

## Kinetics of the Thermal Isomerizations of Gaseous Vinylcyclopropane and Vinylcyclobutane

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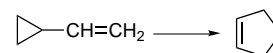
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Rate constants for the thermal isomerizations of vinylcyclopropane to cyclopentene have been measured over a wide temperature range, 577–1054 K, in a static reactor and a single-pulse shock tube; they are well represented by  $\log(A, \text{s}^{-1}) = 14.3$  and  $E_a = 51.7$  kcal/mol. This activation energy is higher than two previously reported values by some 2 kcal/mol; rate constants at high temperatures are about a factor of 2 larger than calculated from the Arrhenius parameters derived from the earlier low-temperature data. The thermal decomposition and isomerization reactions of vinylcyclobutane to give ethene plus 1,3-butadiene and cyclohexene have also been followed in shock-tube kinetic studies at 839–965 K. Combining the new rate constants with those from two lower-temperature studies gives the following: for the total consumption of vinylcyclobutane,  $\log(A, \text{s}^{-1}) = 14.5$  and  $E_a = 49.3$  kcal/mol; for production of ethene and butadiene,  $\log(A, \text{s}^{-1}) = 14.5$  and  $E_a = 49.8$  kcal/mol; and for isomerization to cyclohexene,  $\log(A, \text{s}^{-1}) = 13.4$  and  $E_a = 47.5$  kcal/mol. These values are close to previously reported Arrhenius parameters based on lower temperature static-reactor kinetic investigations. The diradical transition structure for the vinylcyclobutane to cyclohexene isomerization appears to be strain free, while the transition structure for the vinylcyclopropane to cyclopentene conversion retains some  $4.6 \pm 0.9$  kcal/mol of ring strain and torsional strain energy.

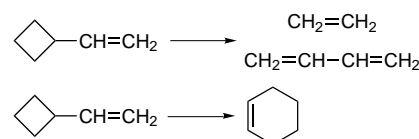
## Introduction

Unimolecular isomerization and fragmentation reactions of relatively small hydrocarbons have long been studied through careful kinetic investigations. Such reactions are often accessible at reasonable temperatures, easy to follow with a variety of quantitative analytical methods, and fairly amenable to various theoretical models. While most kinetic studies of hydrocarbon isomerizations and fragmentations have been limited to the temperatures and pressures accessible in static reactors, more recent work has explored selected reactions of simple hydrocarbons under other conditions using chemical activation, very low pressure pyrolysis, and infrared multiphoton excitation methods. Insofar as these methods usually involve high levels of thermal or nonthermal molecular excitation and low pressures far from the high-pressure limit, comparisons between the kinetic parameters obtained and similar data secured from static-reactor studies over a limited temperature range may be problematic. Extrapolations over many hundreds of degrees may be required. When multiple reaction paths are possible and different product ratios are obtained under widely differing experimental conditions, variations in product ratios may be due to differences in temperatures of thermalized gases or to low collision rates and nonthermal internal energy distributions. Measurements of thermal reaction rates over large temperature ranges at sufficiently high pressures to ensure first-order behavior serve to clarify these uncertainties; they may be made by combining classical static-reactor and single-pulse shock-tube kinetic investigations of individual reactions. This paper reports such studies on two vinylcycloalkanes. The unimo-

lecular isomerization rate of vinylcyclopropane to cyclopentene was studied in both a static reactor and a single-pulse shock tube over a temperature range of 577–1054 K.



The parallel rates of vinylcyclobutane isomerizing to cyclohexene and fragmenting to give ethene and 1,3-butadiene were also measured in the shock tube at 839–965 K.



The isomerization of vinylcyclopropane to cyclopentene instigated thermally, by chemical activation, and through infrared multiphoton excitation has been studied previously. Vogel first reported that cyclopentene is the principal thermal rearrangement product of vinylcyclopropane.<sup>1</sup> Static reactor studies by Flowers and Frey<sup>2</sup> at 612–664 K, by Wellington<sup>3</sup> at 598–663 K, and by Retzlöff, Coull, and Coull<sup>4</sup> at 680–800 K gave essentially identical Arrhenius parameters for the isomerization vinylcyclopropane  $\rightarrow$  cyclopentene:  $\log(A, \text{s}^{-1}) = 13.5$ – $13.6$  and  $E_a = 49.6$ – $49.7$  kcal/mol. Flowers and Frey also reported yields on the order of 1% of their product samples of all three straight-chain pentadienes (1,4-, *cis*-1,3-, and *trans*-1,3-pentadiene) as well as some isoprene (2-methylbutadiene) at the highest temperatures of their study. Wellington found the three pentadiene isomers, each representing about 1% of his product samples and increasing slightly with temperature, but he did not find isoprene in product mixtures. He deduced rate constants for production of each pentadiene:  $E_a$  values

