311G** basis sets. The ground-state geometries are in satisfactory agreement with experiment.[20] The transition state is 60.8 kcal/mol (6-31G* basis set) or 61.5 kcal/mol (6-311G** basis set) higher in energy than the ground state after zero-point energy correction, which is in good agreement with experiment.[21] Interestingly, previous calculations using a similar method but different basis set predicted a 45-kcal/mol barrier.[13]

Propene calculations were carried out in C_s symmetry for both the ground state and transition state (Figure 3, Tables 1 and 2), and also in C_1 symmetry for the transition state, using the 6-31G* basis set. Both the ground-state geometry and the barrier to rotation (62 kcal/mol) are in good agreement with experimental values.[22,23] The C_s transition structure of propene (Figure 3) is a second-order saddle point. There is a large ($1337i$ cm^{-1}) imaginary frequency associated with $C{=}C$ bond rotation and a second, smaller ($195i$ cm^{-1}) imaginary frequency that corresponds to a pyramidalization of the radical at C2. The methyl group in the transition state is staggered with respect to the C1−C2 bond; when the methyl group is eclipsed with the C1−C2 bond, there is an additional imaginary frequency associated with this motion. Relaxation of the symmetry constraint gives a transition structure (Figure 4) which is pyramidalized at the central carbon by 18° (the angle formed by the C−H bond with the C−C−C plane). The $-CH_2$ terminus is pyramidalized by about 8° in both the C_1 and C_s structures. On a vibrationless energy surface, the C_1 structure is calculated to be 0.2 kcal/mol lower in energy than the C_s structure; the C_s structure is the saddle point for interconversion of the C_1 structure shown in Figure 4 with its enantiomer. However, after zero-point energy corrections are applied, the C_s structure is lower in energy than the C_1 structure by 0.3 kcal/mol. The C_s structure probably better represents the "true" transition-state structure, but KIEs were calculated for the C_1 transition structure as well.

Allyl radical was calculated in C_{2v} symmetry (ground state) and C_s symmetry (transition state), using the 6-31G* basis set (Figure 5). The geometry of the ground state is in reasonable agreement with experiment,[24] although the bond lengths are not very close. This lack of close agreement may be attributable to the use of electron diffraction to obtain internuclear distances. The calculated barrier to rotation is 13.7 kcal/mol after zero-point energy correction, which is in good agreement with the experimental value.[25]

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(12) (a) Hehre, W. J.; Radom, L.; v. R. Schleyer, P.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley-Interscience: New York, 1986. (b) Roos, B. O. In *Methods in Computational Molecular Physics*; Diercksen, G. H. F., Wilson, S., Eds.; D. Reidel Publishing: Dordrecht, The Netherlands, 1983; pp 161−187. (c) Werner, H. J. In *Advances in Chemical Physics*; Lawley, K. P., Ed.; Wiley Interscience: New York, 1987; Vol. 69, pp 1−62. (d) Shepard, R. *Ibid.*, pp 63−200.

(13) Yamaguchi, Y.; Osamura, Y.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1983**, *105*, 7506.

(14) (a) Takada, T.; Dupuis, M. *J. Am. Chem. Soc.* **1983**, *105*, 1713. (b) Szalay, P. G.; Császár, A. G.; Fogarasi, G.; Karpfen, A.; Lischke, K. *J. Chem. Phys.* **1990**, *93*, 1246. (c) Peeters, D.; Leroy, G.; Matagne, M. *THEOCHEM* **1988**, *43*, 267. (d) Hammons, J. H.; Coolidge, M. B.; Borden, W. T. *J. Phys. Chem.* **1990**, *94*, 5468.

(15) (a) Kistiakowsky, G. B.; Smith, W. R. *J. Am. Chem. Soc.* **1934**, *56*, 638. (b) Schmiegel, W. W.; Lett, F. A.; Cowan, D. O. *J. Org. Chem.* **1968**, *33*, 3334.

(16) (a) *GAMESS*: Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Koseki, S.; Jensen, J. H.; Gordon, M. S.; Nguyen, K. A.; Windus, T. L.; Elbert, S. T. *QCPE Bull.* **1990**, *10*, 52. (b) *Gaussian 94* (Revision A.1), M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. A. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, and J. A. Pople; Gaussian, Inc.: Pittsburgh, PA, 1995.

(17) Pulay, P.; Hamilton, T. P. *J. Chem. Phys.* **1988**, *88*, 4926.

(18) Saunders, M.; Laidig, K. E.; Wolfsberg, M. *J. Am. Chem. Soc.* **1989**, *111*, 8989.

(19) (a) Bigeleisen, J.; Wolfsberg, M. *Adv. Chem. Phys.* **1958**, *1*, 15. (b) Bigeleisen, J.; Goeppert-Mayer, M. *J. Chem. Phys.* **1947**, *15*, 261.

