J. Am. Chem. Soc. **1992**, *114*, 2085–2093

is somewhat misleading, being probably based upon the possibility of shuttling. Indeed, both the present and MRD–CI calculations indicate that β-chloroethyl is a classical radical. In fact, both calculations predict a tetrahedral arrangement of atoms around C_β at the absolute energy minimum, and that the rotational motion about the C_α–C_β bond is favored over the shuttle motion. The stereochemical control of small entity exercised by the chlorine atom[9] could be due to the high population of the eclipsed rotamer I in conjunction with the nonplanarity of the radical site[13] and/or steric hindrance of the β-substituent rather than due to shuttling since the present calculations show that this motion cannot occur for other β-substituted alkyl radicals (M = S, Si) where an analogous control was observed experimentally. In this connection, it is worthwhile to mention that MRD–CI calculations on β-bromoethyl[11] predicted that the shuttle motion is nearly free and favored over the rotational motion. This theoretical result is consistent with the complete stereochemical control exerted by the bromine atom. Indeed, the ESR spectra of β-bromoalkyl radicals[41] exhibit unusual features for β-substituted alkyl radicals. The spectral analysis of symmetric compounds as a function of temperature indicates that the bromine atom oscillates rapidly between two equivalent sites. However, it was suggested that the spectral features could also be interpreted as due to a rocking motion. Investigation in this direction is now being made.

Conclusion

The structural parameters of β-substituted ethyl radicals containing second- and third-row elements are typical of a classical radical having a nonplanar radical center. Substituents containing second-row elements adopt a gauche conformation, but rotation about the C_α–C_β bond is nearly free. Substituents containing third-row elements are constrained to the eclipsed conformation by a sizable rotation barrier. The shuttle motion of the substituent between the C_α and C_β atoms is less favored with respect to the rotoinversion motion about the C_α–C_β bond. Shuttling is likely for the chlorine atom, highly unlikely for the H_2N, HO, and F groups, and impossible for the other substituents. These results are in contrast to the hypothesis that static or dynamic asymmetric bridging generally occurs in radicals bearing third-row substituents. By contrast, the experimental findings can be explained with the change in the rotoinversion energy surface on going from second- to third-row elements and with the remarkable dependence of the β-splitting on the electronegativity of the substituent in the eclipsed conformation.

Registry No. Ethyl radical, 2025-56-1; 1-propyl radical, 2143-61-5; 2-aminoethyl radical, 4422-53-1; 2-hydroxyethyl radical, 4422-54-2; 2-fluoroethyl radical, 28761-00-4; 2-silylethyl radical, 31452-28-5; 2-phosphinoethyl radical, 88999-41-1; 2-mercaptoethyl radical, 88053-53-6; 2-chloroethyl radical, 16519-99-6.

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Stereomutation of Cyclopropane Revisited. An ab Initio Investigation of the Potential Surface and Calculation of Secondary Isotope Effects

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Abstract: The transition states for single and double methylene group rotation on the singlet trimethylene potential surface have been located at the GVB/6-31G* level of theory, with one pair of electrons correlated. The preference for conrotatory double rotation over single rotation is found to be 0.97 kcal/mol at the GVB level, and is expected to increase slightly with inclusion of additional electron correlation, on the basis of SD-CI calculations on (0,0)- and (0,90)-trimethylene. At the SD-CI level, the transition state for disrotation is expected to be quite close in energy to that for single rotation, and passage over either of these transition states can lead to net one-center epimerization. The H/D kinetic isotope effects for passage over all three of these transition states have been calculated and found to be moderate and normal, with the β isotope effects much smaller than the α effects. On the basis of the isotope effects computed for conrotatory double methylene group rotation, the kinetic preference for cleavage of an isotopically less substituted bond in cyclopropane-*1,2-*$^{2}H_{2}$ (**1**) is calculated to be $z_{12} = 1.13$. This value is in good agreement with that assumed by Berson et al. in their analysis of the stereomutations of **1**. However, this value is very different from the value of $z_{12} = 0.4$ that is required in order to apply a common mechanistic interpretation to the experimental results obtained recently for cyclopropane-*1-*^{13}C-*1,2,3-*$^{2}H_{3}$ (**2**) by Baldwin and co-workers, and to those obtained for **1** by both Berson et al. and Baldwin et al.

Introduction

Even after two decades of careful studies, the thermal stereomutations of cyclopropanes appear resolutely to resist all attempts at a unified mechanistic description.[1] Most experimental and theoretical effort has focused on distinguishing among three limiting stereomutation mechanisms. These three are (i) rotation of a single methylene group—the so-called Smith mechanism,[3] (ii) cleavage of a C–C bond to give a trimethylene diradical intermediate in which random loss of stereochemistry is at least competitive with ring closure—the Benson hypothesis,[4] and (iii) coupled, simultaneous rotation of two methylene groups—the Hoffmann mechanism.[5]

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(1) A number of reviews[2] chronicle the ample experimental literature on the subject, as well as the numerous theoretical studies of the trimethylene potential energy surface.

(2) (a) Borden, W. T. In *Reactive Intermediates*; Jones, M., Moss, R. A., Eds.; Wiley-Interscience: New York, 1985; Vol. 3, pp 151–188. (b) Gajewski, J. J. *Hydrocarbon Thermal Isomerizations*; Academic Press: New York, 1981; pp 27–35. (c) Borden, W. T. In *Reactive Intermediates*; Jones, M., Moss, R. A., Eds.; Wiley-Interscience: New York, 1981; Vol. 2, pp 175–209. (d) Berson, J. A. In *Rearrangements in Ground And Excited States*; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 1, pp 311–390.

(3) (a) Smith, F. T. *J. Chem. Phys.* **1958**, *29*, 235. (b) Kollmar, H. *J. Am. Chem. Soc.* **1973**, *95*, 966.

0002-7863/92/1514-2085$03.00/0

Figure 1. Idealized (0,0)- and (0,90)-trimethylene geometries.

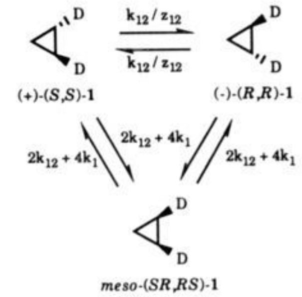
The results of Hoffmann's extended Hückel calculations[5] on (0,0) and (0,90) geometries for singlet trimethylene (Figure 1) provided the motivation for considering the coupled double rotation mechanism. These calculations led to three important predictions: (i) double rotation via a (0,0)-trimethylene intermediate should be favored over single rotation, involving a (0,90)-trimethylene, by 10 kcal/mol, (ii) the barrier preventing (0,0)-trimethylene from closing to cyclopropane is small, amounting to about 1 kcal/mol,[6,7] and (iii) double rotation should occur preferentially in a conrotatory sense, since through-bond interaction in (0,0)-trimethylene results in the p-orbitals of the terminal methylene groups being out of phase in the HOMO.

Subsequent ab initio investigations[8] have focused primarily on (0,90)- and (0,0)-trimethylene as models for, respectively, the rate-determining transition states in single and double methylene group rotations in cyclopropane stereomutations. The results of the ab initio calculations concur with Hoffmann's extended Hückel predictions ii and iii. However, although the ab initio calculations find (0,0)- to be lower in energy than (0,90)-trimethylene, they are also unanimous in predicting a very *small* energy difference (0.4–1.1 kcal) between the two geometries.

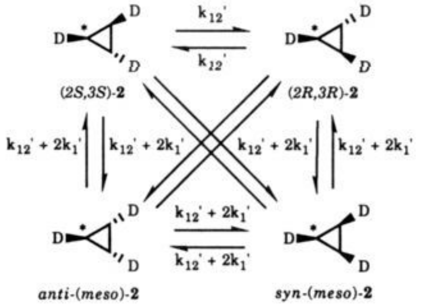
In a pioneering study, Salem and co-workers actually located the transition state for one-center rotation at the ROHF+(3×3)-CI level of theory, using a minimal basis set.[8c,f] This transition state was found to have C_1 symmetry, with the rotating methylene group twisted 5° out of the C–C–C plane. Subsequently, (0,90)-trimethylene, which has C_s symmetry, was identified as the transition state for single rotation at the TCSCF level of theory, with a double-ζ (DZ) basis set.[8p] However, another TCSCF study with the 6-31G basis set again found a C_1 structure, much like Salem's, to be the true transition state.[8q]

Salem and co-workers also determined the approximate location of the transition state for coupled rotation.[8c] Their ROHF+(3×3)-CI calculations showed that pyramidalization in either a syn or anti fashion lowers the energy of (0,0)-trimethylene. Calculations performed by Schaefer and co-workers at the TCSCF/DZ level of theory[8p] found that (0,0)-trimethylene has two imaginary frequencies. This result confirms that (0,0)-trimethylene is a mountaintop, not a transition state on the potential energy surface for cyclopropane stereomutation. The precise location of the transition state for two-center rotation has, to our knowledge, not been reported.

