Concerted and Nonconcerted Pathways for Thermal Conversions of Deuterium-Labeled Cyclohexenes to Butadienes and Ethylenes

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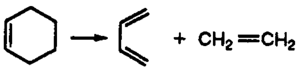
Received June 10, 1993[●]

Abstract: The retro Diels–Alder reactions of cyclohexene-*3,3,6,6*-d_4 and the 4,5-cis isomers of cyclohexene-*1,2,3,4,5,6*-d_6 have been followed using single-pulse shock tube kinetic and tunable diode laser infrared spectroscopic techniques. At temperatures above 1000 K, both labeled cyclohexenes give some products indicative of nonconcerted reaction paths: ethylene-*1,1*-d_2 from the first and *trans*-ethylene-*1,2*-d_2 from the second. Kinetic modeling calculations indicate that the most important pathway for formation of these products is a sequence of steps: cyclohexene → vinylcyclobutane → ethylene plus butadiene. Some relatively minor direct conversion of cyclohexene to ethylene plus butadiene through a stereochemically nonconservative pathway involving a diradical intermediate may also occur.

Introduction

Diels–Alder reactions[1,2] provide vast synthetic versatility, for they are highly stereoselective and are responsive kinetically and regiochemically to substituent effects and reaction conditions. Retro-Diels–Alder reactions (retrodiene reactions) also have substantial synthetic utility.[3] Depending on the full array of substituents and the reaction conditions, the mechanism of a particular Diels–Alder or retro-Diels–Alder reaction may be considered concerted or to involve a diradical or zwitterionic intermediate.[4]

The archetypical Diels–Alder addition and retroaddition processes, the combination of butadiene with ethylene to form cyclohexene[5] and the reverse reaction, the unimolecular thermal decomposition of cyclohexene (**1**) to give butadiene (**2**) and ethylene (**3**),[6,7] have been subjected to extensive theoretical scrutiny in attempts to understand whether they should be viewed as concerted and synchronous, or concerted yet asynchronous, or as proceeding by way of a diradical intermediate. Such studies have led to divergent conclusions that are sensitively dependent on the computational methods employed. The dominant view today based on *ab initio* calculations is that there is a preferred, C_s-symmetrical concerted and synchronous transition structure, but that a transition structure leading to a diradical intermediate is only slightly higher in energy, though very different in geometry.[8]



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Other modes of theoretical analysis have also led to an appreciation that a diradical transition structure could well be a feasible alternative to the traditionally sanctioned concerted one, and could be close enough energetically to be kinetically competitive.[9]

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[●] Abstract published in *Advance ACS Abstracts*, November 1, 1993.

(1) Diels, O.; Alder, K. *Liebigs Ann. Chem.* **1928**, *460*, 98–122.

(2) Oppolzer, W. In *Comprehensive Organic Synthesis*; Paquette, L. A., Ed.; Pergamon Press: Oxford, 1991; Vol. 5, pp 315–399. See also: Singleton, D. A.; Martinez, J. P.; Ndip, G. M. *J. Org. Chem.* **1992**, *57*, 5768–5771, footnote 8.

(3) (a) Kwart, H.; King, K. *Chem. Rev.* **1968**, *68*, 415–447. (b) Ripoll, J.; Rouessac, A.; Rouessac, F. *Tetrahedron* **1978**, *34*, 19–40.

(4) (a) Houk, K. N. *Top. Curr. Chem.* **1979**, *79*, 1–40. (b) Sauer, J.; Sustmann, R. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 729–807. (c) Konovalov, A. I. *Russ. Chem. Rev.* **1983**, *52*, 1064–1080. (d) Houk, K. N.; Li, Y.; Evanseck, J. D. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 682–708.

(5) (a) Hague, E. N.; Wheeler, R. V. *J. Chem. Soc.* **1929**, 378–393. (b) Wheeler, R. V.; Wood, W. L. *J. Chem. Soc.* **1930**, 1819–1828. (c) Küchler, L. *Trans. Faraday Soc.* **1939**, *35*, 874–880. (d) Rowley, D.; Steiner, H. *Discuss. Faraday Soc.* **1951**, *No. 10*, 198–213.

(6) (a) Zelinskii, N. D.; Mikhailov, B. M.; Arbuzov, Yu. A. *Zh. Obshch. Khim.* **1934**, *4*, 856–865; *Chem. Abstr.* **1935**, *29*, 2152.6. (b) Borisov, P. P.; Shakhnazarova, E. M.; Margolis, E. I. *Zh. Obshch. Khim.* **1934**, *4*, 1385–1389; *Chem. Abstr.* **1935**, *29*, 3648.9. (c) Rice, F. O.; Ruoff, P. M.; Rodowskas, E. L. *J. Am. Chem. Soc.* **1938**, *60*, 955–961. (d) Kraus, M.; Vavruska, M.; Bazant, V. *Coll. Czech. Chem. Commun.* **1957**, *22*, 484–488. (e) Smith, S. R.; Gordon, A. S. *J. Phys. Chem.* **1961**, *65*, 1124–1128. (f) Tsang, W. *J. Chem. Phys.* **1961**, *42*, 1805–1809. (g) Uchiyama, M.; Tomioka, T.; Amano, A. *J. Phys. Chem.* **1964**, *68*, 1878–1881. (h) Tsang, W. *Int. J. Chem. Kinet.* **1970**, *2*, 311–323. (i) Tardy, D. C.; Ireton, R.; Gordon, A. C. *J. Am. Chem. Soc.* **1979**, *101*, 1508–1514. (j) Lewis, D. K.; Bergmann, J.; Manjoney, R.; Paddock, R.; Kalra, B. L. *J. Phys. Chem.* **1984**, *88*, 4112–4116. (k) Kiefer, J. H.; Shah, J. A. *J. Phys. Chem.* **1987**, *91*, 3024–3030. (l) Kiefer, J. H.; Shah, J. A. *J. Phys. Chem.* **1990**, *94*, 8380.

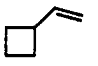
(7) For an earlier example now clearly recognizable as a simple retro-Diels–Alder reaction, the thermal conversion of limonene to isoprene, see Staudinger, H.; Klever, H. W. *Ber. Dtsch. Chem. Ges.* **1911**, *44*, 2212–2215. These authors presciently suggested that the reaction could be generalized to other cyclohexenes.