(20) Kuchitsu, K. *J. Chem. Phys.* **1966**, *44*, 906.

(21) Douglas, J. E.; Rabinovitch, B. S.; Looney, F. S. *J. Chem. Phys.* **1955**, *23*, 315.

(22) Lide, D. R.; Christensen, D. *J. Chem. Phys.* **1961**, *35*, 1374.

(23) Flowers, M. C.; Jonathan, N. *J. Chem. Phys.* **1969**, *50*, 2805.

(24) Vajda, E.; Tremmel, J.; Rozsondai, B.; Hargittai, I.; Maltsev, A. K.; Kagramanov, N.; Nefedov, O. M. *J. Am. Chem. Soc.* **1986**, *108*, 4352.

Table 1. Optimized Ground-State Structures

molecule	ethylene	ethylene	propene	allyl radical
MCSCF calculation	[2e/2o]/6-31G*	[2e/2o]/6-311G**	[2e/2o]/6-31G*	[3e/3o]/6-31G*
symmetry	D_{2h}	D_{2h}	C_s	C_{2v}
energy (hartrees)	−78.06025	−78.08247	−117.09927	−116.48359
zero-point energy (kcal/mol; scaled)	31.2	30.8	48.1	39.6
selected bond distances (Å) and angles (deg)[a]				
C1−C2	1.3382	1.3368 (1.330)	1.3389 (1.336)	1.3899 (1.428)
C2−C3			1.5040 (1.501)	same
H_{cis}−C1	1.0756	1.0764 (1.076)	1.0766 (1.091)	1.0749 (1.069)
H_{trans}−C1	(same)	(same)	1.0752 (1.081)	1.0732 (1.069)
H−C2	(same)	(same)	1.0785 (1.090)	1.0780 (1.069)
H_{cis}−C1−C2	121.73	121.63 (121.7)	121.78 (120.5)	121.21 (120.9)
H_{trans}−C1−C2	(same)	(same)	121.59 (121.5)	121.44 (120.9)
C1−C2−H	(same)	(same)	118.89 (119.0)	117.68 (118.2)
C1−C2−C3			124.94 (124.3)	124.65 (124.6)

[a] Experimental data (parentheses) are taken from refs 20 and 22.

Table 2. Optimized Transition-State Structures

molecule	ethylene	ethylene	propene	propene	allyl radical
MCSCF calculation	[2e/2o]/6-31G*	[2e/2o]/6-311G**	[2e/2o]/6-31G*	[2e/2o]/6-31G*	[3e/3o]/6-31G*
symmetry	D_{2d}	D_{2d}	C_s	C_1	C_s
energy (hartrees)	−77.95570	−77.97772	−116.99377	−116.99405	−116.46214
zero-point energy (kcal/mol; scaled)	26.4	26.5	44.2	44.7	38.9
selected bond distances (Å) and angles (deg)					
C1−C2[a]	1.4692	1.4709	1.4720	1.4741	1.4765
C2−C3			1.5028	1.5038	1.3058
H−C1	1.0754	1.0762	1.0767	1.0769, 1.0756	1.0827
H−C2	(same)	(same)	1.0759	1.0778	1.0923
H−C1−C2	121.32	121.22	121.27	121.21, 121.14	120.18
C1−C2−H	(same)	(same)	119.26	118.15	116.31
C1−C2−C3			121.56	120.92	124.96
pyram. at C1[b]	0.0	0.0	7.31	7.65	19.80
pyram. at C2[b]	(same)	(same)	0.0	18.32	0.0
H_{cis}−C3−C2					121.77
H_{trans}−C3−C2					121.53

[a] Where C1 is the radical carbon, in the case of allyl radical. [b] Pyramidalization at that carbon, i.e., the improper angle.

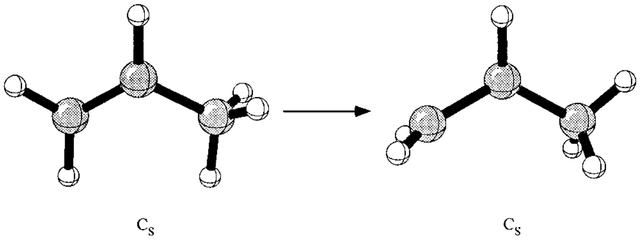

Figure 3. CASSCF/6-31G* [2e/2o] structures of propene: ground state (left); transition state (right).