Scheme I



Scheme II



The current mechanistic understanding of cyclopropane stereomutations from experiment is also less than satisfactory. The predominant stereomutation mechanism appears to be highly dependent on the choice of substituents. For example, single rotation appears to be the dominant mode of stereomutation in methyl 1,2-diphenylcyclopropanecarboxylate,[9] while a random diradical intermediate provides the most plausible description of the rearrangements of *anti*-(2*RS*,3*SR*)-vinylcyclopropane-*2,3*-$^2H_2$.[10] On the other hand, *trans*-1,2-diphenylcyclopropane[11] appears to show at least some propensity for double rotation. The balance of the substituted cyclopropanes studied[2b,d] show competition between at least two of these mechanisms.

In the absence of a single general mechanism for the stereomutation of substituted cyclopropanes, subsequent experimental efforts shifted toward elucidating the mechanism of stereomutation in cyclopropane bearing only isotopic substituents. Berson and co-workers[12] reported the first of these, a tour de force investigation of the stereomutations of (+)-(*S,S*)-cyclopropane-*1,2*-$^2H_2$ (**1**). A simplified kinetic analysis of the kinetic behavior of this system is shown in Scheme I.

Scheme I assumes that the overall kinetic behavior can be treated as a competition between discrete one- (k_1) and two-center (k_{12}) rotation reactions.[13] The quantity z_{12} in Scheme I is the

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(4) (a) Benson, S. W. *J. Chem. Phys.* **1961**, *34*, 521. (b) Benson, S. W.; Nangia, P. S. *J. Chem. Phys.* **1963**, *38*, 18. (c) O'Neal, H. E.; Benson, S. W. *J. Chem. Phys.* **1968**, *72*, 1866. (d) O'Neal, H. E.; Benson, S. W. *Int. J. Chem. Kinet.* **1970**, *2*, 42. (e) Benson, S. W.; O'Neal, H. E. *Kinetic Data on Gas Phase Unimolecular Reactions*; U.S. Department of Commerce, National Bureau of Standards, 1970. (f) Benson, S. W. *Thermochemical Kinetics*; Wiley: New York, 1971; p 83.

(5) Hoffmann, R. *J. Am. Chem. Soc.* **1968**, *90*, 1475.

(6) The implication that the enthalpy barrier to closure of trimethylenes should be small or nonexistent is at variance with Benson's original thermochemical analysis,[4] but is in accord with a more recent one,[7] based on revised heats of formation for ethyl radical and for the transition state for cis–trans isomerization of 1,2-cyclopropane-$^2H_2$.

(7) Doering, W. von E. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 1695.

(8) (a) Buenker, R. J.; Peyerimhoff, S. C. *J. Phys. Chem.* **1969**, *73*, 1299. (b) Siu, A. K. O.; St. John, W. M.; Hayes, E. F. *J. Am. Chem. Soc.* **1970**, *92*, 7249. (c) Jean, Y.; Salem, L.; Wright, J. S.; Horsley, J. A.; Moser, C.; Stevens, R. M. *Pure Appl. Chem., Suppl. (23rd Congr.)* **1971**, *1*, 197. (d) Jean, Y.; Salem, L. *J. Chem. Soc., Chem. Commun.* **1971**, 382. (e) Hayes, E. F.; Siu, A. K. O. *J. Am. Chem. Soc.* **1971**, *93*, 2090. (f) Horsley, J. A.; Jean, Y.; Moser, C.; Salem, L.; Stevens, R. M.; Wright, J. S. *J. Am. Chem. Soc.* **1972**, *94*, 279. (g) Hay, P. J.; Hunt, W. J.; Goddard, W. A. *J. Am. Chem. Soc.* **1972**, *94*, 638. (h) Yamaguchi, K.; Fueno, T. *Chem. Phys. Lett.* **1973**, *22*, 471. (i) Jean, Y.; Chapuisat, X. *J. Am. Chem. Soc.* **1974**, *96*, 6911. (j) Chapuisat, X.; Jean, Y. *J. Am. Chem. Soc.* **1975**, *97*, 6325. (k) Yamaguchi, K.; Ohta, K.; Yabushita, S.; Fueno, T. *Chem. Phys. Lett.* **1977**, *49*, 555. (l) Yamaguchi, K.; Nishio, A.; Yabushita, S.; Fueno, T. *Chem. Phys. Lett.* **1978**, *53*, 109. (m) Kato, S.; Morokuma, K. *Chem. Phys. Lett.* **1979**, *65*, 19. (n) Doubleday, C.; McIver, J. W.; Page, M. *J. Am. Chem. Soc.* **1982**, *104*, 6533. (o) Goldberg, A. H.; Dougherty, D. A. *J. Am. Chem. Soc.* **1983**, *105*, 284. (p) Yamaguchi, Y.; Osamura, Y.; Schaefer, H. F. *J. Am. Chem. Soc.* **1983**, *105*, 7506. (q) Doubleday, C.; McIver, W. M.; Page, M. *J. Phys. Chem.* **1988**, *92*, 4367.

(9) Chmurny, A.; Cram, D. J. *J. Am. Chem. Soc.* **1973**, *95*, 4237.

(10) Willcott, M. R.; Cargle, V. H. *J. Am. Chem. Soc.* **1969**, *91*, 4310.

(11) Crawford, R. J.; Lynch, T. R. *Can. J. Chem.* **1968**, *46*, 1457.

(12) (a) Berson, J. A.; Pedersen, L. D. *J. Am. Chem. Soc.* **1975**, *97*, 238. (b) Berson, J. A.; Pedersen, L. D.; Carpenter, B. K. *J. Am. Chem. Soc.* **1976**, *98*, 122.

(13) Berson and co-workers performed separate kinetic analyses for the three limiting mechanisms mentioned above, as well as for a triple methylene rotation mechanism, and for a diradical intermediate in which random internal rotation and closure are competitive. The analysis given here more closely resembles that given by Carpenter.[14] The scheme in his Figure 4.7 on p 63 reduces to our Scheme I, upon making the following substitutions: $k_d = k_{12}$, $k_s = 2k_1$, and $k_o = 0$ (k_o is the rate constant for cleavage of cyclopropane to give a random diradical intermediate). The factor of 2 in he expression for k_s arises because cleavage of two different C–C bonds allows rotation of the same carbon.

(14) Carpenter, B. K. *Determination of Organic Reaction Mechanisms*; Wiley-Interscience: New York, 1984.

factor by which coupled rotation of C(1)–C(2) is slower than coupled rotation of C(1)–C(3) or of C(2)–C(3), due to the combination of α and β secondary deuterium isotope effects. Analysis of Scheme I yields expressions for the first-order rate constants for trans–cis isomerization (k_i) and for loss of optical activity (k_α) in terms of k_1, k_{12}, and z_{12}. The ratio of these two phenomenological rate constants, k_i and k_α, is given in eq 1.

$$\frac{k_i}{k_\alpha} = \frac{2(2k_1 + k_{12})}{2k_1 + k_{12}(1 + 1/z_{12})} \qquad (1)$$

For **1** at 422.5 °C, Berson and co-workers[12] measured $k_i/k_\alpha = 1.07 \pm 0.04$. This result has recently been corroborated by Baldwin and co-workers,[15] who measured $k_i/k_\alpha = 1.09 \pm 0.05$ for **1** at the same temperature. Using the value $k_i/k_\alpha = 1.07$ and assuming a modest, normal isotope effect of $z_{12} = 1.10$, eq 1 gives the ratio of double to single rotation rates as $k_{12}/k_1 = 98/2$. On the basis of this finding, Berson and co-workers concluded that "...there is no doubt that the double rotation mechanism predominates by a substantial factor".[12b]

This interpretation has recently been challenged by Baldwin and co-workers.[16] In an elegant experiment, these researchers investigated the thermal stereomutations of (2*S*,3*S*)-cyclopropane-*1*-^{13}*C*-*1,2,3*-$^2H_3$ (**2**). Every carbon atom in **2** bears the same substituents, since the stereogenicity is engendered by the ^{13}C label. Consequently for **2**, no assumption about the magnitude of secondary H/D isotope effects needs be made. This is in contrast to **1**, for which a value of z_{12} must be assumed.