(8) (a) Burke, L. A.; Leroy, G.; Sana, M. *Theor. Chim. Acta* **1975**, *40*, 313–321. (b) Townshend, R. E.; Ramunni, G.; Segal, G.; Hehre, W. J.; Salem, L. *J. Am. Chem. Soc.* **1976**, *98*, 2190–2198. (c) Burke, L. A.; Leroy, G. *Theor. Chim. Acta* **1977**, *44*, 219–221. (d) Ortega, M.; Oliva, A.; Lluch, J. M.; Bertrán, J. *Chem. Phys. Lett.* **1983**, *102*, 317–320. (e) Brown, F. K.; Houk, K. N. *Tetrahedron Lett.* **1984**, *25*, 4609–4612. (f) Bernardi, F.; Bottoni, A.; Robb, M. A.; Field, M. J.; Hillier, I. H.; Guest, M. F. *J. Chem. Soc., Chem. Commun.* **1985**, 1051–1052. (g) Burke, L. A. *Theor. Chim. Acta* **1985**, *68*, 101–105. (h) Burke, L. A. *Int. J. Quantum Chem.* **1986**, *29*, 511–518. (i) Houk, K. N.; Lin, Y.-T.; Brown, F. K. *J. Am. Chem. Soc.* **1986**, *108*, 554–556. (j) Bernardi, F.; Bottoni, A.; Field, M. J.; Guest, M. F.; Hillier, I. H.; Robb, M. A.; Venturini, A. *J. Am. Chem. Soc.* **1988**, *110*, 3050–3055. (k) Bach, R. D.; McDouall, J. J. W.; Schlegel, H. B.; Wolber, G. J. *J. Org. Chem.* **1989**, *54*, 2931–2935. (l) Storer, J. W.; Raimondi, L.; Houk, K. N. *Abstracts of Papers*, 201st National Meeting of the American Chemical Society, Altanta, GA, April 1991; American Chemical Society: Washington, DC, 1991; ORGN 96. (m) Li, Y.; Houk, K. N. *J. Am. Chem. Soc.* **1993**, *115*, 7478–7479. (n) Storer, J. W.; Raimondi, L.; Houk, K. N. *J. Am. Chem. Soc.* **1993**, *115*, in press.

(9) (a) Dewar, M. J. S.; Olivella, S.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1986**, *108*, 5771–5779. (b) Huybrechts, G.; Poppelsdorf, H.; Maesschalck, L.; Van Mele, B. *Int. J. Chem. Kinet.* **1984**, *16*, 93–102. (c) Doering, W. von E.; Roth, W. R.; Breuckmann, R.; Figge, L.; Lennartz, H.-W.; Fessner, W.-D.; Prinzbach, H. *Chem. Ber.* **1988**, *121*, 1–9.

0002-7863/93/1515-11728$04.00/0

Experimental work relevant to the mechanism of the two reactions has been fairly limited. Bartlett and Schueller showed that at 175 °C and 6000 psi butadiene and ethylene gave cyclohexene and vinylcyclobutane (**4**) in a 5000:1 ratio;[10] the latter product was presumed to be formed through a stepwise, diradical-mediated mechanism. Further, they demonstrated that vinylcyclobutane was stable under the reaction conditions used.



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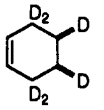

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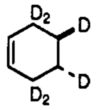

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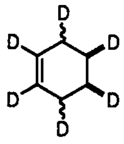
Houk, Lin, and Brown combined butadiene-*1,1,4,4*-d_4 and *cis*-ethylene-*1,2*-d_2 (or *trans*-ethylene-*1,2*-d_2) at 185 °C and 1800 psi to form the cyclohexene-*3,3,4,5,6,6*-d_6 isomers **5** and **6** with a very high degree of preservation of stereochemistry about the ethylene-derived unit, on the order of 100:1.[8i] This ratio was deduced from proton NMR spectroscopic integration data secured for the epoxides derived from product mixtures of **5** and **6**. A diradical process would have resulted in some loss of stereochemistry for the deuterium labels at C4 and C5 of the products.

The reverse reaction (**1** → **2** + **3**) recently has been subjected to molecular beam photofragmentation translational energy spectroscopy experiments by Lee and co-workers,[11] using both ultraviolet (193 nm) and multiphoton infrared excitation. Molecules were raised to internal energies as high as 148 kcal/mol, which is more than twice the activation energy for the retro-Diels–Alder reaction. The observed translational energy distributions of the products, monitored at *m/e* 53 and 28 (in the 193 nm time-of-flight spectra) and at *m/e* 52 and 26 (in the CO_2 laser multiphoton excitation time-of-flight spectra), were viewed as consistent with a concerted as opposed to a diradical potential energy surface for the reaction of cyclohexene giving butadiene and ethylene. No estimate was given of how much of a nonconcerted pathway might have gone undetected in these experiments.

Thus, the simplest Diels–Alder cycloaddition and the corresponding retro-Diels–Alder reaction apparently take place largely or exclusively in a concerted, stereochemically conservative fashion; yet recent theoretical work on the concerted versus diradical alternatives implies that products derived from a diradical intermediate might well be in evidence for reactions conducted at elevated temperatures or in reaction mixtures examined with sensitive analytical methods. The question addressed here concerns the extent to which diradical mediated, stereochemically nonconservative mechanistic alternatives for the retro-Diels–Alder reaction **1** → **2** + **3** might be kinetically competitive. To address this issue, deuterium-labeled cyclohexenes **7** and **8** were converted to butadienes and ethylenes in single-pulse shock tube kinetic experiments, which gave access to kinetic and stereochemical data for these retro-Diels–Alder reactions at relatively high temperatures. The rate of cis,trans isomerization of ethylene-*1,2*-d_2 isomers was also measured directly, in the presence of reacting cyclohexene. The deuterium-labeled ethylenes formed from **7** and **8** were quantified through tunable diode laser (TDL) infrared spectroscopy. Some *trans*-ethylene-*1,2*-d_2 was formed from **7**, and some ethylene-*1,1*-d_2 from **8**; the relative abundances of both nonconcerted reaction products rose with increasing temperatures. Kinetic modeling calculations were done to aid in interpreting the product distributions as functions of temperature.