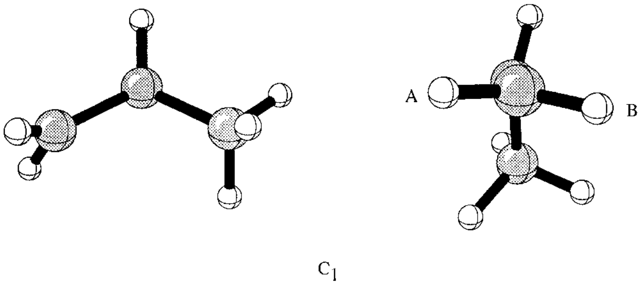

Figure 4. Two views of the CASSCF/6-31G* [2e/2o] structures of propene (C_1 symmetry; see text). Note the pyramidalization at the central carbon atom. The compound isotope effects for atoms H_A and H_B, designated on the view at right, were essentially the same (ΔKIE < 0.02).

Frequencies of Ground States and Transition States

The vibrational frequencies of ground-state ethylene[26] and propene[27] are reasonably reproduced by the MCSCF calculations when scaled[12a] (Table 3; the frequencies of isotopomers of ethylene and propene in both ground states and transition states are tabulated in the supporting information). As shown in Table 3, one ground-state vibrational mode is entirely lost in the transition state, becoming an imaginary frequency, but other modes are reduced in magnitude as well. Aside from the reaction coordinate motion, the most striking reduction in vibrational frequencies is seen in the out-of-plane wagging motions of the methylene groups, which are far looser in the transition state than in the reactant state. The reduction in these frequencies is about 700 cm^{-1} in these two cases. Other vibrations associated with C−H bonds are reduced by 30−300 cm^{-1}.

In propene, an out-of-plane bending mode at C2 of the twisted species has an imaginary frequency if the C−H bond is held coplanar with the carbon skeleton. Although with a zero-point energy correction the planar geometry is the lowest-energy species, the out-of-plane motion is a very loose vibration with negligible associated zero-point energy.

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(25) Korth, H.-G.; Trill, H.; Sustmann, R. *J. Am. Chem. Soc.* **1981**, *103*, 4483.

(26) Shimanouchi, T. *Tables of Molecular Vibrational Frequencies, Consolidated Volume*; National Bureau of Standards: Washington, DC, 1972; NSRDS-NBS 39.

(27) Silvi, B.; Labarbe, P.; Perchard, J. P. *Spectrochim. Acta, Part A* **1973**, 29A, 263.

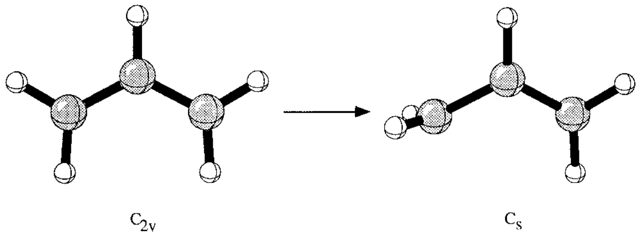

Figure 5. CASSCF/6-31G* [3e/3o] structures of allyl radical: ground state (left); transition state (right).

Table 3. MCSCF/6-311G** Vibrational Frequencies (cm^{-1}) of Ethylene[a,b]

ground-state freq		transition-state freq	
CH_2 rock	803 (826)	CH2 twist	1611*i*
CH_2 wag	830 (943)	CH2 wag	160
CH_2 wag	867 (949)	CH2 wag	162
CH_2 twist	1011 (1023)	CH_2 wag	938
CH_2 rock	1238 (1236)	CH_2 wag	948
CH_2 scissor	1324 (1342)	CC stretch	1079
CH_2 scissor	1474 (1444)	CH_2 scissor	1444
CC stretch	1622 (1623)	CH_2 scissor	1475
CH_2 sym stretch	3024 (2989)	CH_2 stretch	3027
CH_2 asym stretch	3040 (3026)	CH_2 stretch	3034
CH_2 asym stretch	3094 (3103)	CH_2 stretch	3118
CH_2 sym stretch	3120 (3106)	CH_2 stretch	3122

[a] Experimental values in parentheses are from ref 26. [b] Calculated frequencies scaled by 0.93.

The scaled MCSCF frequencies of the ground-state allyl radical reasonably reproduce experimental values.[28] In contrast to ethylene and propene, the simple disappearance of a single torsional mode is a good approximation of the changes in vibrational frequency associated with the rotational process. The magnitude of the imaginary frequency (221*i* cm^{-1}) is also far lower than in the alkenes (1291*i* to 1611*i* cm^{-1}).