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ranged from 53.6 to 57.3 kcal/mol. The three pentadiene isomers formed as minor products in vinylcyclopropane thermalyses are also formed from cyclopentene at considerably higher temperatures.<sup>5</sup>

The chemical activation studies of Crane and Rose<sup>6</sup> involving the addition of methene from the photolysis of diazomethane to 1,3-butadiene provided data on the reactions of vibrationally excited vinylcyclopropane; higher relative yields of pentadienes were obtained, and the isoprene produced was inferred to be the product of a direct insertion reaction. Farneth and co-workers reported an infrared multiphoton excitation study of vinylcyclopropane isomerizations; cyclopentene and the three pentadienes were again the observed products.<sup>7</sup> While overall product yields and compositions were found to vary considerably with excitation fluence, intensity, and wavelength, the pentadiene concentrations were greater under all conditions than those reported in other studies.

In related work, Lewis, Baldwin, and Cianciosi<sup>8</sup> measured the rate of the reversible degenerate unimolecular interconversion of cyclopentene-3-<sup>13</sup>C and cyclopentene-4-<sup>13</sup>C at temperatures near 1200 K in a single-pulse shock tube. This interconversion is believed to occur by way of the intermediate vinylcyclopropane-2-<sup>13</sup>C. The observed rates were about a factor of 2 larger than expected from the calculated equilibrium constant<sup>9</sup> coupled with a 500 K upward extrapolation of the rate constants for vinylcyclopropane isomerization to cyclopentene measured in static reactors.<sup>2-4</sup> This finding prompted speculation that the activation energy for the vinylcyclopropane-to-cyclopentene isomerization may be somewhat greater than previously reported.

The isomerization and fragmentation of vinylcyclobutane have been studied in static reactors by Pottinger and Frey<sup>10</sup> and by Micka.<sup>11</sup> Both investigations led to essentially the same Arrhenius parameters: for vinylcyclobutane → ethene + 1,3-butadiene,  $\log(A, \text{s}^{-1}) = 14.7 - 14.9$  and  $E_a = 50.2 - 50.7$  kcal/mol; for vinylcyclobutane → cyclohexene,  $\log(A, \text{s}^{-1}) = 13.7 - 13.9$  and  $E_a = 48.2 - 48.6$  kcal/mol. No other significant reaction channels were observed.

A study of the thermal decomposition of ethylcyclobutane to ethene plus 1-butene gave  $\log(A, \text{s}^{-1}) = 15.6$  and  $E_a = 62.0 \pm 1$  kcal/mol;<sup>12</sup> the difference in  $\log A$  values for this reaction and the vinylcyclobutane → ethene + 1,3-butadiene cyclorversion is consistent with expectations while the difference in  $E_a$  values,  $11.5 \pm 1$  kcal/mol, is within experimental uncertainties of the resonance energy of the allyl radical determined by Tsang and Walker,  $12.2 \pm 1$  kcal/mol.<sup>13</sup>

A related reaction is the retro-Diels-Alder fragmentation of cyclohexene to ethene plus 1,3-butadiene. Most experimental and computational studies of the interconversion of ethene plus 1,3-butadiene with cyclohexene have favored a concerted mechanism, but a recent shock-tube study of the decomposition of deuterium-labeled cyclohexenes indicated that stereochemically nonconservative processes are important at high temperatures.<sup>14</sup> Whether vinylcyclobutane is involved as a reactive intermediate may be probed through careful measurements of branching ratios for vinylcyclobutane → ethene + 1,3-butadiene and vinylcyclobutane → cyclohexene over a broad range of temperatures and then modeling the contributions of direct (cyclohexene to ethene + 1,3-butadiene) and indirect (cyclohexene to vinylcyclobutane to ethene + 1,3-butadiene) paths.<sup>14</sup>

Small but potentially significant uncertainties in activation parameters for the isomerization reactions of vinylcyclopropane and for the isomerization and fragmentation reactions of vinylcyclobutane prompted the present work, extending to high temperatures rate constant measurements for the vinylcyclo-

propane → cyclopentene, vinylcyclobutane → ethene + 1,3-butadiene, and vinylcyclobutane → cyclohexene reactions.