The kinetic analysis of **2**, shown in Scheme II, yields eq 2 for the ratio of the phenomenological rate constants (k_i' and k_α') in terms of the rate constants for single (k_1') and double (k_{12}') rotation. Assuming that primary and secondary ^{13}C isotope effects in **2** are negligible, no terms involving isotope effects appear in eq 2. Consequently, eq 2 can be solved unambiguously for k_{12}'/k_1'.

$$\frac{k_i'}{k_\alpha'} = \frac{2k_1' + k_{12}'}{k_1' + k_{12}'} \qquad (2)$$

For **2** at 407.0 °C, Baldwin and co-workers[16] measured $k_i' = (4.59 \pm 0.09) \times 10^{-5}\ \mathrm{s}^{-1}$ and $k_\alpha' = (3.10 \pm 0.07) \times 10^{-5}\ \mathrm{s}^{-1}$, which yields $k_i'/k_\alpha' = 1.48 \pm 0.04$ and $k_{12}'/k_1' = 1.05 \pm 0.10 \cong 51/49$. Therefore, these researchers concluded that the single and double rotation mechanisms contribute essentially equally to the stereomutations of **2**. Furthermore, they suggested that the conclusion drawn by Berson and co-workers[12] for **1** and quoted above is incorrect because of "...some reasonable but nevertheless erroneous assumptions regarding kinetic isotope effects which were employed...".[16]

Although Baldwin and co-workers[16] seem implicitly to assume that **1** and **2** undergo stereomutation by the same combination of one- and two-center rotation mechanisms (i.e., $k_{12}'/k_1' = k_{12}/k_1$), they stop short of explicitly stating the magnitude of z_{12} in **1** that is required by this assumption. This value can be derived by appropriate algebraic manipulation of eq 1. Substituting $k_{12}'/k_1' = 1.05 \pm 0.10$ measured for **2**[16] for the analogous ratio, k_{12}/k_1, in **1**, and using the value of $k_i/k_\alpha = 1.09 \pm 0.05$ found in **1**,[12,15] gives $z_{12} = 0.41 \pm 0.06$. The existence of a net inverse isotope effect (comprised of both α and β secondary deuterium isotope effects) of this magnitude is necessary in order to apply a common mechanistic interpretation to the experimental results obtained for the trideuteriocyclopropane (**2**), and to those obtained for the dideuterio system (**1**).

Although a net inverse secondary deuterium isotope effect of this size, particularly at temperatures above 400 °C, would be without precedent,[17] this does not a priori exclude such an effect from the realm of possibility in the case of cyclopropane stereomutations. However, another possible explanation for the difference between the results obtained for **1** and for **2** is that the difference in their isotopic substitution results in a difference between the relative contributions of one-center and two-center rotation mechanisms to the stereomutations of these two cyclopropanes. Thus, in addition to determining the magnitude of z_{12} in **1**, isotope effects could also cause the ratio k_{12}/k_1 in **1** to differ from the ratio k_{12}'/k_1' in **2**.

In order to estimate the size and nature of the isotope effects that are likely to be manifested in cyclopropane stereomutations, we have performed ab initio calculations. We have (i) located the transition states for single and double methylene group rotations, (ii) calculated the vibrational force constants for these transition states and for cyclopropane, and (iii) computed the effects of isotopic substitution on the vibrational frequencies and, hence, on the reaction rates. Herein we report the results of our calculations.

Computational Methodology

All calculations were performed using the 6-31G* basis set.[18] Geometry optimization and vibrational analysis of cyclopropane were carried out at the RHF level, while those of the various singlet trimethylenes were performed at the GVB level, with one pair of electrons correlated. The RHF and GVB calculations were done with the Gaussian 88[19] package of ab initio programs.

In order to investigate the effects of including additional electron correlation, SD-CI calculations were performed on those optimized trimethylene structures having an element of symmetry. Unfortunately, SD-CI calculations on structures with C_1 symmetry were beyond our computational resources. The SD-CI calculations utilized two-configuration reference wave functions, except in the case of (0,90)-trimethylene (**4**). The C_s symmetry plane present in the (0,90) geometry allowed the utilization of an ROHF reference wave function. The CI calculations were performed using MELDF.[20]

Secondary deuterium isotope effects, as well as primary and secondary ^{13}C isotope effects, were calculated with the RHF/6-31G* force constants for cyclopropane, and the GVB/6-31G* force constants for the transition states. The calculated vibrational frequencies and force constants were used without scaling (vide infra). The program QUIVER[21] was used to carry out the isotope effect calculations.

Results and Discussion

Trimethylene Potential Energy Surface. We have located eight stationary points on the potential energy surface (PES) for singlet trimethylene. The optimized geometries are shown pictorially in Figure 2. Vibrational analyses showed two of these (**3** and **4**) to be mountaintops, two more (**5** and **6**) to be local minima, and the remaining four (**7–10**) to be transition states on the PES. The most important geometric parameters for **3–10** are defined in Figure 3, and summarized in Table I. The energies calculated for **3–10** at the GVB and SD-CI levels of theory are given in Table II. Complete listings of the GVB/6-31G* optimized geometries and vibrational frequencies for **3–10** are available as supplementary material.[22]

The GVB/6-31G* vibrational analysis of the (0,0) geometry **3** reveals two imaginary frequencies, consistent with the results previously obtained with an unpolarized DZ basis set.[8p] One of these imaginary modes (b_1, $\nu = 334i\ \mathrm{cm}^{-1}$) corresponds principally to syn pyramidalization of the two terminal methylene groups, coupled with some disrotation, while the other (a_2, $\nu = 317i\ \mathrm{cm}^{-1}$) corresponds principally to anti pyramidalization, coupled with some conrotation.

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(20) Developed at the University of Washington by McMurchie, L.; Elbert, S.; Langhoff, S.; Davidson, E. R. Modified by Feller, D.; Rawlings, D.

(21) Saunders, M.; Laidig, K. E.; Wolfsberg, M. *J. Am. Chem. Soc.* **1989**, *111*, 8989. We thank Professor Saunders for supplying us with a copy of this program.

(22) Ordering information is given on any current masthead page.

Table I. Important Structural Features Calculated for Cyclopropane and for Singlet Trimethylenes **3–10**

	distances (Å)		angles (deg)				
structure	C(1)–C(2)	C(2)–C(3)	C–C–C	θ_1[a]	θ_3[a]	ϕ_1[b]	ϕ_3[b]
3	1.501	1.501	115.3	0.0	0.0	0.0	0.0
4	1.504	1.508	114.0	0.0	90.0	0.0	−22.2
5	1.503	1.503	115.1	−16.6	16.6	21.9	21.9
6	1.502	1.502	113.6	30.6	30.6	20.2	20.2
7	1.506	1.506	110.4	−39.3	39.3	18.1	18.1
8	1.502	1.502	112.8	38.6	38.6	16.8	16.8
9	1.502	1.502	114.9	8.2	27.1	−12.4	21.4
10	1.507	1.507	114.3	5.0	97.0	21.0	−21.4
c-C_3H_6	1.497	1.497	60.0	90.0	90.0	30.0	30.0

[a] Methylene twist angle. Positive and negative values refer, respectively, to counterclockwise and clockwise twists, relative to (0,0)-trimethylene (**3**). [b] A positive value of ϕ_1 indicates the terminal methylene group is pyramidalized so that the partially occupied orbital at C(1) is tilted toward C(3), while a negative value indicates this partially occupied orbital is tilted away from C(3).

Table II. Calculated Energies for Cyclopropane and for Singlet Trimethylenes **3–10**

	GVB/6-31G*		SD-CI	
structure	E_{calc}[a]	E_{rel}[b]	E_{calc}[a]	E_{rel}[b]
3	−116.988 882	0.00	−117.342 687	0.00
4	−116.987 686	0.75	−117.340 826	1.17
5	−116.989 696	−0.51	−117.342 132	0.35
6	−116.990 343	−0.92	−117.342 932	−0.15
7	−116.988 758	0.08	−117.341 011	1.05
8	−116.990 307	−0.89	−117.343 247	−0.35
9	−116.989 538	−0.41		−0.4[c]
10	−116.987 989	0.56		1.0[d]
c-C_3H_6	−117.058 865[e]	−43.92	−117.438 281	−59.99

[a] Energy in hartrees. [b] Energy in kilocalories per mole. [c] Estimated from the relative energies of **3** and **9** at the GVB level. [d] Estimated from the energy of **10**, relative to **4**, at the GVB level and from the effect of SD-CI on the relative energies of **3** and **4**. [e] RHF/6-31G* energy.