Calculated Kinetic Isotope Effects

The Bigeleisen equation,[19]

$$\frac{k_{\mathrm{H}}}{k_{\mathrm{D}}} = \frac{\nu_{i(\mathrm{H})}^{\ddagger}}{\nu_{i(\mathrm{D})}^{\ddagger}} \cdot \mathrm{VP} \cdot \mathrm{EXC} \cdot \mathrm{ZPE}$$

expresses the isotope effect in terms of the ratio of imaginary frequencies and three terms, each of which is a function of the ground-state and transition-state vibrational frequencies:

$$\mathrm{VP} = \prod_{n}^{3n-6} \nu_{n(\mathrm{D})}/\nu_{n(\mathrm{H})}/\prod_{n}^{3n^{\ddagger}-7} \nu_{n(\mathrm{D})^{\ddagger}}/\nu_{n(\mathrm{H})^{\ddagger}}$$

$$\mathrm{EXC} = \prod_{n}^{3n-6} 1 - \mathrm{e}^{-u_n(\mathrm{H})}/1 - \mathrm{e}^{-u_n(\mathrm{D})}/\prod_{n}^{3n^{\ddagger}-7} 1 - \mathrm{e}^{-u_n(\mathrm{H})^{\ddagger}}/1 - \mathrm{e}^{-u_n(\mathrm{D})^{\ddagger}}$$

$$\mathrm{ZPE} = \prod_{n}^{3n-6} \mathrm{e}^{(u_n(\mathrm{H})/2)}/\mathrm{e}^{(u_n(\mathrm{D})/2)}/\prod_{n}^{3n^{\ddagger}-7} \mathrm{e}^{(u_n(\mathrm{H})^{\ddagger}/2)}/\mathrm{e}^{(u_n(\mathrm{D})^{\ddagger}/2)}$$

where $u_n = h\upsilon_n/\kappa T$, and υ_n are the fundamental vibrational frequencies. The isotope effect can also be corrected for tunneling (see below).

Table 4. MCSCF/6-31G* Vibrational Frequencies (cm^{-1}) of Allyl Radical[a,b]

ground state freq		transition-state freq	
CH_2 rock	416 (−)	CH_2 twist	222*i*
CCC bend	502 (502−510)	CCC bend	374
CCC oop bend	532 (−)	CCC oop bend	499
CH_2 wag	636 (−)	CH_2 wag	526
CH_2 wag	651 (801−802)	CH wag	803
CH_2 oop bend	917 (−)	CH_2 wag	924
CH_2 wag	937 (983−985)	CCC bend	936
CCC stretch	994 (−)	CCC bend	996
CCC stretch	1092 (−)	C−C stretch	1073
CCC stretch	1232 (1242)	CCC stretch	1287
CH_2 scissor	1395 (1388−1389)	CH_2 scissor	1422
CCC stretch	1483 (1463)	CH_2 scissor	1458
CCC stretch	1507 (1477)	C=C stretch	1611
CH stretch	3013 (3016−3019)	CH stretch	3009
CH_2 asym stretch	3041 (−)	CH_2 asym stretch	3018
CH_2 sym stretch	3055 (3048−3051)	CH_2 asym stretch	3033
CH_2 asym stretch	3124 (3105−3107)	CH_2 asym stretch	3089
CH_2 sym stretch	3136 (−)	CH_2 sym stretch	3115

[a] Experimental values in parentheses are from ref 28. [b] Calculated frequencies scaled by 0.91.

ZPE represents the KIE due to differences in zero-point energy changes for H and D. EXC gives the contributions due to different populations of excited vibrational levels for H and D. VP, the vibrational product, and the ratio of imaginary frequencies come from the replacement of the MMI term, which gives translational and rotational contributions to the KIE.[19]

Isotope effects calculated using scaled frequencies are given in Tables 5 and 6 for temperatures ranging from 25 to 400 °C. The components of the isotope effects from the Bigeleisen equation are given in the tables.

The calculated isotope effect for rotation of ethylene at room temperature (Table 5) is large ($k_H/k_D = 1.32$). The contribution of zero-point energy differences (1.35) is somewhat larger than the net values, because the excitation term is inverse. The temperature dependence of the KIE is mainly due to the Arrhenius behavior arising from differences in activation energies.

Isotope effects for both the C_s and C_1 structures of twisted propene are provided in Table 5. The ratio of imaginary frequencies makes a significant contribution. ZPE factors are also large; for alkenes, they are larger than the total KIE, because the EXC factors are inverse or near unity. Although there is a component of the KIE which can reasonably be ascribed to rehybridization (especially in lower-frequency out-of-plane C−H vibrations), the magnitudes of the isotope effects are larger than secondary isotope effects typically encountered upon simple rehybridization. Adding a $-CH_3$ (or $-CH_2^{\bullet}$ group, see Table 6) on the terminus of the double bond opposite from the side of the deuterium substituent increases k_H/k_D. The 1-deuteropriopene isotope effect is 1.22 at 473 K. Adding a $-CH_3$ to the same terminus of the double bond has little effect. The k_H/k_D becomes 1.19 (at 473 K); adding a $-CH_2^{\bullet}$ to form 2-deuterioallyl decreases k_H/k_D to 1.05 (at 473 K). The particularly small KIE in the case of the 2-deuterioallyl radical indicates that rotation is centered mainly on C1.