## Experimental Section

**Materials.** Vinylcyclopropane was prepared from cyclopropyl methyl ketone (Aldrich, 99%) in two steps, by way of the tosylhydrazone. Analysis by GC indicated 99.77% vinylcyclopropane, 0.15% cyclopentene, 0.06% *trans*-1,3-pentadiene, and 0.02% *cis*-1,3-pentadiene. There was no detectable 1,4-pentadiene or cyclopentadiene. Vinylcyclobutane was prepared in a similar two-step reaction sequence from cyclobutyl methyl ketone (Aldrich, 98%). The purified reactant contained no detectable (>0.01%) impurities. Cyclobutane (Columbia Biochemical Co., 99%) was included in vinylcyclopropane reaction mixtures as an internal thermometer. The single observed impurity, believed to be *n*-butane, was unreactive at the temperatures of the present study and was not removed. Calibration samples for products were prepared from samples obtained as follows: ethene and 1,3-butadiene (Matheson CP lecture bottles); cyclohexene and 1,4-pentadiene (Aldrich); *cis*- and *trans*-1,3-pentadiene (API Standards). The diluent gas for the shock tube and static reactor experiments was Matheson Research Grade argon. Linde helium was used as the shock tube driver gas.

The reactants (vinylcyclopropane, vinylcyclobutane, and cyclobutane) were degassed through multiple freeze-pump-thaw cycles in a glass high-vacuum system, transferred to 1 dm<sup>3</sup> glass storage flasks equipped with greaseless stopcocks, and diluted to 10.0% with argon. Portions of these stock samples were further diluted and mixed as appropriate for the shock tube runs; other portions were used undiluted in the static reactor.

**Apparatus.** The static reactor and single-pulse shock tube used in this study, and procedures for their operation, have been described previously.<sup>15,16</sup> Reactant and product samples were analyzed on a Varian 1440-20 gas chromatograph with hydrogen flame detector, using a 1.5 m 5% *n*-octane on Poracil C column at 50 °C.

**Vinylcyclopropane Kinetic Runs.** For the static reactor runs, 35–50 Torr samples of 10.0% vinylcyclopropane in argon were heated for 15–30 min. At the end of the reaction period, the products were passed through a U-tube at 77 K to trap the organic fraction, which was then chromatographed. Shock-tube experiments were run on a mixture of 1.0% vinylcyclopropane in argon and on three mixtures of vinylcyclopropane plus cyclobutane diluted in argon: 0.50%/0.54%, 0.50%/0.50%, and 0.20%/0.18%. Samples ranging from 119 to 205 Torr were heated for  $(8.0 \pm 0.5) \times 10^{-4}$  s. Product samples were chromatographed without prior removal of the argon diluent.

**Vinylcyclobutane Kinetic Runs.** Single-pulse shock-tube experiments were run on a mixture containing 0.50% vinylcyclobutane plus 0.50% vinylcyclopropane, the latter included to determine reaction temperatures. Samples ranging from 110 to 200 Torr were heated, and the products were analyzed as in the vinylcyclopropane reactions.

**Calculations.** Concentrations of hydrocarbon gases in product samples were determined from GC peak heights, corrected for sensitivity differences determined from prepared calibration samples. Then rate constants for vinylcyclopropane, vinylcyclobutane, and cyclobutane depletion were calculated from the integrated rate equation for irreversible first-order reactions. The rate constant for total vinylcyclobutane loss was then apportioned to fragmentation (to ethene and 1,3-butadiene) and isomerization (to cyclohexene) according to the relative 1,3-butadiene and cyclohexene concentrations in the product

samples, assuming parallel first-order reactions. The reactions vinylcyclobutane  $\rightarrow$  ethene plus 1,3-butadiene and cyclobutane  $\rightarrow$  2ethene are essentially irreversible at the high temperatures and relatively low partial pressures of these experiments. Although the vinylcyclopropane  $\rightarrow$  cyclopentene and vinylcyclobutane  $\rightarrow$  cyclohexene reactions are reversible, the  $K_p$  values are very large; under the present conditions the assumption of irreversibility in the analysis should introduce no significant error. Small quantities of cyclopentadiene observed in the vinylcyclopropane isomerization experiments were added to the cyclopentene product concentrations, following the assumption that the cyclopentadiene came from dehydrogenation of cyclopentene.