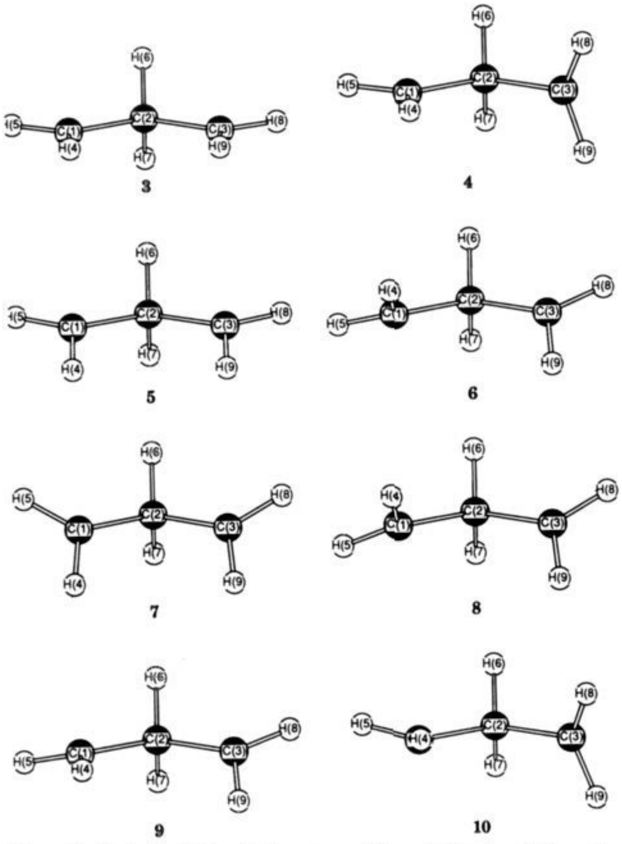

Figure 2. Optimized trimethylene geometries: (0,0)-trimethylene (**3**), C_{2v}; (0,90)-trimethylene (**4**), C_s; disrotatory local minimum (**5**), C_s; conrotatory local minimum (**6**), C_2; disrotatory transition state (**7**), C_s; conrotatory transition state (**8**), C_2; conrotatory–disrotatory interconversion transition state (**9**), C_1; single rotation transition state (**10**), C_1.

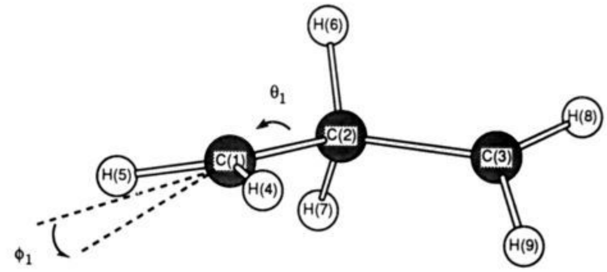

Figure 3. Internal coordinates θ and ϕ for trimethylenes **3–10**. For the sake of consistency with Hoffman's (0,0)- and (0,90)-trimethylene nomenclature,[5] the twist angle θ_n is defined as the dihedral angle between the normals to the H–C(n)–H and C–C–C planes. Each pyramidalization angle ϕ_n is defined as the angle formed by the extension of the C(2)–C(n) bond and the bisector of the H–C(n)–H angle.

Distortion of **3** along the b_1 imaginary mode lowers the symmetry to C_s. Optimization of the resulting C_s structure leads to a geometry in which the terminal methylenes are rotated by an angle (Figure 3) of $\theta = 16.6°$. Vibrational analysis indicates that this C_s structure **5**, which lies 0.51 kcal/mol below **3**, is a minimum on the PES.

Increasing θ beyond 16.6° in a disrotatory fashion causes the energy to increase monotonically up to $\theta = 39.3°$. The resulting C_s structure **7**, which lies 0.59 kcal/mol above the disrotatory minimum **5**, is a true transition state having a single imaginary frequency (a′, ν = 306i cm^{-1}), which corresponds to coupled modulation of θ and of the C–C–C bond angle.[23]

Increasing θ beyond its value in the disrotatory transition state **7** leads to a significant contraction of the C–C–C bond angle. For example, increasing θ from 40° to 50° in a disrotatory fashion causes the optimized C–C–C angle to drop from 110° to 75°. This contraction of the C–C–C bond angle is accompanied by a rapid drop in energy as trimethylene closes to cyclopropane.

A small distortion imposed on **3** along the secondary imaginary mode (a_2) lowers the symmetry to C_2. Geometry optimization in C_2 symmetry leads to a new minimum (**6**) on the PES at θ = 30.6°, 0.92 kcal/mol below **3**. Increasing the twist angle to θ = 38.6° leads to a conrotatory transition state (**8**) with a single imaginary frequency (a, ν = 159i cm^{-1}), which corresponds to coupled modulation of θ and the C–C–C bond angle. Since **8** lies only 0.03 kcal/mol above the conrotatory minimum **6**, neither is chemically significant; the minimum corresponding to **6** could easily vanish with a different basis set.

Thus, for all practical purposes, conrotation leads from the (0,0) geometry **3** to cyclopropane without an energy barrier. By contrast, disrotatory closure starting from **3** encounters a barrier, 0.08

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(23) After our calculations were completed, we were informed of the results of recent calculations by Yamaguchi, Schaefer, and Baldwin.[24] They have also located a disrotatory transition state, nearly identical in structure to that of **7**, and their results lead to the same qualitative conclusions regarding the relative energies of **3**, **4**, and **7** as do ours (vide infra).

(24) Yamaguchi, Y.; Schaefer, H. F.; Baldwin, J. E. *Chem. Phys. Lett.*, submitted for publication. We thank Professor Schaefer for providing us with a copy of this paper prior to publication.

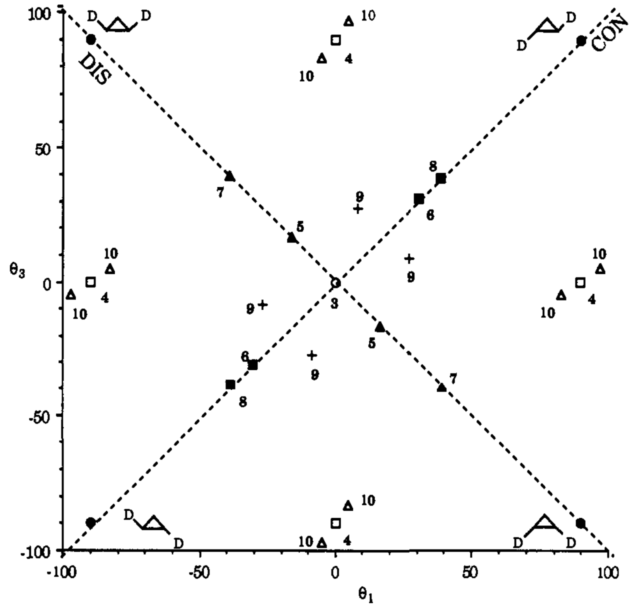

Figure 4. Location of stationary points on the cyclopropane–trimethylene PES in terms of the twist angles θ_1 and θ_3 at the terminal methylenes (C(1) and C(3)). Deuterium substitution on cyclopropane corresponding to **1** is shown, in order to clarify the stereochemical outcome of each reaction path: ●, cyclopropanes (D_{2h}); ○, (0,0)-trimethylene (C_{2v}); ■, conrotatory stationary points (C_2); ▲, disrotatory stationary points (C_s); +, conrotatory–disrotatory (CON-DIS) transition states (C_1); □, (0,90)-trimethylenes (C_s); △, single rotation transition states (C_1).

kcal/mol higher in energy than **3** and 0.59 kcal/mol above the disrotatory minimum **5**.

These findings are in accord with Hoffmann's analysis,[5] since conrotatory closure of **3** is "allowed", while disrotatory closure is "forbidden". However, (0,0)-trimethylene (**3**) is really a diradical, and in its wave function the ratio of the squared coefficients for the two configurations, composed of different symmetry combinations of the terminal methylene p AO's is 1.20.[25] Upon going from **3** to the disrotatory transition state **7**, the relative weights of these configurations reverse, and the ratio of the squared coefficients becomes 0.80. Nevertheless, because of the large (45%) contribution from the second configuration to the wave function of **3**, upon going to transition state **7** the energy increases by only 0.08 kcal/mol.

As noted above, **3** is a mountaintop on the singlet PES, so that it cannot be involved in cyclopropane stereomutation as an intermediate or as a transition state. Opening of cyclopropane by coupled rotation, either con- or disrotatory, must therefore break symmetry before **3** is reached. Consequently, the transition state for coupled rotation must lack any symmetry element.

We searched for a C_1 transition state that would link the disrotatory (**5**) and conrotatory (**6**) minima by rotating and inverting one of the terminal methylene groups while holding the other relatively fixed. A true transition state (**9**), 0.41 kcal/mol below **3** and 43.5 kcal/mol above the RHF energy of cyclopropane, was located. We verified that the single vibration with an imaginary frequency (ν = 140i cm^{-1}) calculated for **9** connects **9** to **5** and **6**.