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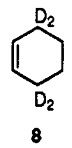

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Experimental Section

Materials. Birch reduction of benzene-d_6 (Aldrich; 99.5 atom % D) with sodium in liquid ammonia–ethanol–ether[12] gave 1,4-cyclohexadiene-*1,2,3,4,5,6*-d_6, which was purified by preparative GC on a 20% $\beta\beta'$-ODPN column: ^{1}H NMR δ 2.63 ppm (s); ^{13}C NMR 124.1, 25.1 ppm (both triplets, from ^{13}C–D coupling). For commercial 1,4-cyclohexadiene: ^{1}H NMR δ 5.70, 2.68 ppm; ^{13}C NMR δ 124.4, 25.8 ppm. The labeled diene was reduced with diimide generated from potassium azodicarboxylate and acetic acid in dioxane[13] to give cis isomers of cyclohexene-*1,2,3,4,5,6*-d_6 (**7**): ^{1}H NMR δ 1.96 (s, 2H), 1.59 ppm (s, 2H); ^{13}C NMR δ 126.1, 24.4, 22.0 ppm (all triplets, from ^{13}C–D coupling). For unlabeled cyclohexene: ^{13}C NMR δ 127.2, 25.3, 22.9 ppm.[14] Both the intermediate cyclohexadiene-d_6 and the product cyclohexene-d_6 (**7**) had analytical capillary GC characteristics identical to those shown by authentic unlabeled samples; the deuterium-labeled cyclohexene **7** used for kinetic work, after preparative GC purification on a 20% $\beta\beta'$-ODPN column, was better than 97% pure according to capillary GC analyses, with less than 3% dioxane as the major contaminant. Ethylene-*d* was prepared by adding D_2O dropwise to a solution of vinylmagnesium bromide in THF; the gaseous product was passed through a trap at −78 °C and collected in a trap cooled with liquid nitrogen; by capillary GC criteria, it was a 100% homogeneous ethylene sample.

Cyclohexene-*3,3,6,6*-d_4 (**8**; 98 atom % D), *cis*-ethylene-*1,2*-d_2 (98 atom % D), *trans*-ethylene-*1,2*-d_2 (98 atom % D), and ethylene-*1,1*-d_2 (99.1 atom % D) were obtained from Merck, Sharpe and Dohme. Each was degassed two or more times at 77 K before use. Analyses of these compounds by capillary GC showed that each was >99.9% structurally homogeneous. Analysis of cyclohexene-*3,3,6,6*-d_4 (**8**) by ^{1}H NMR showed no significant proton absorption signal for allylic protons.

Infrared absorption spectroscopic analyses were performed on *cis*- and *trans*-ethylene-*1,2*-d_2 (*cis*-**ET** and *trans*-**ET**). The cis isomer contained <0.5% of the trans isomer, and the trans isomer contained 2.4% of the cis isomer; each also contained a few percent ethylene-*d* and traces of ethylene (**3**), but no (<0.5%) ethylene-*1,1*-d_2 (1,1-ET). The following materials were used as supplied, except for degassing at 77 K, for preparation of GC calibration mixtures: ethylene (Matheson, >99.5%), 1,3-butadiene (Matheson, >99.0%), cyclohexene (Aldrich, >99%), and argon (Matheson, >99.9995%). The shock tube driver gas was helium (Linde, 99.995%).

Instrumentation and Operating Procedures. Gas mixtures were prepared on a bakeable all-metal vacuum line which could be pumped to <1 × 10^{-5} Torr with an oil-free turbo-pump and were stored in glass containers sealed with greaseless stopcocks. All kinetic runs were performed in a single-pulse shock tube, which has been previously described.[15] Two product samples (35 and 200 mL) were extracted in succession from the downstream end of the apparatus immediately after running each shock. The first sample (a) was subjected to two or more GC analyses (Varian 1440-20 flame ionization GC), and relative concentrations of residual reactant cyclohexene and product butadiene were measured. Reaction temperatures were calculated for each experiment from the extent of reaction, assuming irreversible first-order kinetics, the well-established rate parameters log (A, s^{-1}) = 15.2 and E_a = 66.6 kcal/mol,[6h] and the 8.0 × 10^{-4} s characteristic reaction time for samples adjacent to the downstream end of this shock tube.

The second, larger sample (b) from each experiment was also analyzed by GC, and the effective average reaction time experienced for that sample (range: 6.0 to 6.5 × 10^{-4} s) was calculated from the extent of cyclohexene conversion to products, assuming the same reaction temperature as determined for sample (a). The shorter reaction times for gas removed from further upstream is a consequence of the sequence of heating and

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[10] Bartlett, P. D.; Schueller, K. E. *J. Am. Chem. Soc.* **1968**, *90*, 6071–6077.

[11] Zhao, X.; Continetti, R. E.; Yokoyama, A.; Hintsa, E. J.; Lee, Y. T. *J. Chem. Phys.* **1989**, *91*, 4118–4127.

[12] Paquette, L. A.; Barrett, J. H. *Organic Syntheses*; Wiley: New York, 1973; Collect. Vol. V, pp 467–471.

[13] Pasto, D. J.; Taylor, R. T. *Org. React.* **1991**, *40*, 91–155.

[14] Johnson, L. F.; Jankowski, W. C. *Carbon-13 NMR Spectra*; Wiley-Interscience: New York, 1972; spectrum 176.

[15] (a) Lewis, D. K.; Giesler, S. E.; Brown, M. S. *Int. J. Chem. Kinet.* **1978**, *10*, 277–294. (b) Lewis, D. K.; Baldwin, J. E.; Cianciosi, S. J. *J. Phys. Chem.* **1990**, *94*, 7464–7467.

cooling waves which propagate along the apparatus during the experiment.[15b] Sample (b) was frozen at 77 K, degassed to remove argon, which had been added as a diluent for the shock tube runs, and then warmed to 143 K in a pentane slush bath to separate the ethylene fraction from cyclohexene and butadiene.

Ratios of ethylene, ethylene-*d*, and the three ethylene-d_2 isomers were measured by infrared absorption spectroscopy using a ultra high resolution tunable diode laser spectrometer, which has been previously described.[16] For this study, a new data acquisition/processing method was developed and employed. Successive frequency scans of the diode, covering approximately 0.1 cm^{-1}, were directed alternately through 1.20-m gas cells filled with sample and reference gases by a phase-locked bow-tie chopper and combined onto the face of a single detector. The amplified output was streamed into 32 megabits of memory in a Macintosh IIfx computer through National Instruments NB-A2000 and NB-DMA2800 boards synchronized with the laser and chopper so as to co-add the sweeps in two separate registers. Typically, 50 scans of each cell were made per acquisition, at a diode scan rate of 100 Hz. This arrangement allows improved resolution (12 bit, vertical and horizontal). The signal-to-noise ratio is also improved because the full intensity of the laser beam is directed through whichever cell is being sampled.