The temperatures reached in the shock tube runs on vinylcyclopropane + cyclobutane mixtures were calculated from the measured extent of the cyclobutane  $\rightarrow$  2ethene reaction, using the well-established kinetic parameters  $\log(A, \text{s}^{-1}) = 15.6$  and  $E_a = 62.5$  kcal/mol.<sup>17</sup> Temperatures reached in the vinylcyclobutane plus vinylcyclopropane mixtures were then determined from the progress of the vinylcyclopropane  $\rightarrow$  cyclopentene reaction and are therefore directly referenced to cyclobutane  $\rightarrow$  2ethene reaction rates.

## Data and Results

**Vinylcyclopropane Reactions.** Figure 1 shows an Arrhenius plot for rate constants from 15 shock-tube experiments and six static-reactor runs and a linear least-squares fit for that data. The data for the vinylcyclopropane  $\rightarrow$  cyclopentene isomerization are well represented by

$$\log(A, \text{s}^{-1}) = 14.3 \pm 0.1; \quad E_a = 51.7 \pm 0.5 \text{ kcal/mol} \quad (1)$$

Figure 1 includes for comparison data reported by Wellington.<sup>3</sup> While the latter appear to fall directly on the line of this study, they give a 2 kcal/mol lower slope; extrapolation of the Wellington rate constants to temperatures reached in shock-tube experiments predicts rate constants about a factor of 2 lower than observed in the present study.

**Vinylcyclobutane Reactions.** Figures 2, 3, and 4 show Arrhenius plots for rate constants from six shock-tube runs for vinylcyclobutane  $\rightarrow$  all products, vinylcyclobutane  $\rightarrow$  ethene + 1,3-butadiene, and vinylcyclobutane  $\rightarrow$  cyclohexene. Also shown are the static reactor data reported by Pottinger and Frey<sup>10</sup> and linear least-squares fits through both high- and low-temperature data.

for vinylcyclobutane  $\rightarrow$  all products:

$$\log(A, \text{s}^{-1}) = 14.5 \pm 0.1; \quad E_a = 49.3 \pm 0.4 \text{ kcal/mol} \quad (2)$$

for vinylcyclobutane  $\rightarrow$  ethene + 1,3-butadiene:

$$\log(A, \text{s}^{-1}) = 14.5 \pm 0.1; \quad E_a = 49.8 \pm 0.4 \text{ kcal/mol} \quad (3)$$

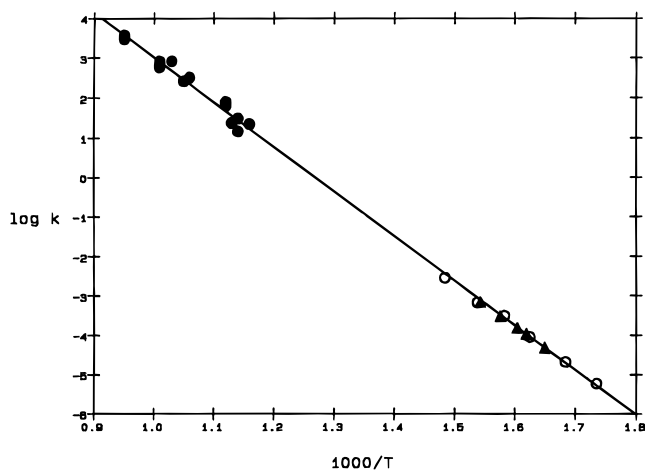
for vinylcyclobutane  $\rightarrow$  cyclohexene:

$$\log(A, \text{s}^{-1}) = 13.4 \pm 0.1; \quad E_a = 47.5 \pm 0.5 \text{ kcal/mol} \quad (4)$$