In the 1-deuterioallyl radical, there are two different types of methylene rotation, one involving rotation of the CHD, the other involving rotation of CH_2. The deuterium slows the rotation of the methylene group to which it is attached, but it speeds up the rotation of the opposite methylene. There is a small fractionation-factor preference for deuterium to be on an olefinic site, since the bending force constants are larger for olefin than for allyl radical sp^2 carbon−hydrogen bonds.[29]

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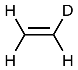
(28) (a) Maltsev, A. K.; Korolov, V. A.; Nefedov, O. M. *Bull. Acad. Sci. USSR, Chem. Ser.* **1982**, *31*, 2131. (b) Maier, G.; Reisenauer, H. P.; Rohde, B.; Dehnicke, K. *Chem. Ber.* **1982**, *16*, 732.

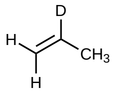
Table 5. Kinetic Isotope Effects (k_H/k_D) upon Alkene Rotation

Ethylene-*1-d* (MCSCF/6-311G**)



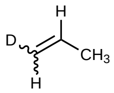
T (K)	$\nu_H^‡/\nu_D^‡$	VP	EXC	ZPE	KIE
298	1.068	1.052	0.872	1.347	1.322
373			0.868	1.269	1.240
473			0.869	1.206	1.180
573			0.872	1.168	1.147
673			0.874	1.150	1.129

2-Deuteriopropene Rotation (C_s) MCSCF/6-31G*



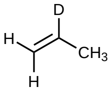
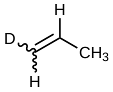
T (K)	$\nu_H^‡/\nu_D^‡$	VP	EXC	ZPE	KIE
298	1.088	0.837	0.986	1.505	1.352
373			0.999	1.370	1.246
473			1.016	1.282	1.186
573			1.032	1.228	1.154
673			1.053	1.191	1.142

1-Deuteriopropene Rotation (C_s average of *cis* and *trans*) MCSCF/6-31G*



T (K)	$\nu_H^‡/\nu_D^‡$	VP	EXC	ZPE	KIE
298	1.095	0.920	0.910	1.512	1.385
373			0.920	1.391	1.290
473			0.936	1.297	1.222
573			0.949	1.239	1.185
673			0.952	1.210	1.161

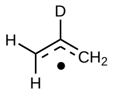
Deuteriopropene Rotations (C_1) (MCSCF/6-3G*)

	2-deuteriopropene	1-deuteriopropene
		
T (K)	KIE	KIE
298	1.313	1.386
373	1.235	1.288
473	1.179	1.204
573	1.115	1.169
673	1.099	1.157

[a] Average of *cis*-propene-*1-d* going to H8 or H9 and *trans*-propene-*1-d* going to H8 or H9; all give essentially the same result.

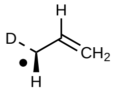
Table 6. MCSCF/6-31G* Kinetic Isotope Effects of Allyl Radical Rotation.

2-Deuterioallyl Radical



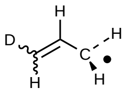
T (K)	$\nu_H^‡/\nu_D^‡$	VP	EXC	ZPE	KIE
298	1.020	0.984	0.991	1.089	1.082
373			0.990	1.071	1.062
473			0.990	1.055	1.048
573			0.952	1.046	0.998

1-Deuterioallyl Radical (Average of *exo* and *endo*)



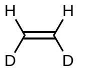
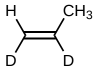
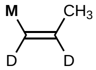
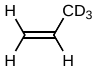
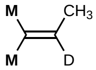
T (K)	$\nu_H^‡/\nu_D^‡$	VP	EXC	ZPE	KIE
298	1.165	0.855	1.034	1.284	1.318
373			1.041	1.224	1.270
473			1.052	1.173	1.234
573			1.067	1.141	1.215

1-Deuterioallyl Radical (Average of *exo* and *endo*)



T (K)	$\nu_H^‡/\nu_D^‡$	VP	EXC	ZPE	KIE
298	1.005	0.994	1.021	0.946	0.965
373			1.024	0.956	0.980
473			1.026	0.965	0.991
573			1.027	0.972	0.998

Table 7. Calculated Isotope Effects of Variously Substituted Alkenes

molecule	$\nu^‡_H/\nu^‡_D$	KIE (H/D)	KIE (tunnel corrected)
	$-1599/-1394 = 1.147$	1.330 at 300 °C	1.657 at 300 °C
	$-1337/-1099 = 1.217$	1.396 at 300 °C	1.678 at 300 °C
	$-1108/-807 = 1.373$	1.580 at 300 °C	1.871 at 300 °C
	$-1337/-1335 = 1.001$	1048 at 25 °C	
	$-830/-631 = 1.315$	1.632 at 25 °C	2.363 at 25 °C