Fully resolved and non-overlapping vibration–rotation features of the five ethylene species listed above were identified within 0.1-cm^{-1} spectral width regions at 923 and 947 cm^{-1}, and a Beer's law plot was constructed for each authentic sample over the pressure range 0–0.20 Torr to ensure linearity of response. The absorbance of each species in each kinetic sample was then determined relative to the absorbance of a known pressure of the authentic species placed in the other cell. Fortunately, absorption lines of both *cis*-ET and *trans*-ET, and of both **3** and 1,1-ET, were found in the same spectral regions. This made it possible to measure absorbance ratios for both ethylenic products in a kinetic sample against their absorbances in carefully prepared reference mixtures without having to change diode frequency.

A reaction mixture from cyclohexene **8** partially converted to butadienes and ethylenes in a shock-tube run at 1077 K was examined by capillary GC and then the cyclohexene was reisolated and examined by ^{1}H NMR spectroscopy. In addition to cyclohexene and butadiene, there were no other components evident, except one with a retention time slightly shorter than that of cyclohexene and approximately 0.3–0.4% as intense; it was present as well as a trace impurity in the starting material. An authentic, gas chromatographically purified sample of vinylcyclobutane was prepared from cyclobutanemethanol (Aldrich) through oxidation with pyridinium chlorochromate in the presence of powdered 3A molecular sieves and sodium acetate in CH_2Cl_2,[17] followed by a Wittig reaction employing methyltriphenylphosphonium bromide and sodium hydride in DMSO.[18] The retention times of this vinylcyclobutane sample on ultra-performance Hewlett-Packard cross-linked methyl silicone and 5% phenyl methyl silicone 25 m × 0.2 mm × 0.33 μm capillary GC columns did not correspond to retention times of the trace impurity. The amount of cyclohexene-*3,3,4,4-d*$_4$ present in the recovered cyclohexene material was negligible, for the ^{1}H NMR spectral absorption intensity near δ 1.96 ppm appropriate to allylic hydrogens in that cyclohexene was undetectable.

Kinetic Results

Retro-Diels–Alder Reaction of Cyclohexene 7. The deuterium-labeled cyclohexene **7**, having deuterium labels at C4 and C5 in a well-defined cis relationship, was diluted to 2.00% in argon. Three shock-tube kinetic runs using this **7**-in-argon mixture gave the products summarized in Table I. The cis and trans isomers of ethylene-*1,2-d*$_2$ were found to be the dominant ethylene components; trace amounts of ethylene and of ethylene-*d* were detected, but no ethylene-*1,1-d*$_2$ was seen. The column in Table I titled "% *trans*-ET" lists the percentages of ethylene-*1,2-d*$_2$ determined to be the trans isomer from the TDL spectroscopic analyses. Where two values are listed, they were calculated from the relative absorbances at two different pairs of *cis*- and *trans*-ethylene-*1,2-d*$_2$ spectroscopic features, on separate occasions. The percentage of trans product increases dramatically at higher temperatures.

Table I. Shock-Tube Kinetic Runs for Deuterium-Labeled Cyclohexene **7**

run no.	temp (K)	conversion[a] (%)	% *trans*-ET
1	1094	4.3	5.1 ± 1.0
1	1094	4.3	6.0 ± 0.6
2	1180	33.6	8.8 ± 1.0
2	1180	33.6	9.3 ± 0.6
3	1244	82.8	33.1 ± 1.3

[a] Conversion of cyclohexene **7** to deuterium-labeled butadienes and ethylenes.

Table II. Shock-Tube Kinetic Runs for Deuterium-Labeled Cyclohexene **8**

run no.	temp (K)	conversion[a] (%)	% 1,1-ET
4	1077	2.7	3.4 ± 0.4
5	1113	9.4	4.2 ± 0.6
6	1129	13.9	4.3 ± 0.4
7	1152	18.6	4.6 ± 0.4
8	1195	53.6	5.4 ± 0.4

[a] Conversion of cyclohexene **8** to deuterium-labeled butadienes and ethylenes.

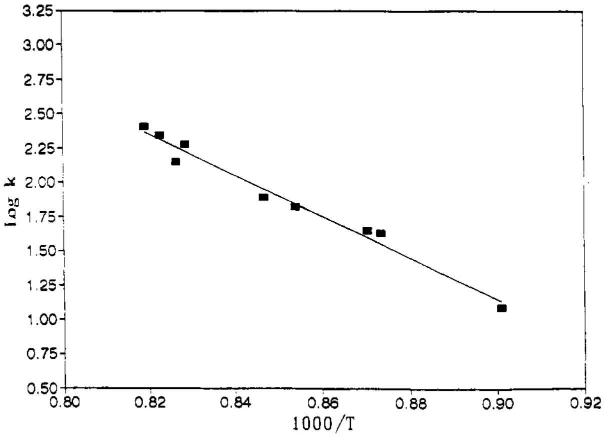

Figure 1. Rate constants for cis,trans equilibration of ethylene-*1,2-d*$_2$ isomers.

Isomerization and Retro-Diels–Alder Reaction of Cyclohexene 8. Samples containing either 3.00% or 5.00% cyclohexene **8** in argon were prepared and shock-heated in five kinetic runs. Reaction conditions and product distributions for these runs are summarized in Table II. The ethylene products were ethylene and ethylene-*1,1-d*$_2$, plus a trace of ethylene-*d*; the cis and trans isomers of ethylene-*1,2-d*$_2$ were not observed. As noted in Table II, the percentage of ethylene-*1,1-d*$_2$ showed only a small dependence upon temperature, rising from 3.6% to 5.4% over the temperature range covered, 1077 to 1196 K.