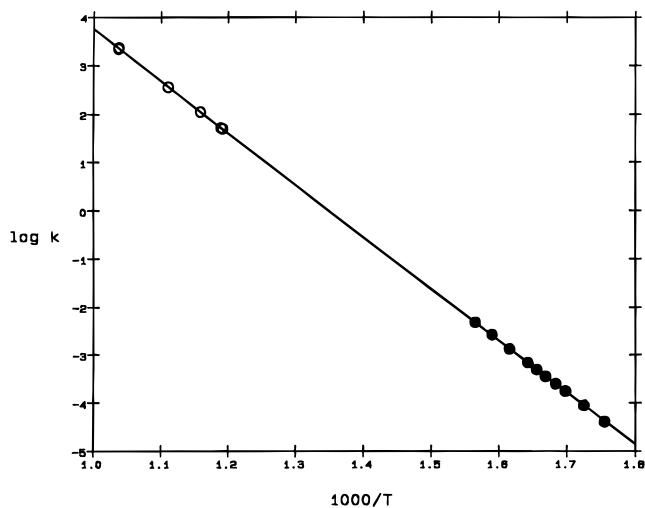
Extrapolation of the low-temperature data alone<sup>10</sup> would slightly overestimate the observed high-temperature values of  $k$  (vinylcyclobutane  $\rightarrow$  all products); the discrepancy amounts to a temperature difference of some 10 deg at 900 K.

## Discussion

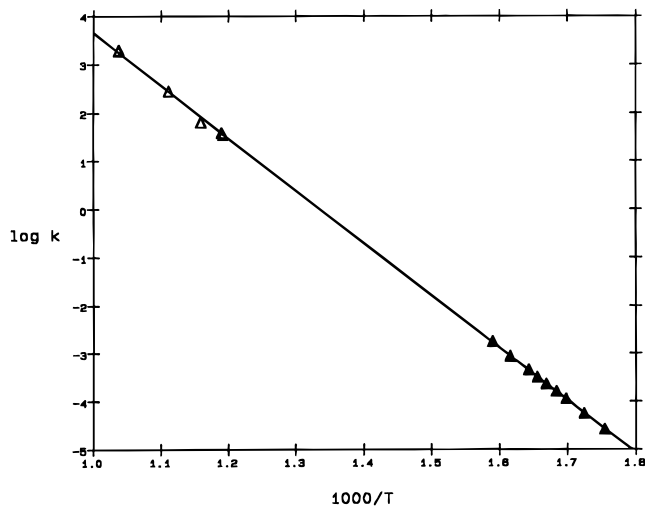
The newly determined  $E_a$  values for vinylcyclobutane  $\rightarrow$  ethene + 1,3-butadiene and for vinylcyclobutane  $\rightarrow$  cyclohexene



**Figure 1.** Rate constants  $k$  for the isomerization of vinylcyclopropane to cyclopentene: (●) this study, single-pulse shock tube data; (▲) this study, static-reactor data; (○) static-reactor data of Wellington.<sup>3</sup>

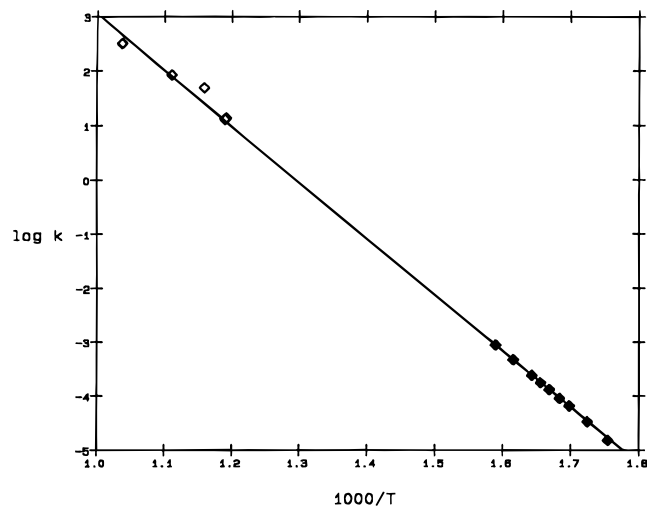


**Figure 2.** Rate constants  $k$  for total conversion of vinylcyclobutane to ethene + 1,3-butadiene and to cyclohexene: (○) this study, single-pulse shock-tube data; (●) static-reactor data of Pottinger and Frey.<sup>10</sup>