Minimization of steric interactions between inward-rotating methylene hydrogens may be responsible for the fact that the energy of transition state **9** is lower than that of the (0,0) geometry **3**.[26] In the vicinity of **3** steric repulsion between H(4) and H(9) (see Figure 2) increases, as the H(4)–H(9) distance decreases, reaching a minimum value of about 2.5 Å in **3**. An effective relief for the steric crowding that would be encountered if coupled rotation passed through **3** can be achieved by inverting and rotating C(1) and C(3) in an asynchronous fashion, so that H(4) and H(9) do not simultaneously occupy the C–C–C plane.

Figure 4 shows a schematic depiction of the reaction path for coupled rotation, using the independent rotations (θ_1 and θ_3) of the terminal methylene carbons of trimethylene.[27] The dotted lines that lie along the diagonals of Figure 4 are the axes for conrotation, which maintains C_2 symmetry, and for disrotation, which maintains C_s symmetry. These two axes intersect at the (0,0) geometry **3**, which has C_{2v} symmetry.

The minimum energy pathway for coupled methylene rotation begins as purely conrotatory as it passes from cyclopropane (e.g., starting from $\theta_1 = \theta_3 = -90°$) through transition state **8** ($\theta_1 = \theta_3 = -38.6°$) and the very shallow local minimum **6** ($\theta_1 = \theta_3 = -30.6°$). In the region $-30.6 < \theta < -27.1$ an intersection is reached from which two degenerate pathways diverge, each corresponding principally to rotation and flattening of a different one of the two terminal methylenes. Each pathway leads to a transition state with the structure of **9** ($\theta_1 = -8.2°$, $\theta_3 = -27.1°$; or $\theta_1 = -27.1°$, $\theta_3 = -8.2°$), in which one methylene group has inverted, but has not yet passed through the C–C–C plane (ϕ has changed signs, θ has not; see Table I). From the transition state **9**, the energy decreases as the inverted carbon rotates through the C–C–C plane (θ changes sign), and the second methylene begins to rotate. This motion leads to a C_s local minimum with the structure of **5** ($\theta_1 = -\theta_3 = 16.6°$; or $\theta_1 = -\theta_3 = -16.6°$) as the disrotatory coordinate axis is reached.

From this point on the PES, the minimum energy pathway for coupled rotation is symmetric in the forward and reverse directions. In the forward direction, the energy increases as the second methylene carbon rotates through the C–C–C plane and begins to flatten, until another transition state of structure **9** is reached ($\theta_1 = 27.1°$, $\theta_3 = 8.2°$; or $\theta_1 = 8.2°$, $\theta_3 = 27.1°$). Both degenerate pathways decrease in energy from transition state **9**, until they intersect near the very shallow local minimum **6** ($\theta_1 = \theta_3 = 30.6°$) on the conrotatory coordinate axis. Passage over conrotatory transition state **8** ($\theta_1 = \theta_3 = 38.6°$) leads via conrotatory cyclization to the doubly epimerized cyclopropane ($\theta_1 = \theta_3 = 90°$).

Disrotation in cyclopropane also involves passage twice over transition state **9** since, as in the case of conrotation, symmetry breaking to avoid passage over **3** represents the lowest energy pathway connecting the disrotatory minima **5** at $\theta_1 = -\theta_3 = 16.6°$ and $\theta_1 = -\theta_3 = -16.6°$. However, the disrotatory transition state **7** ($\theta_1 = -\theta_3 = 39.3°$; or $\theta_1 = -\theta_3 = -39.3°$) lies 0.49 kcal/mol *above* **9**, so that **7** is the highest energy point on the pathway for disrotatory opening and closure. Since **9**, the highest energy point on the path for conrotatory closure, lies below **7**, a molecule with sufficient energy to open via the disrotatory transition state **7** can close in either a con- or a disrotatory fashion.

In addition to finding the transition states for both con- and disrotatory coupled methylene rotation, we also located the transition state for rotation of a single methylene group. Toward this end, we began by optimizing (0,90)-trimethylene (**4**) in C_s symmetry. In contrast to the previous finding with the DZ basis set,[8p] our vibrational analysis revealed two imaginary frequencies for **4**. One of these (a″, ν = 370i cm^{-1}) corresponds primarily to pyramidalization of the $\theta = 0°$ methylene group, the other (a″, ν = 319i cm^{-1}) to its rotation. Both modes, however, also involve small rotations of the $\theta = 90°$ methylene group.

A moderate distortion, corresponding to the pyramidalization mode, was imposed on **4**, and a search in C_1 symmetry led to a true transition state (**10**) for single rotation, 0.21 kcal/mol lower in energy than **4**. As shown in Table I, the geometry of **10** is characterized by a 5° twist of the rotating methylene group, C(1),

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[25] At the disrotatory minimum **5**, this ratio is 1.17, nearly the same as that in **3**.

[26] Salem and co-workers[8c] postulated that steric interactions between internal C–C and C–H bonds are responsible for the decrease in energy of (0,0)-trimethylene upon both syn and anti pyramidalization.

[27] Two dimensions are, of course, inadequate to depict all the important geometric changes that occur in cyclopropane stereomutation, which would also include, at the very least, the pyramidalization angles ϕ_1 and ϕ_3 and the C–C–C bond angle. The coordinates θ_1 and θ_3 were chosen for Figure 4, since changes in the θ's are clearly important components of the reaction path along its entire length. Changes in the ϕ's are most important in the vicinity of **3**, while changes in the C–C–C angle are most important in the vicinity of cyclopropane.

and a small (7°) conrotatory twist of the nonrotating methylene group, C(3), relative to the (0,90) geometry **4**. The single imaginary frequency in **10** (ν = 302i cm^{-1}) corresponds principally to rotation of C(1), coupled with a small amount of disrotation at C(3). We verified that the energy decreases monotonically in both directions along the reaction coordinate.

This result may at first seem curious. As shown in Figure 2, C(1) in **10** is pyramidal (ϕ = 21.0°), and orbital overlap and subsequent σ-bonding between C(1) and C(3) should develop much more rapidly if C(1) rotates in a counterclockwise sense than if it rotates clockwise. However, a careful examination of the geometry of, and the energy changes in, **10** along the reaction coordinate suggests the existence of a second factor.

Rotating C(1) counterclockwise by a small increment does in fact increase the orbital overlap between C(1) and C(3), but as shown in Figure 2, it simultaneously decreases the distance between H(4) and H(8). On the other hand, the distance between these two hydrogen atoms increases steadily with rotation of C(1) in a *clockwise* sense. Consequently, rotation of C(1) in either direction from the geometry of **10** lowers the energy.

The single rotation pathway differs from the coupled rotation pathway in requiring passage over a single transition state (**10**). For example, beginning with the cyclopropane shown in the lower left-hand corner of Figure 4 ($\theta_1 = \theta_3 = -90°$), rotating the left-hand (C(1)) methylene group leads to one of two transition states having structure **10** ($\theta_1 = -5.0°$, $\theta_3 = -97.0°$; or $\theta_1 = 5.0°$, $\theta_3 = -83.0°$), depending on whether the sense of rotation is clockwise or counterclockwise. From either of these points, the energy decreases monotonically until closure to the epimerized cyclopropane ($\theta_1 = -\theta_3 = 90°$) is achieved.

Table II shows that at the GVB level the PES in the trimethylene region is quite flat. In fact, a scant 1.6 kcal/mol range encompasses all the stationary points **3**–**10**. The energy difference between the transition states for single (**9**) and double (**10**) rotation amounts to only 0.97 kcal/mol, which increases to 1.27 kcal/mol when zero-point energies are included.

The heat capacities of **9** and **10** are calculated to be 14.1 and 13.7 gibbs/mol, respectively. This means that in calculating $\Delta\Delta H^{\ddagger}$ between transition states **9** and **10** at temperatures around 400 °C, the greater zero-point energy of **10** is almost exactly canceled by the greater heat capacity of **9**. The calculated entropies (298 K) for **9** and **10** are 64.8 and 65.0 gibbs/mol, respectively. Consequently, even at temperatures around 400 °C the $\Delta\Delta G^{\ddagger}$ between **9** and **10** should be nearly equal to the $\Delta\Delta H^{\ddagger}$ between them.

The benchmark for the calculated preference for coupled over single rotation has usually been taken to be the difference in energy between the (0,0) and (0,90) geometries. Our value of 0.75 kcal/mol for the energy difference between **3** and **4**[28] is consistent with the results of previous ab initio calculations.[8] At the SD-CI level, this energy difference increases by approximately 0.4 kcal/mol, to 1.17 kcal/mol.

By virtue of the through-bond interaction between the symmetric combination of terminal methylene p AO's and the central methylene group,[5] **3** can be regarded as electronically more delocalized than **4**. In **4**, symmetry precludes both through-bond and through-space interactions between radical centers. Since inclusion of additional electron correlation usually benefits the more delocalized of two structures preferentially,[29] it is not surprising that **3** is found to be selectively stabilized, relative to **4**, by the SD-CI calculations.