The effects of varying the masses of substituents and the location of deuterium substituents are further explored in Table 7. One notable example is 3,3,3-trideuteriopropene; even at 25 °C, k_H/k_{D3} is only 1.048 (using the C_s transition structure) or 1.036 (using the C_1 transition structure), which is only 1.012–1.016 per D. These atoms are only indirectly involved in the reaction coordinate and have little effect on the KIE. The small effect is due to an increase in hyperconjugation involving the interaction of the methyl group with the radical center at C2 in the transition state. Also in Table 7 are KIEs for a series of deuterated olefins, with various masses added. **M** signifies a hypothetical hydrogen of mass = 15 to simulate the mass effect of a methyl group.[5] Adding mass to the alkene increases the overall KIE per D; more reaction coordinate motion resides in the remaining hydrogens as heavier substituents are added to the double bond.

We tested whether the change in translational and rotational partition functions upon deuteration had any substantial influence on the isotope effects. For this purpose, UHF/6-31G* calculations on ground-state and D_{2d} ethylene were performed. When $\Delta G^‡$ values were calculated from the translational, rotational, and vibrational partition functions, only the vibrational terms are significantly different in the undeuterated and deuterated compounds.

The large tunnel corrections[30] reported in Table 7 should be looked on with skepticism, since the single Bell correction is not expected to be accurate for such cases.

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(29) (a) Houk, K. N.; Gustafson, S. M.; Black, K. A. *J. Am. Chem. Soc.* **1992**, *114*, 8565. (b) Gajewski, J. J.; Olson, L. P.; Tupper, K. J. *J. Am. Chem. Soc.* **1993**, *115*, 4548.

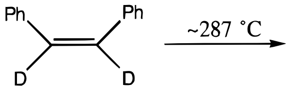

Figure 6. Experimental study.

Table 8. Experimental Kinetic Isotope Effects for Thermal Isomerization of *cis*-Stilbene and α,α′-Dideuterio-*cis*-stilbene at 287 ± 3 °C.[a]

run no.	KIE (k_H/k_{D2})[b]	
A1	1.25	
A2	1.60	
A3	1.41	
A4	1.53	A1−A4 av: 1.45
B1	1.45	
B2	1.61	
B3	1.59	
B4	1.39	
B5	1.29	
B6	1.64	B1−B6 av: 1.50
overall av:	1.47 ± 0.13 (σ_n)	

[a] 560 ± 3 K. [b] KIEs corrected for incomplete deuterium incorporation, assuming the following: $(k_H/k_D)^2 = k_H/k_{D2}$; (fraction D_0) = (% H/100)^2; and (fraction D_1) = 1 − [(fraction D_2) + (fraction D_0); and (fraction D_2) = (% D/100)^2.

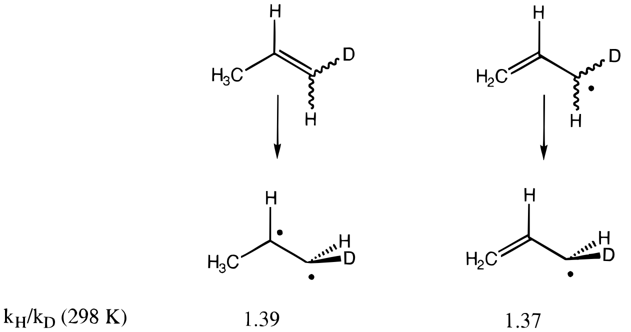

Figure 7. MCSCF KIE for propene and allyl.

Experimental Measurements of Stilbene Rotational KIE

In order to test several of our general theoretical predictions concerning alkene isomerization KIEs, we pyrolyzed *cis*-stilbenes (Figure 6). Two sets of KIE data were obtained (Table 8), with the samples in each set synthesized, purified, pyrolyzed, and analyzed independently from the other set, by different investigators.

The two sets of data have been corrected for incomplete deuterium incorporation in the deuterated samples (94% D incorporation in samples A1−A4; 88% D incorporation in samples B1−B6). Overall, the two sets of data agree with each other very well. Despite careful pretreatment of the pyrolysis tubes, the greatest source of error in the measured KIEs is probably due to residual surface catalysis which might affect one sample more than the other in any given run; this error should be random, however. Presumably, the experimental error in the KIE could be reduced by taking extreme care to eliminate all surface catalysis; nonetheless, the essential result is clear: even at its lower bound, the KIE is substantial. The large experimental KIE in this case (k_H/k_{D2} = (1.47 ± 0.13) (σ) at 287 °C) agrees with the calculated KIE for a model *cis*-disubsituted alkene (entry 3, Table 7; k_H/k_{D2} = 1.58 at 300 °C). Deuterium has a pronounced effect on the isomerization rate even at the elevated temperature of 287 °C.