Interconversion of Cis and Trans Isomers of Ethylene-*1,2-d*$_2$. Reactant mixtures were prepared containing either 2.00% *cis*-ET plus 0.25% cyclohexene **1** in argon or 2.00% *trans*-ET plus 0.25% **1** in argon. Nine shock tube experiments were run at temperatures ranging from 1101 to 1221 K. Rate constants calculated from the integrated form of the rate equation for a reversible first-order reaction with an equilibrium constant equal to unity are shown in Figure 1. The standard linear regression line, with all error attributed to the *y*-axis variable, gives log (*A*, s^{-1}) = 14.7, E_a = (68.6 ± 3.9) kcal/mol. The measured E_a value lies within one standard deviation of the generally accepted value

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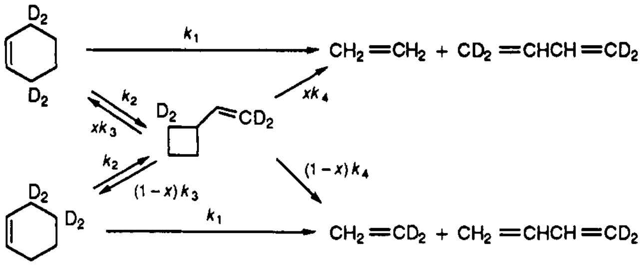
(16) (a) Glenar, D. A.; Hill, A. *Rev. Sci. Instrum.* **1986**, *57*, 2493–2498. (b) Glenar, D. A.; Lewis, D. K. *Appl. Spectrosc.* **1989**, *43*, 283–288. (c) Baldwin, J. E.; Cianciosi, S. J.; Glenar, D. A.; Hoffman, G. J.; Wu, I.-W.; Lewis, D. K. *J. Am. Chem. Soc.* **1992**, *114*, 9408–9414.

(17) (a) Herscovici, J.; Antonakis, K. *J. Chem. Soc., Chem. Commun.* **1980**, 561–562. (b) McMurry, J. E.; Bosch, G. K. *J. Org. Chem.* **1987**, *52*, 4885–4893.

(18) Greenwald, R.; Chaykovsky, M.; Corey, E. J. *J. Org. Chem.* **1963**, *28*, 1128–1129.

Scheme I



of 65.0 kcal/mol;[19] forcing the data to that slope gives a pre-exponential factor of $10^{14.0}$. Thus the interconversion of *cis*-ET and *trans*-ET in this temperature range and in the presence of reacting cyclohexene is well represented by eq 1. This A factor is an order of magnitude larger than the frequency factor deduced from low-pressure static reactor experimental data at 723–823 K,[19a] but close to the value estimated from thermochemical calculations.[19b]

$$\log (k, \mathrm{s}^{-1}) = 14.0 - (65.0 \times 10^3/4.576T) \qquad (1)$$

The first of these three sets of experiments shows that some *trans*-ethylene-*1,2*-d_2 is formed during the retro-Diels–Alder reaction of cyclohexene **7**. The second set shows that some ethylene-*1,1*-d_2 is formed as cyclohexene **8** is heated to give butadienes and ethylenes, a result most easily rationalized by postulating isomerization of cyclohexene **8** to form a vinylcyclobutane, which could decompose to form either ethylene or ethylene-*1,1*-d_2. The third set of experiments indicates that at the higher end of the temperature range used for the retro-Diels–Alder kinetic runs, direct cis,trans interconversion of ethylene-*1,2*-d_2 isomers is a significant contributor to the overall stereochemical outcomes observed.

To move beyond these qualitative inferences, kinetic modeling calculations were performed.

Kinetic Modeling Results

Isomerization and Retro-Diels–Alder Reaction of Cyclohexene 8. The isomerization and conversion of cyclohexene **8** to butadienes and ethylenes was modeled at intervals over the temperature range 1000–1250 K, according to Scheme I, using a digital integration routine. Step sizes ranged from 1.0×10^{-5} to 1.0×10^{-7} s, depending upon temperature; in all cases the step size was less than 5% of $(\ln 2)/k_4$, the half-life of the fastest reaction in Scheme I. Calculations were checked by repeating with different ordering of the reactions steps, or by allowing the computer to randomly select the order of calculating the concentration changes from each reaction at each time increment to avoid the possibility of cumulative errors.

Three of the four rate constants as functions of temperature needed for calculations based on this model are known[6h,20] and are summarized in eqs 2–4.

$$\log (k_1, \mathrm{s}^{-1}) = 15.2 - (66.6 \times 10^3/4.576T) \qquad (2)$$

$$\log (k_3, \mathrm{s}^{-1}) = 13.4 - (47.5 \times 10^3/4.576T) \qquad (3)$$

$$\log (k_4, \mathrm{s}^{-1}) = 14.5 - (49.8 \times 10^3/4.576T) \qquad (4)$$

For the rate constant for isomerization of cyclohexene to vinylcyclobutane (k_2), E_a was taken to be 72.3 kcal/mol, which is E_a for the reverse reaction (k_3) plus ΔH_{1140} for the isomerization of cyclohexene to vinylcyclobutane. The unknown log (A, s^{-1}) term was expected to be between 15 and 16, by analogy with the previously studied conversion of cyclopentene to vinylcyclopropane.[15b] Calculations were first performed with the parameter x set equal to 0.5, appropriate to the assumption that no secondary deuterium kinetic isotope effect sensitive deviations of the branching ratio for the vinylcyclobutane-d_4 intermediate to **8** and to cyclohexene-*3,3,4,4*-d_4, or to ethylene and ethylene-*1,1*-d_2 (1,1-ET), need to be considered, and with various assumed values of log (A, s^{-1}). Relative percentages of 1,1-ET expected after a reaction time of 6.00×10^{-4} s were calculated at temperature increments of 50 K. These were compared with the percentages of 1,1-ET measured experimentally in the 200-mL sample (b) from each shock tube experiment. With a log (A, s^{-1}) value of 15.34 for k_2, the model tracks the data points extremely well. Repeating the calculations for a longer reaction time of 6.50×10^{-4} s resulted in no appreciable changes in theoretical percentages for ethylene-*1,1*-d_2 as a function of temperature.