The lack of any symmetry element in **9** or **10** made SD-CI calculations impracticable for these two structures. However, it seems reasonable to infer from their relationships to **3** and **4**, respectively, that inclusion of additional correlation would tend slightly to increase the energy difference between **9** and **10**. If the preferential stabilization of **9** over **10** amounted to about 0.4 kcal/mol, as it does in the case of **3** versus **4**,[30] the energy gap between **9** and **10** would be expected to increase from 0.97 kcal/mol at the GVB level to about 1.4 kcal/mol at the SD-CI level.

At 422.5 °C, an energy gap of 1.4 kcal/mol corresponds to a ratio of rate constants for double versus single rotation of k_{12}/k_1 = 73/27. This ratio is slightly less than that of 85/15 estimated by Berson and co-workers[12] to be the minimum ratio allowed by their experimental data for **1**. Dynamical effects, however, apparently favor coupled rotation,[8i,j] and might thus be expected to increase the ratio k_{12}/k_1.

As shown in Table II, SD-CI selectively stabilizes cyclopropane, whose RHF wave function contains no correlation between electrons of opposite spin, relative to **3** and **4** (and also, by inference, to transition states **9** and **10**), whose GVB wave functions correlate one pair each. Correcting the SD-CI energy difference of 61.0 kcal/mol between **10** and cyclopropane for zero-point energies (49.2 and 54.8 kcal/mol, respectively) and heat capacities (13.7 and 9.9 gibbs/mol, respectively) gives a calculated $\Delta H^{\ddagger}$ = 58.2 kcal/mol for trans–cis isomerization of cyclopropane at 476 °C. This computed value may be compared with the experimental value of 59.8 kcal/mol obtained for **1** at this temperature.[31]

Within the coupled rotation manifold, our results agree with the previous theoretical studies[5,8] in finding that conrotation is preferred over disrotation. The highest energy transition state along the (predominantly) conrotatory pathway is **9**, which is favored over the disrotatory transition state **7** by 0.49 kcal/mol at the GVB level, and by 0.78 kcal/mol when zero-point energies are included. Since the energy difference between **3** and **7** increases by 0.97 kcal/mol upon inclusion of SD-CI, at this level **7** might be anticipated to lie about 1.5 kcal/mol above **9**.

As shown in Table II, at the GVB level of theory the energy of the disrotatory transition state **7** is slightly lower than that of the transition state **10** for rotation of a single methylene group. At the SD-CI level, these two transition states are estimated to have essentially equal energies. Since a molecule that passes over **7** has sufficient energy for either con- or disrotatory closure, it follows that passage over **7** (like passage over **10**) provides a pathway for epimerization of a single methylene group in cyclopropane.

In predicting a preference for conrotation over either disrotation or single rotation, our results do not differ qualitatively from those of previous ab initio studies, which were largely based on assumed transition-state geometries. However, our primary reason for locating the transition states on the trimethylene PES was to perform vibrational analyses at these geometries and to use the force constants thus obtained to compute the secondary deuterium isotope effects on cyclopropane stereomutation. The results of these calculations are presented and discussed in the next section.

Kinetic Isotope Effects. Kinetic isotope effects (KIEs) on one- and two-center methylene rotation were calculated using the

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(28) Preliminary calculations performed on pentane-2,4-diyl at the GVB/6-31G* level of theory show that substitution of methyl groups onto the terminal carbons of trimethylene in the sterically least demanding fashion reduces this energy gap from 0.75 to 0.16 kcal/mol. This finding suggests that the small preference for (0,0)- over (0,90)-trimethylene is likely to be overwhelmed by the electronic and steric changes introduced by even alkyl substituents. Thus, it is not surprising that alkyl-substituted cyclopropanes do not show any preference for coupled rotation.[2]

(29) Davidson, E. R.; Borden, W. T. *J. Phys. Chem.* **1983**, *87*, 4783.

(30) Since **9** is less planar and, hence, presumably less delocalized than **3**, SD-CI probably affords slightly less stabilization to **9** than to **3**. Therefore, it seems likely, especially considering the flatness of the GVB potential surface in the region around **9**, that at the SD-CI level the transition state for double rotation moves closer to the geometry of **3**. Such a change in the geometry for this transition state would be consistent with the findings that, at the SD-CI level **5**, the disrotatory minimum which lies below both **3** and **9** at the GVB level actually lies slightly above **3** and that the relative SD-CI energies of **6** and **8**, the conrotatory stationary points, are in the opposite order from those at the GVB level and closer to the SD-CI energy of **3**.

(31) Waage and Rabinovitch[32] determined that at 476 °C the Arrhenius activation energy for trans–cis isomerization is approximately 3.7 kcal/mol less than the 65.0 kcal/mol measured for the cyclopropane to propene isomerization.[33] The resulting E_a = 61.3 for the trans–cis isomerization corresponds to an enthalpy of activation $\Delta H^{\ddagger}$ = 59.8 kcal/mol at 476 °C.

(32) Waage, E. V.; Rabinovitch, B. S. *J. Phys. Chem.* **1972**, *76*, 1695.

(33) Chambers, T. S.; Kistiakowski, G. B. *J. Am. Chem. Soc.* **1934**, *56*, 399.

Table III. Calculated KIEs on Double Methylene Rotation of Cyclopropane, via Transition State **9**

	k_H/k_D			$k_{^{12}C}/k_{^{13}C}$	
substitution	407.0 °C	422.5 °C	substitution	407.0 °C	422.5 °C
α deuterium			primary ^{13}C		
8-^2H	1.097	1.093	*1-^{13}C*	1.013	1.012
9-^2H	1.106	1.102	*3-^{13}C*	1.011	1.011
4-^2H	1.370	1.365			
5-^2H	1.142	1.138			
β deuterium			secondary ^{13}C		
6-^2H	1.023	1.023	*2-^{13}C*	1.001	1.001
7-^2H	1.042	1.041			

Table IV. Calculated KIEs on Double Rotation of *t*-**1** via Transition State **9** at 422.5 °C

cleavage of more substituted bond	k_H/k_D	cleavage of less substituted bond	k_H/k_D
4,9-$^2H_2$	1.514	*6,9-$^2H_2$*	1.125
5,8-$^2H_2$	1.241	*7,8-$^2H_2$*	1.138
		4,7-$^2H_2$	1.428
		5,6-$^2H_2$	1.165

Bigeleisen equation.[34] This equation gives the ratio of the rates for the unsubstituted (A) and isotopically substituted (A*) species in terms of the one imaginary vibrational frequency, $\nu_L^{\ddagger}$, for each in the transition state, and the real vibrational frequencies for A and A*, both in the reactant and in the transition state. The rate ratio is given by the expression

$$\frac{k(\mathrm{A})}{k(\mathrm{A}^*)} = \frac{\nu_L^{\ddagger}(\mathrm{A})}{\nu_L^{\ddagger}(\mathrm{A}^*)} \prod_{i=1}^{3N^{\ddagger}-7} \frac{\mu_i^{\ddagger}(\mathrm{A})}{\mu_i^{\ddagger}(\mathrm{A}^*)} \frac{1 - \exp[-\mu_i^{\ddagger}(\mathrm{A}^*)]}{1 - \exp[-\mu_i^{\ddagger}(\mathrm{A})]} \times \frac{\exp[\mu_i^{\ddagger}(\mathrm{A}^*)/2]}{\exp[\mu_i^{\ddagger}(\mathrm{A})/2]} \prod_{i=1}^{3N-6} \frac{\mu_i(\mathrm{A}^*)}{\mu_i(\mathrm{A})} \frac{1 - \exp[-\mu_i(\mathrm{A})]}{1 - \exp[-\mu_i(\mathrm{A}^*)]} \frac{\exp[\mu_i(\mathrm{A})/2]}{\exp[\mu_i(\mathrm{A}^*)/2]} \quad (3)$$

where $\mu_i = h\nu_i/kT$. The symmetry numbers (σ) which usually appear in the Bigeleisen equation have been removed for the sake of consistency with the definition of *microscopic* rate constants that are implicit in Schemes I and II.

The program QUIVER[21] was used to evaluate the right-hand side of eq 3 for three different transition states (**7**, **9**, and **10**). The frequencies were derived using the appropriate isotopic masses, together with the force constants obtained at the RHF/6-31G* level for the reactant (cyclopropane), and at the GVB/6-31G* level for each of the transition states. Isotope effects arising from a single isotopic label (^{2}H or ^{13}C) were calculated at 407.0 and 422.5 °C. Isotope effects arising from the 1,2-dideuterio substitution in **1** were calculated at 422.5 °C and were found to be essentially equal to the product of the appropriate individual isotope effects calculated at this temperature. Isotope effects for **2** were calculated at 407.0 °C and again were found to be nearly equal to the product of individual isotope effects at this temperature.