Discussion

Large KIEs are calculated for rotation about the restricted C−C bonds of alkenes and allyl radical. In the case of alkenes, the calculations do not support the notion that only one $-CH_2$ torsional vibration is affected in the transition state for methylene rotation.[1b,5] Rather, a number of modes are involved in creating the large KIE. Nonetheless, the predicted significant loss of zero-point energy[1b,5] is borne out by the calculations on alkenes. Allyl radical, on the other hand, has a much smaller loss of zero-point energy in its rotation process. Still, from Table 6, the ZPE term is quite significant.

In alkene rotations, similar mass effects to those observed in amide rotations[10,11] are seen; the terminus of the rotating bond with the heavier substituents has less motion in the transition state. This leads to a smaller KIE with deuterium on the more heavily-substituted terminus relative to the KIE with deuterium on the less-substituted terminus. For example, the KIE is largest with deuterium on C1 of propene.

No KIEs for allyl radical isomerizations seem to have been reported; however allyl radical is a model for a number of reactions with putative allyl-radical-like intermediates or transition states, where methylene rotation must occur in order for the reaction (e.g., ring closure) to occur. The [1,3] shifts of vinylcyclopropanes and vinylcyclobutanes may involve transition states or intermediates resembling an allyl radical tethered to another radical site. The observed KIEs at approximately 300 °C are k_H/k_{D2} = 1.14−1.18 for vinylcyclopropane rearrangements[2] and k_H/k_{D2} = 1.07 for a vinylcyclobutane rearrangements[4] when the methylene termini are deuterated. These values are significantly lower than k_H/k_{D2} = 1.46, which we predict for allyl radical rotation at that temperature. These reactions, however, consist of considerable nuclear motion aside from simple hydrogen motion, and almost certainly a certain degree of carbon rehybridization, depending on the degree of bond formation. Nonetheless, the source of the observed kinetic isotope effect in these cases should be similar in principle to that of allyl radical, and substantial KIEs should be observed even at elevated temperatures in many reactions where rotational motion of hydrogen through space is an important component of the reaction coordinate. These KIEs could be partly caused by fractionation between vinyl and allyl carbon.

Another interesting point is observed in the calculations: methylene twisting (as experienced by C1) is a similar process in propene and allyl radical (Figure 7). Despite significant differences in the rotational barriers as well as the magnitude of various terms in the Bigeleisen equation, the calculated KIEs are nearly the same; the MCSCF calculation of doublet allyl radical provides a similar KIE result to that of singlet biradical propene.

Three distinct features become apparent from inspection of Tables 5−7. (**i**) Even at a high temperature, significant KIEs are predicted. The calculations suggest that this is primarily a consequence of the large zero-point energy terms and the large ratios of imaginary frequencies in the Bigeleisen equation. The loss or diminution of several ground-state modes and the considerable hydrogen motion required for twisting about the C=C bond are reflected here. (**ii**) The KIE per deuterium is predicted to increase with increased substituent mass, because the zero-point energy term becomes *more sensitive* to each deuterium substituent when there are *fewer* hydrogens overall which are involved in the reaction coordinate. As examples, note the increase in KIEs in Table 7 along the series dideuterioethylene, propene, and butene (simulated). In the experiment of Caldwell *et al.*[5] as well as our own (Table 8) the masses connected to the twisting double bond are considerable. (**iii**) Large KIEs are predicted in the C=C rotation of normal, unstrained alkenes (as was also predicted by Caldwell *et al.*[5]). Using the hypothetical trisubstituted alkene (entry 5 in Table

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(30) Bell, R. P. *Trans. Faraday Soc.* **1959**, *55*, 1.

7), where 2-deuteriopropene has been substituted at C1 with two hydrogens of mass = 15 (**M**), the calculated KIE is 1.632 at 25 °C; with a tunneling correction[31] applied, this value increases to 2.365 (based on an imaginary frequency of 830*i* cm^{-1} for the nondeuterated and 631*i* cm^{-1} for the deuterated species). With or without the tunneling correction, the calculated value compares reasonably well with the experimental value of 2.0,[5] considering the difference between the hypothetical trisubstituted alkene and *trans*-1-phenylcyclohexene. Experiment also showed that k_H/k_{D3} for *trans*−*cis* isomerization of 2,6,6-trideuteriophenylcyclohexene differed little from k_H/k_D for isomerization of 2-deuteriophenylcyclohexene.[5] This is consistent with our calculations, which show that there is only a small KIE associated with the isomerization of 3,3,3-trideuteriopropene (Table 7).

Conclusions

Our experiments with *cis*-stilbenes (Table 8) demonstrate the points (**i**, **ii**, and **iii**) discussed above: at a high temperature, an unstrained alkene with ponderous substituents exhibits a large secondary deuterium KIE on thermal isomerization.