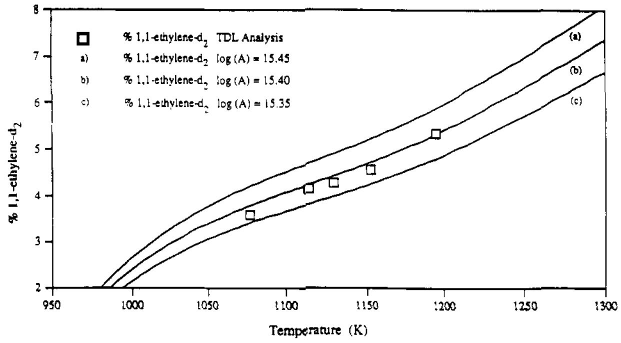


Figure 2. Comparison of experimental percent 1,1-ET from reactions of cyclohexene **8** and percentages predicted from Scheme I. For an explanation of curves a, b, and c, see text.

A small normal secondary deuterium kinetic isotope effect might contribute to the kinetic picture outlined in Scheme I, and this possibility was modeled for the case $x = 0.55$ and $(1 - x) = 0.45$, a branching ratio of 1.22, or 10% per deuterium on the cyclobutane ring. The effect is that somewhat less of the vinylcyclobutane formed becomes cyclohexene-*3,3,4,4*-d_4 and 1,1-ET, and that log A for k_2 must be raised by about 0.05 for the model to match the data. This comparison of model with experimental data is shown in Figure 2; expected percentages of ethylene product appearing as 1,1-ET are plotted versus temperature for choices of log A for k_2 ranging from 15.35 to 15.45, and the experimental points are those from Table II. The exactness of the fit evident in Figure 2 implies that Scheme I accurately reflects the important reactions of cyclohexene **8** under the experimental conditions[21] and that the isomerization of **8** to vinylcyclobutane-d_4 in this temperature range is well represented by eq 5.

$$\log (k_2, \mathrm{s}^{-1}) = 15.4 - (72.3 \times 10^3/4.576T) \qquad (5)$$

Isomerization and Retro-Diels–Alder Reaction of Cyclohexene 7. The thermal reactions of cyclohexene **7** were modeled according to Scheme II over the temperature range 950–1300 K, for assumed reaction times of 6.00×10^{-4} s. The model includes the effects of both reversible interconversion of cyclohexenes and vinylcyclobutanes and cis,trans isomerization of ethylene-*1,2*-d_2 isomers. Equations 1–5 were used for the five rate constants in the model, k_1 through k_5. The results are shown in Figure 3, a plot of expected

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[19] (a) Douglas, J. E.; Rabinovitch, B. S.; Looney, F. S. *J. Chem. Phys.* **1955**, *23*, 315–323. (b) Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley-Interscience: New York, 1976; p 105.

[20] Lewis, D. K.; Charney, D. J.; Kalra, B. L.; Plate, A.-M.; Woodard, M. H.; Cianciosi, S. J.; Baldwin, J. E. Kinetics of the Thermal Isomerizations of Gaseous Vinylcyclopropane and Vinylcyclobutane; manuscript in preparation.

[21] As one referee has suggested, it is conceivable that a reversible isomerization of cyclohexene with bicyclo[3.1.0]hexane might also contribute to the formation of 1,1-ET from **8**; this possibility has not yet been pursued through appropriate experiments. Cf.: Frey, H. M.; Smith, R. C. *Trans. Faraday Soc.* **1962**, *58*, 697–701. Chang, S.-j.; McNally, D.; Shary-Tehrany, S.; Hickey, M. J.; Boyd, R. H. *J. Am. Chem. Soc.* **1970**, *92*, 3109–3118.

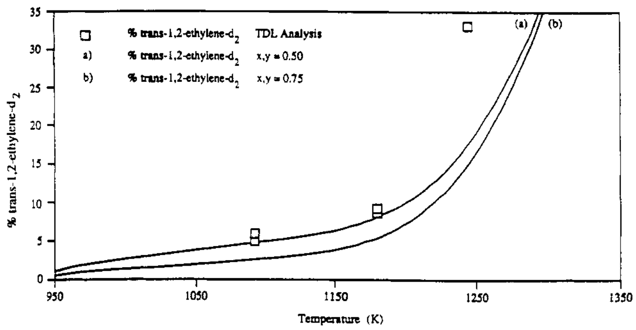
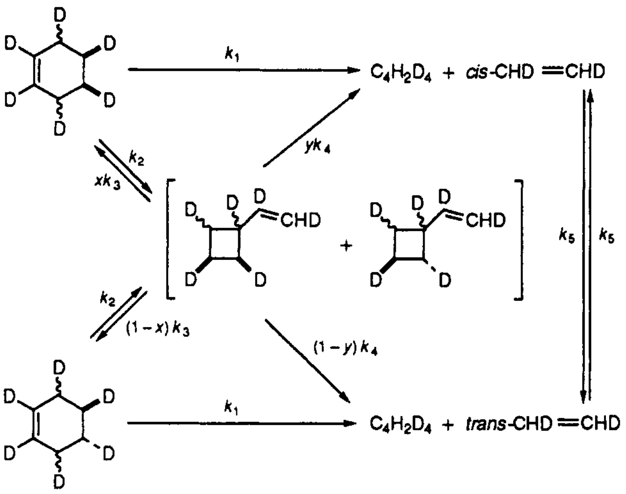


Figure 3. Comparison of experimental percent *trans*-ET produced from reaction of cyclohexene 7 and percentages predicted from Scheme II. For an explanation of curves a and b, see text.

Scheme II



relative percentages of *trans*-ET after 6.00 × 10^{-4} s against temperature. Also included in Figure 3 for comparison with the model-based calculations are the five experimental data points from Table I, showing the percentages of *trans*-ET measured in the ethylene products of shock tube kinetic runs of cis cyclohexene 7 at 1094, 1180, and 1244 K. In these calculations, isotope-dependent differences in rates of bond cleavages are not an issue, since every cyclohexene and every vinylcyclobutane intermediate has one deuterium atom at each carbon. Another complication, however, had to be addressed: the stereochemistry of 1,3-carbon migrations and of vinylcyclobutane to butadiene plus ethylene reactions.

For the first calculation (curve b of Figure 3), one positing a maximum preservation of stereochemistry, the parameters were taken to be $x = y = 0.75$. The 1,3-shifts interrelating cyclohexene and vinylcyclobutane then occur with complete retention, and the ethylene formed reflects the stereochemical disposition of deuterium labels in the cyclohexene or vinylcyclobutane precursor. The cis stereochemistry of the cyclohexene 7 would be retained at two adjacent ring positions in the vinylcyclobutane intermediate, according to this model, and would be passed on preferentially to the product ethylenes. Two different bonds in the vinylcyclobutane could be broken; one would lead only to 7 or *cis*-ET, and the other would lead to equal amounts of cis and trans cyclohexene-d_6 isomers, and of *cis*-ET and *trans*-ET. The net effect is that ethylenes generated through vinylcyclobutane would consist of 75% *cis*-ET and 25% *trans*-ET. This "maximum preservation of stereochemistry" model predicts the absolute minimum percentages of *trans*-ET which should be formed at these temperatures, taking into consideration the paths to this product included in Scheme II.