The RHF and GVB force constants and vibrational frequencies used for these calculations were unscaled. We did investigate, however, the effect of scaling the calculated harmonic frequencies by 10% in order to account for anharmonicity and other effects.[35] We found that all calculated isotope effects were reduced in magnitude by about this amount, roughly 10%. Nevertheless, our fundamental interest was in the ratios of isotope effects for pairs of transition states, and scaling had little quantitative effect on these ratios and no qualitative effect on the conclusions drawn from them.

The calculated isotope effects, arising from a single isotopic substitution, on coupled methylene rotation via transition state **9** are given in Table III. All the calculated isotope effects are normal (i.e., the rate is predicted to be greater in the unsubstituted system). At 422.5 °C, the α deuterium isotope effects fall in the range 1.093–1.365 and the β deuterium effects in the range 1.023–1.041. At this same temperature, the two possible primary ^{13}C effects were both computed to be about 1.011, and the secondary ^{13}C effect (1.001) was found to be essentially nonexistent.

The C_1 symmetry of transition state **9** causes all atoms to be nonequivalent, and so each in principle has a different sensitivity to isotopic substitution. The magnitude of the isotope effect at each site appears mainly to reflect the "loosening" of vibrations at that site on going to the transition state. In other words, the larger the decrease in torsional and rotational frequencies associated with displacement of a given hydrogen atom in the transition state, the larger the normal isotope effect associated with deuterium substitution at that site.[36] The largest decrease in torsional and rotational frequencies should occur for atoms showing the greatest motion along the reaction coordinate at the transition state, i.e., in the mode whose frequency is imaginary. Indeed, we find that the sites that have the largest displacements in this mode are the sites exhibiting the largest normal isotope effects.

For example, the imaginary frequency (ν = 140i cm^{-1}) in **9** corresponds mostly to rotation and pyramidalization of the C(1) methylene group. This mode incorporates a significant displacement of H(4), a slightly smaller displacement of H(5), and still smaller displacements of H(8) and H(9), at C(3). Consequently, as shown in Table III, the calculated α deuterium isotope effect is largest for deuterium substitution at H(4), next largest for H(5), and smaller for H(8) and H(9). Also, as shown in Table III, the β deuterium effects at C(2) are calculated to be quite small.

The isotope effects calculated for double rotation in *trans*-cyclopropane-*1,2-$^2H_2$* (*t*-**1**) are summarized in Table IV. The isotope effects were calculated relative to the all-protio system, and are given for cleavage of both the more and the less substituted bonds of *t*-**1**. The kinetic isotope effects (KIEs) listed in Table IV are essentially equal to the products of the corresponding KIEs for a single isotopic substituent, as given in Table III.

A net isotope effect can be assigned to cleavage and double methylene rotation of the more substituted bond in **1** via transition state **9**. This net effect is given by the ratio of the sums of the relative rates for the two possible dideuterio substitutions in **9**. Using the data in Table IV, we find that the net isotope effect on coupled rotation of the methylene groups at the more substituted bond of *t*-**1** is

$$\left(\frac{k_H}{k_D}\right)_{\mathrm{net}}^{\mathrm{more}} = \left(\frac{\sum k_i(\mathrm{H})}{\sum k_i(\mathrm{D})}\right)_{\mathrm{net}}^{\mathrm{more}} = \left(\frac{\sum k_i(\mathrm{D})}{\sum k_i(\mathrm{H})}\right)_{\mathrm{more}}^{-1} = \left(\frac{1}{2}\sum_{i=1}^{2}\left(\frac{k_D}{k_H}\right)_i\right)_{\mathrm{more}}^{-1} = \left(\frac{0.661 + 0.806}{2}\right)^{-1} = \frac{1}{0.733} = 1.36 \quad (4)$$

Likewise, for the cleavage of one of the less substituted bonds in *t*-**1**, the data in Table IV lead to the prediction that

$$\left(\frac{k_H}{k_D}\right)_{\mathrm{net}}^{\mathrm{less}} = \left(\frac{0.889 + 0.879 + 0.700 + 0.858}{4}\right)^{-1} = \frac{1}{0.832} = 1.20 \quad (5)$$

The isotope effect z_{12} is defined by Scheme I and eq 1. Physically, z_{12} expresses the kinetic preference for cleavage and double rotation of the less substituted bond in **1**. Computationally,

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(34) There are many excellent texts giving the derivation of the Bigeleisen equation from semiclassical transition-state theory. A recent example is Melander, L.; Saunders, W. H. *Reaction Rates of Isotopic Molecules*; Wiley-Interscience: New York, 1984.

(35) Hess, B. A.; Schaad, L. J.; Cársky, P.; Zahradnîk, R. *Chem. Rev.* **1986**, *86*, 709. Strictly speaking, anharmonic frequencies should not be used for the terms in the Bigeleisen equation that involve products of frequencies, and which represent products of moments of inertia.[34] Uniform scaling, however, does not change the ratio of these products. The main error in scaling the frequencies in eq 3 is to overestimate the anharmonic corrections to the zero-point energies. Consequently, the actual effect of anharmonicity is less than that estimated by uniform scaling of all frequencies in eq 3.

(36) For a brief discussion in the context of pericyclic and diradical reactions, see ref 17a.

Table V. Calculated KIEs on Single Rotation of Cyclopropane via Transition State **10** at 422.5 °C

	k_H/k_D			$k_{^{12}C}/k_{^{13}C}$	
substitution	407.0 °C	422.5 °C	substitution	407.0 °C	422.5 °C
α deuterium			primary ^{13}C		
8-^{2}H	1.101	1.097	*1-^{13}C*	1.011	1.011
9-^{2}H	1.108	1.104	*3-^{13}C*	1.011	1.011
4-^{2}H	1.192	1.188			
5-^{2}H	1.304	1.299			
β deuterium			secondary ^{13}C		
6-^{2}H	1.023	1.023	*2-^{13}C*	1.002	1.002
7-^{2}H	1.010	1.010			

z_{12} is simply the ratio of the two net isotope effects for passage over transition state **9**.

$$z_{12} = (k_H/k_D)^{\text{more}}_{\text{net}}/(k_H/k_D)^{\text{less}}_{\text{net}} = 1.36/1.20 = 1.13 \quad (6)$$

This calculated value of z_{12} is very close to that of 1.10 assumed by Berson and co-workers[12] in their analysis of the stereomutations of **1**.

The only direct measurement of secondary deuterium isotope effects on a cyclopropane stereomutation was made by Baldwin and Carter for 1-cyano-2-phenylcyclopropane.[37] On the basis of the observation that this system undergoes stereomutation only by single rotations of the two substituted carbons, these researchers found that the α deuterium effect on this process at 242 °C is 1.07, while the β effect is 1.13. To account for the fact that the observed β effect is larger than the α effect, these researchers invoked the argument[38] that, in (0,0)-trimethylene, C–D bonds at the central methylene hyperconjugate less effectively than do C–H bonds at the same position. This leads to the expectation of a normal ($k_H/k_D > 1$) β deuterium isotope effect.

The data in Table III clearly show that our calculations do find normal β deuterium isotope effects. Nevertheless, the calculations give no evidence that the β deuterium isotope effects are larger in magnitude than the α effects in the double epimerization of cyclopropane via transition state **9**.

However, 1-cyano-2-phenylcyclopropane apparently undergoes stereomutation by exclusive single rotations.[37] Therefore, we have used the single rotation transition state **10** to investigate whether a single rotation mechanism in the parent cyclopropane should give rise to such effects. The calculated isotope effects arising from a single isotopic substitution are given in Table V. The calculated isotope effects are normal, with the α deuterium isotope effects in the range 1.097–1.299 and the much smaller β deuterium effects in the range 1.010–1.023. The ^{13}C effects are again calculated to be quite small, with a primary effect of 1.011 and a secondary effect of 1.002.

As discussed in the previous section, epimerization of a single methylene group of cyclopropane can also be achieved by a process involving disrotatory opening via transition state **7**, followed by conrotatory closure via **9**. The reverse of this process would also achieve the same result. Since either sequence provides an alternative mechanism (to passage over **10**) for single rotation, we have also calculated the isotope effects for passage over the disrotatory transition state **7**. The KIEs calculated for a single isotopic substitution are given in Table VI, and are similar in magnitude to those calculated for passage over transition state **10** (Table V).

Calculated deuterium isotope effects (α and β) generally increase as the temperature is lowered, and the Baldwin and Carter experiments were performed at 242 °C, not at the temperatures for which the data in Tables III, V, and VI were calculated. However, we find that even at 25 °C the calculated α effects are all substantially larger than the calculated β effects. This is true whether the isotope effects are computed for coupled rotation via transition state **9**, single rotation via **10**, or disrotatory opening via **7**. Our calculations of the α and β H/D isotope effects on the stereomutation of the parent cyclopropane may, of course, not be applicable to the kinetic isotope effects measured in 1-cyano-2-phenylcyclopropane.