We also conclude that the results of Caldwell *et al.*[5] are not due to a spurious effect caused by trace catalysts in the nondeuterated sample or trace inhibitors in the deuterated sample, as has been suggested.[10] Furthermore, the description of the alkene rotational KIE as a "quasi-primary" isotope effect[5] seems appropriate; although there is not simply a single torsion which is lost in the transition state, the considerable hydrogen motion and the loss of zero-point energy in the rotational process are indeed reminiscent of primary KIEs.

We also predict large rotational KIEs in the isomerization of allyl radicals substituted with deuterium at the radical termini. This is a testable hypothesis.

Experimental Section

cis-Stilbene was obtained from Aldrich. ^1H NMR spectra were recorded at 360 MHz using a Bruker AM360 spectrometer. Capillary gas chromatography was performed using a Hewlett-Packard HP-1 methylsilicone column (25 m × 0.2 mm id) installed in a Hewlett-Packard 5890 Series II chromatograph equipped with flame ionization detection (FID). *cis*- and *trans*-stilbenes were assumed to have the same FID sensitivity factor.

***(Z)*-1,2-(^{2}H)-Diphenylethene**. This procedure is a slightly modified version of a published method[31] for selective reduction of alkynes to *cis*-alkenes. A zinc−copper−silver couple was prepared as follows: $Cu(OAc)_2 \cdot H_2O$ (70 mg) was added to a stirred suspension of Zn dust (0.7 g) in 4 mL of D_2O. After 15 min, $AgNO_3$ (70 mg) was added. After an additional 15 min, the suspension was filtered, and the filtrant was washed successively with D_2O (5 mL), CH_3OD (5 mL), dry acetone (8 mL), and dry ethyl ether (8 mL). The activated zinc was then resuspended in 4 mL of CH_3OD/D_2O (5:3 v/v). Diphenylacetylene (0.10 g, 0.56 mmol) was added to the suspension, and it was stirred under argon at room temperature for 16 h; then the mixture was refluxed for 6 h (at which point no starting material was detectable by thin-layer chromatography (UV detection; hexane/silica gel)). The mixture was filtered, and most of the solvent was evaporated. The product was extracted with pentane (3 × 20-mL portions) and dried ($MgSO_4$). After evaporation of solvent, the residue was distilled (bulb-to-bulb, 90 °C/3 Torr) and purified by chromatography on silica gel (hexane). Bulb-to-bulb distillation was then repeated twice to give 73 mg of product (68% yield), >99% pure by capillary GC. Deuterium incorporation was 88% in one sample and 94% in the other, as determined by careful collection (20-s pulse delays) and integration of the ^1H NMR spectra. ^1H NMR (360 MHz, acetone-d_6): δ 6.64 (br s, 0.12H), 7.22−7.30 (m, 10H).

Pyrolysis. The pyrolysis tubes were cleaned with concentrated chromic acid, rinsed with distilled water, soaked overnight in 1 M HNO_3, rinsed with distilled water, soaked for 3 days in a dilute solution of Na_2EDTA, rinsed with distilled water and concentrated ammonium hydroxide, and then oven-dried. The interior surfaces were wetted with freshly distilled Me_2SiCl_2; after evaporation of the silane, the tubes were rinsed with ethyl acetate, dried, rinsed with dilute ammonium hydroxide and glass-distilled water, and dried in an oven (120 °C) for two days.

Samples of purified *cis*-stilbene (3 μL) were vacuum-sealed after two cycles of freeze−pump−thaw degassing in the pyrolysis tubes. Pyrolyses were carried out using a tube furnace equilibrated at 287 ± 3 °C. Fine temperature control was not used, because the quantity of interest was the *ratio* of rate constants, which should vary little over this small temperature range. The furnace was fitted with a large Pyrex sleeve (sealed at one end and loosely packed with glass wool at the other end) into which the pyrolysis tubes were inserted. Deuterated and nondeuterated samples were inserted and removed simultaneously, and the large Pyrex sleeve was rotated several times during pyrolysis to ensure a homogeneous temperature environment. Pyrolysis was carried out over 0.5 to 2 half-lives of isomerization, that is, from 30 min to 2 h in different runs. Analysis of stilbenes was by capillary gas chromatography, with several determinations of each sample averaged to determine the *cis*−*trans* ratio. No significant side products were observed by gas chromatography.

Acknowledgment. We are grateful to the National Science Foundation for financial support of this research.

Supporting Information Available: Tables of MCSCF/6-311G** frequencies (11 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

JA952046B

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[31] Avignon-Tropis, M.; Pougny, J. R. *Tetrahedron Lett.* **1989**, *30*, 4951.