For a second calculation (curve a of Figure 3), one positing a complete loss of stereochemistry over both the cyclohexene to vinylcyclobutane to cyclohexene sequence and the cyclohexene to vinylcyclobutane to ethylene sequence, the parameters were taken to be $x = y = 0.50$. This "minimum preservation of stereochemistry" model predicts the maximum percentages of *trans*-ET which should be formed through stereochemically randomizing versions of the paths included in Scheme II leading to and from vinylcyclobutane.

The second of these models (curve a of Figure 3) is in better accord with the experimental data than the model presupposing a maximum retention of stereochemistry (curve b). In the lower portion of the temperature range considered, the curves of Figure 3 look much like those of Figure 2, for the cyclohexene to vinylcyclobutane to ethylene route provides the dominant path leading to *trans*-ET. The cis-to-trans isomerization of *cis*-ET produces less the 0.5% *trans*-ET at temperatures below 1100 K, but it becomes the dominant source of that product above 1200 K. Very little ethylene comes from the trans isomer of the labeled cyclohexene 7, for k_4/k_3 (Scheme II) is about 4.5; the relative concentration of that trans isomer in the shock-tube kinetic runs is always much smaller than the concentration of the cis isomer, 7.

Discussion

An important finding from this study is that the thermal conversion of cyclohexene to butadiene and ethylene gives ethylene with a substantial degree of conservation of stereochemistry, even at very high reaction temperatures. When post-reaction cis,-trans isomerization of ethylene-*1,2-d*$_2$ isomers is included in the kinetic model, the initially formed ethylene isomers are inferred to show greater than 90% retention of the stereochemical disposition of deuterium labels at C4–C5 of the cyclohexene reactant at temperatures up to at least 1200 K (Figure 3). On this point the present study agrees with and extends earlier experimental work.[8i,11] Yet the presence of greater quantities of *trans*-ET in product mixtures than can be attributed to cis-to-trans isomerization of product *cis*-ET indicates that some stereochemically nonconservative processes are also of significant importance in the cyclohexene to butadiene plus ethylene reaction at $T > 1000$ K. This modest defect in stereospecificity was not detected in earlier studies; indeed, the modeling analysis confirms that stereochemically nonconservative channels should not have been observable (<1%) at the much lower temperatures employed in the study of the stereochemistry of combination of deuterium-labeled butadienes and ethylenes.[8i]

The four experimental data points for percent *trans*-ET production from cyclohexene 7 at 1094 and 1180 K (Figure 3) lie slightly above curve a, but the range of uncertainty associated with each measurement does overlap that curve. Thus it may be concluded that Scheme II with $x = y = 0.5$ (complete loss of stereochemistry on the cyclohexene to vinylcyclobutane to ethylene route) adequately describes the retro-Diels–Alder reaction of cyclohexene up to 1200 K. The data allow, however, the production of up to 2% more *trans*-ET than Scheme II predicts at 1094 and 1180 K, and the possible implications of this fact need to be examined.

A higher *trans*-ET percentage would be expected if there were a preference for inversion at the migrating carbon in the cyclohexene to vinylcyclobutane isomerization, followed by a preference for suprafacial production of ethylene from vinylcyclobutane. While some possible experimental precedents for such stereochemical preferences may be cited,[22,23] they depend on work with differently constrained bicyclic hydrocarbons at much lower temperatures, where amplitudes of molecular vibrations would

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[22] (a) Baldwin, J. E.; Belfield, K. D. *J. Am. Chem. Soc.* **1988**, *110*, 296–297. (b) Klärner, F.-G.; Drewes, R.; Hasselmann, D. *J. Am. Chem. Soc.* **1988**, *110*, 297–298.

[23] Baldwin, J. E.; Ford, P. W. *J. Am. Chem. Soc.* **1969**, *91*, 7192.

be much less than at the high temperatures of the present study. Such a combination of stereochemical preferences seems unlikely at $T > 1000$ K. The inverse of this scenario, preferential retention of stereochemistry at the migrating carbon in the cyclohexene to vinylcyclobutane reaction, followed by net antarafacial fragmentation of ethylene from vinylcyclobutane, would also predict a model curve higher than curve a, but this seems even less likely.

Higher *trans*-ET product concentrations could also be accommodated by adding to the kinetic scheme a direct path between cyclohexene **7** reactant and *trans*-ET product, one not involving formation of a vinylcyclobutane intermediate. This direct path would involve cleavage of a cyclohexene C3–C4 bond and formation of a diradical intermediate. Indeed, the transitory existence of vinylcyclobutane in the overall cyclohexene reaction scheme demonstrates the probable presence of such a diradical, which could either revert to cyclohexene or give vinylcyclobutane or fragment to produce ethylene plus butadiene, depending upon the phase relationships and directions of vibrations and internal rotations. If the assumptions implicit in developing model curve a in Figure 3 are adopted—all stereochemistry is lost in the formation of vinylcyclobutane from cyclohexene **7**—then no more than 4% of the ethylene product (2% trans plus 2% cis) can have come from a direct stereochemically nonconservative channel at temperatures lower than 1200 K. If, on the other hand, there is some net retention of stereochemistry in the cyclohexene to vinylcyclobutane to ethylene process, then the observed amount of *trans*-ET cannot be accounted for by the cyclohexene to vinylcyclobutane to ethylene route alone (Scheme II) and another path, a stereochemically nonconservative direct path from cyclohexene **7** to *trans*-ET, must be involved. Experiments to test this possibility are underway.

The third shock-tube experiment on cyclohexene **7**, run at a temperature (calculated from the extent of cyclohexene depletion) of 1244 K, produced a *trans*-ET percentage about 15% greater than predicted by Scheme II (Figure 3). Three experimental complications must be considered, however, before attributing this excess to a direct stereochemically nonconservative channel.