Table VI. Calculated KIEs for Passage of Cyclopropane over Transition State **7** during Either Ring Opening or Ring Closure at 422.5 °C

	k_H/k_D			$k_{^{12}C}/k_{^{13}C}$	
substitution	407.0 °C	422.5 °C	substitution	407.0 °C	422.5 °C
α deuterium			primary ^{13}C		
4(9)-^{2}H^a	1.100	1.096	*1(3)-^{13}C^a*	1.013	1.012
5(8)-^{2}H^a	1.227	1.222			
β deuterium			secondary ^{13}C		
6-^{2}H	0.996	0.997	*2-^{13}C*	1.004	1.004
7-^{2}H	1.034	1.034			

[a] There are two symmetry equivalent sites corresponding to this isotope effect.

In summary, our calculations find no evidence that β H/D isotope effects are larger than α H/D isotope effects in any mechanism for cyclopropane stereomutation. This general finding is reflected in our calculated value of $z_{12} = 1.13$, which gives the isotope effect favoring cleavage of the less substituted bond in passage of **1** over transition state **9** for double rotation. Our computational results do not support a value of $z_{12} < 1$, much less the value of $z_{12} = 0.41$ that is required to fit the experimental results for **1** and **2**, if k_{12}/k_1 in **1** is assumed to be equal to k_{12}'/k_1' in **2**.

As discussed in the Introduction, another possibility that we considered is that the change in isotopic substitution on going from **1** to **2** might alter the relative contributions of the single and double rotation mechanisms in these two compounds, thus invalidating the assumption that $k_{12}/k_1 = k_{12}'/k_1'$ in Schemes I and II. Therefore, we performed calculations to investigate isotope effects on the ratios of microscopic rate constants for coupled and single rotations. The results, which are given and discussed in detail in the supplementary material for this paper,[22] show that such effects do exist, but that they are small.

For example, we calculate that $k_{12}/k_1 = 1.11(k_{12}'/k_1')$. The predicted isotope effect on the rate ratios is largely due to the fact that although k_1 and k_1' are both rate constants for rotation of a single CHD group, k_{12} is the rate constant for double rotation of one CH$_2$ and one CHD group in **1** but k_{12}' is the rate constant for two CHD groups in **2**. For the same reason that rotation of one CH$_2$ group and one CHD group is predicted to be faster than rotation of two CHD groups in **1** ($z_{12} = 1.13$), rotation of one CH$_2$ group and one CHD group in **1** is computed to be faster than rotation of two CHD groups in **2** by a factor of $1.11(k_1/k_1')$.

Our finding that $k_{12}/k_1 = 1.11(k_{12}'/k_1')$ implies that double rotation should contribute about 10% more to the steromutation of **1**, involving cleavage of the less substituted bond, than to the stereomutation of **2**. However, this predicted isotope effect still requires a value of $z_{12} = 0.44$ in order to reconcile the experimental results on **1**[12,15] with those on **2**.[16] As discussed above, our calculations yield a value of z_{12} more than 2.5 times larger than 0.44.

Conclusions

Our GVB/6-31G* calculations find a small energetic preference for double over single methylene group rotation amounting to 0.97 kcal/mol. SD-CI calculations on (0,0)- and (0,90)-trimethylene suggest that this gap will increase by about 0.4 kcal/mol when the effect of additional electron correlation is taken into account. At the SD-CI level, the transition state **7** for disrotation is expected to be quite close in energy to that (**10**) for single rotation, and passage over either transition state can result in net one-center epimerization.

At the GVB/6-31G* level, the minimum energy pathway on the singlet PES for double rotation is predominantly conrotatory, but breaks C_2 symmetry to avoid passing through C_{2v} (0,0)-tri-

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[37] (a) Baldwin, J. E.; Carter, C. G. *J. Am. Chem. Soc.* **1978**, *100*, 3042. (b) Baldwin, J. E.; Carter, C. G. *J. Am. Chem. Soc.* **1979**, *101*, 1325.

[38] First postulated in the context of a (0,0)-trimethylene intermediate by Al-Sayed and Crawford,[39] to account for the β deuterium isotope effect in the thermolysis of 1-pyrazoline.

[39] Al-Sayed, B. H.; Crawford, R. J. *Can. J. Chem.* **1968**, *46*, 3301.

methylene (**3**). The symmetry breaking entails rotation and inversion of one methylene group, passing over a C_1 transition state (**9**), crossing the C_s symmetric disrotation coordinate, and inverting the second methylene via another transition state of structure **9**, before rejoining the C_2 conrotatory pathway. The reaction pathway for single rotation also breaks symmetry to avoid C_s (0,90)-trimethylene (**4**), and passes through a single transition state (**10**) of C_1 symmetry.

We have used the highest energy transition state **9** on the pathway for two-center rotation to calculate the α and β deuterium isotope effects on double rotation. Both α and β isotope effects at 422.5 °C are calculated to be moderate and normal, with the β H/D isotope effects much smaller than the α effects. In cyclopropane-*1,2*-$^2H_2$ (**1**), these individual isotope effects give rise to a calculated overall kinetic preference of $z_{12} = 1.13$ for C(1)–C(3) (or C(2)–C(3)) over C(1)–C(2) coupled rotation. This value of z_{12} is quite close to that assumed by Berson and coworkers[12] in their original analysis of the stereomutations of **1**.

Our calculated value $z_{12} = 1.13$ for **1** is very different from the value of about $z_{12} = 0.4$ that is necessary for the result obtained by Baldwin[16] for cyclopropane-*1*-^{13}C-*1,2,3*-$^2H_3$ (**2**) to be compatible with the results obtained both by Berson[12] and by Baldwin[15] for **1**. Our calculations do find that the difference in isotopic substitution between **1** and **2** should alter the relative contributions of the single and double methylene group rotation mechanisms in these two cyclopropanes, but the effect is computed to be small, amounting only to about a 10% difference in the ratios of the rates for single and double rotation. On the basis of these computational findings, we conclude that there is no apparent way to reconcile the experimental results obtained for **1**, which indicate a clear preference for double rotation, with those obtained for **2**, which indicate that single and double methylene group rotations proceed at essentially equal rates.

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Registry No. Trimethylene, 32458-33-6; cyclopropane, 75-19-4; deuterium, 7782-39-0.

Supplementary Material Available: Complete GVB/6-31G* optimized geometries and vibrational frequencies for **3**–**10** and results of calculations of isotope effects on ratios of microscopic rate constants (23 pages). Ordering information is given on any current masthead page.

Three-Membered Rings of Carbon, Silicon, and Germanium: An Analysis of Thermodynamic Stability to Fragmentation

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Abstract: Ab initio quantum mechanical methods have been used to determine the strain energies of all possible saturated three-membered rings, c-$XH_2YH_2ZH_2$, and the energetics of the decomposition reactions c-$XH_2YH_2ZH_2 \rightarrow :XH_2 + H_2Y{=}ZH_2$ for X, Y, Z = C, Si, Ge. The three-membered-ring (3MR) decomposition enthalpy can be semiquantitatively predicted from a simple model using the strain energies along with published single bond dissociation energies, π-bond energies, and divalent state stabilization energies. Of the ten rings studied, germirane (c-$GeH_2CH_2CH_2$) is by far the least stable with respect to dissociation, being only about 20 kcal/mol more stable than $GeH_2 + H_2C{=}CH_2$. Thus the lack of success of experimental efforts to form a germirane has a thermochemical origin. This observation also helps account for observed differences in methylene, silylene, and germylene addition reactions to dienes. The estimation of substituent effects on ring decomposition enthalpies is facilitated by this model.

Introduction

In recent years the three-membered rings comprising group 14 elements have received considerable attention.[1-6] Small-ring compounds seem to be inherently and enduringly interesting to chemists, due in large part to their high strain, novel ring bonding, and, in the case of group 14 cyclotrimetallanes, reactive bonds between heavy atoms (e.g. Si–Ge). The group 14 cyclotrimetallanes are not only interesting, they are also synthetically useful as convenient sources of highly reactive carbene-like species and dimetallenes, because they decompose photolytically via the reaction

$$\text{c-}XR_2YR_2ZR_2 \rightarrow :XR_2 + R_2Y{=}ZR_2 \qquad (1)$$

where X, Y, Z = group 14 elements.[2,3] In some cases thermolysis yields the same products.[3,4,7,8]

Of the ten cyclotrimetallane rings made up of C, Si, and Ge, all have been synthesized to date except the three which contain a single Ge atom. Among the latter group the germirane (GeC_2) ring is especially notable for its elusiveness. Germiranes have been

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