First, the substantial endothermicity of the retro-Diels–Alder reaction coupled with the large extent of cyclohexene decomposition in this experiment means that the gas temperature dropped many tens of degrees during the reaction time and that the calculated temperature represents a weighted kinetic average value. Since the retro-Diels–Alder reaction and the ethylene cis,trans isomerization have virtually identical activation energies, potential errors introducted by this temperature averaging should in principle cancel. However, the probability that the gas temperature approached 1300 K at the very beginning of the experiment raises concern about a possible acceleration of the ethylene isomerization rate by radical-induced processes.

Second, products sampled from single-pulse shock-tube experiments always include a small amount (typically 1% to 5%) of unreacted "boundry layer" gas which resided at or near the shock tube walls and which remained cool during the pulse. Therefore, rate constants deduced from single-pulse shock-tube measurements can be lower than the true values, especially at high temperatures where large extents of reaction are achieved.[24] Given the large extent of retro-Diels–Alder reaction in the 1244 K experiment, the true average temperature was probably a few degrees higher. The ethylene isomerization would not appear slowed by the same factor, owing to the lower expected extent of reaction.

Third, we chose for cis,trans isomerization of ethylene-*1,2-d*$_2$ in Scheme II rate constants calculated from eq 1; this equation is both an acceptable (within error limits) representation of the data shown in Figure 1 and in fair agreement with earlier measurements of E_a and thermochemical estimates of A.[19] Equation 1, however, predicts a rate constant at 794 K more than three times larger than that reported by Douglas, Rabinovitch, and Looney, and an order of magnitude larger than that calculated with their preferred activation parameters.[19a] If, on the other hand, the best linear regression line through the present isomerization data, corresponding to log $(A, \text{s}^{-1}) = 14.7$ and $E_a = 68.6$ kcal/mol, is extrapolated downward to 794 K, it overshoots the rate constant reported in 1955[19a] by less than a factor of 2. If the higher activation energy suggested by this comparison is correct, then ethylene isomerization rates at $T > 1200$ K are slightly greater than those given by eq 1, and the discrepancy between curve a of Figure 3 and the 1244 K data point is reduced. Additional experiments to resolve this question are in progress.

Mindful of these three concerns, and of the steep rise of the curves of expected percent *trans*-ET with temperature (Figure 3), we refrain from claiming that the 1244 K experiment proves the existance of a substantial component of a direct stereochemically nonconservative path from cyclohexene **7** to *trans*-ET. Such a path, however, cannot be ruled out by the present data.

From the vantage point offered by these high-temperature experiments and model calculations, together with the many theoretical and the few experimental studies that have gone before, a more detailed perspective on the behavior of cyclohexene molecules undergoing the retro-Diels–Alder rection emerges. An extensive *ab initio* study of the cyclohexene to butadiene plus ethylene energy surface located a diradical saddle point only about 2 kcal/mol above the energy of the lowest energy barrier for the C_s-symmetric concerted process.[8j] If the statistical chances of approaching these two saddle points are the same, then the rates of passage over the two barriers would differ by less than a factor of 3 at 1000 K. One may wonder, then, whether there may be an even greater extent of decomposition by way of diradical intermediates than required by the present data and the model outlined in Scheme II. Could the abundance of diradicals actually be greater than required by Scheme II, and the subsequent decay to ethylene plus butadiene be so rapid that ethylene-*1,2-d*$_2$ is formed from the short-lived diradical in a largely stereochemicaly conservative manner? Could it be that the reaction is subjected to a kinetic as well as quantum mechanical control of overall reaction stereochemistry?

Further insight may be gained by consideration of the complexity of vibrational motions, the 42 normal modes, in gaseous cyclohexene. The most stable conformation is a "half-chair",[25] not the planar conformation commonly pictured; the reported activation energy for ring inversion through planarity is 5.3 kcal/mol,[26] less than 10% of the energy barrier to the retro-Diels–Alder reaction. For cyclohexene at 1200 K, $C_p{}^\circ = 72$ cal/(mol·K), about 79% of the classical high-temperature limit, excluding electronic excitation. Most cyclohexene molecules sufficiently energized to react would be undergoing extensive out-of-plane twisting. Even if the lowest energy saddle point for reaction is a C_s-symmetric configuration of atoms, the actual paths by which individual molecules traverse the barrier ought to be governed by both energetic and statistical considerations and be dependent upon the dynamic histories of individual reacting molecules.

When a cyclohexene molecule has barely sufficient internal energy to react, it will explore configurations for a long time until finally arriving at, and passing over, the lowest energy saddle point; but when much more internal energy is available, the molecule is not so restricted and may proceed over the barrier through other configurations as well. Although the lowest energy saddle point may be associated with a C_s-symmetric configuration of atoms, in a collection of reacting molecules with a distribution of internal energies and a random relationship between the phases

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[24] Skinner, G. B. *Int. J. Chem. Kinet.* **1977**, *9*, 863–865.

[25] (a) Chiang, J. F.; Bauer, S. H. *J. Am. Chem. Soc.* **1969**, *91*, 1898–1901. (b) Scharpen, L. H.; Wollrab, J. E.; Ames, D. P. *J. Chem. Phys.* **1968**, *49*, 2368–2372.

[26] Anet, F. A. L.; Haq, M. Z. *J. Am. Chem. Soc.* **1965**, *87*, 3147–3150. Anet, F. A. L.; Freedberg, D. I.; Storer, J. W.; Houk, K. N. *J. Am. Chem. Soc.* **1992**, *114*, 10969–10971.

of excited vibrations, it is likely that many molecules will react along paths that involve some degree of asymmetry, because such configurations are statistically much more numerous and not much higher in energy. The higher the temperature, the greater the likelihood of a molecule reacting by way of a highly distorted or, in the limit, a diradical structure. At very high temperatures, molecules can virtually pour over the barrier at numerous configurations. At the higher internal energies attendant upon higher reaction temperatures, the likelihood of diradical mediated paths and loss of stereochemistry in the ethylene fragment increases.

Acknowledgment. We thank the National Science Foundation for support of the work at Colgate University through Grant No. CHE 90-23319 and at Syracuse University through Grant No. CHE 91-00246. We also thank Samuel Bonacorsi, Jr., Steven J. Cianciosi, and Karla A. Villarica at Syracuse University and Bansi L. Kalra and Carl E. Lewis at Colgate University for their assistance.