**Figure 3.** Rate constants  $k$  for vinylcyclobutane  $\rightarrow$  ethene + 1,3-butadiene: (△) this study; (▲) Pottinger and Frey.<sup>10</sup>

are only slightly lower than the activation energies reported by Pottinger and Frey<sup>10</sup> and by Micka.<sup>11</sup> There are related small differences in preexponential factors, but the temperature-dependent partitioning ratios calculated using either the older parameters or the new  $\log(A, \text{s}^{-1})$  and  $E_a$  constants are not significantly different. One may thus have reinforced confi-

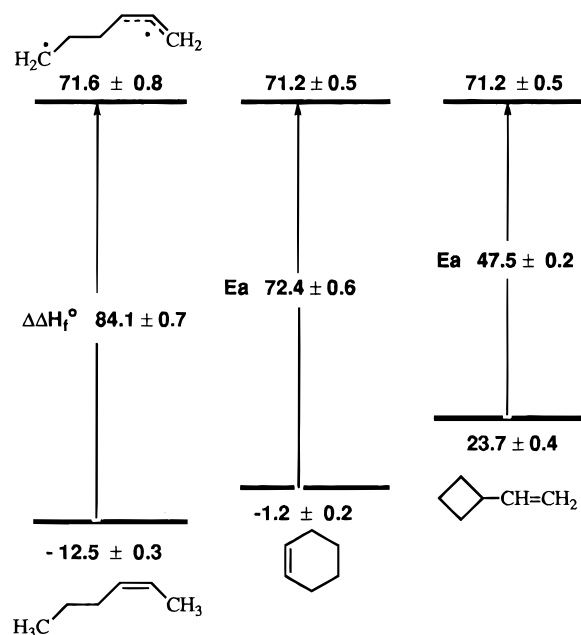


**Figure 4.** Rate constants  $k$  for vinylcyclobutane  $\rightarrow$  cyclohexene: ( $\diamond$ ) this study; ( $\blacklozenge$ ) Pottinger and Frey.<sup>10</sup>

dence in the applicability of the activation parameters already in the literature, even when they are applied at temperatures hundreds of degrees above the temperatures used in the kinetic studies used to derive them. The conclusions based in part on modeling the thermal reactions of cyclohexene giving ethene + 1,3-butadiene through both direct and indirect (by way of vinylcyclobutane) routes which utilized the earlier parameters are accordingly supported.<sup>14</sup> The participation of diradical chemistry and the production of vinylcyclobutane as a reaction intermediate in direct kinetic competition with a stereochemically conservative fragmentation of cyclohexene to ethene + 1,3-butadiene are thus consistent with both stereochemical and kinetic evidence.

The  $\Delta\Delta E_a$  contrast between the (2 + 2) cycloreversions of ethylcyclobutane and of vinylcyclobutane is now  $12.2 \pm 1.1$  kcal/mol, a fine match with the resonance energy of allyl radical.<sup>13</sup> The transition structure related to the fragmentation of vinylcyclobutane, compared with the structure leading from ethylcyclobutane to ethene and 1-butene, seems to have full development of that resonance stabilization.

A consideration of thermochemical relationships pertinent to the interconversion of vinylcyclobutane and cyclohexene based on a diradical model for transition structures, a model exercised earlier in analyses of the thermal interconversions of vinylcyclopentane with cycloheptene and of vinylcyclohexane with *cis*-cyclooctene,<sup>18</sup> is depicted in Figure 5. Gas-phase  $\Delta H_f^\circ$  values for (*Z*)-2-hexene,<sup>19</sup> cyclohexene,<sup>19</sup> and vinylcyclobutane<sup>20</sup> establish the lower reference energies. The calculated energy difference between (*Z*)-2-hexene and the (*Z*)-2-hexen-1,6-diyl diradical is  $84.1 \pm 0.7$  kcal/mol, the sum of the differences in gas-phase heats of formation of ethane and the ethyl radical,  $49.0 \pm 0.1$  kcal/mol,<sup>22</sup> and of propene and the allyl radical,  $35.1 \pm 0.6$  kcal/mol;<sup>23</sup> the  $\Delta H_f^\circ$  value for the (*Z*)-2-hexen-1,6-diyl diradical is thus estimated to be  $71.6 \pm 0.8$  kcal/mol. When the measured activation energy for vinylcyclobutane  $\rightarrow$  cyclohexene is added to  $\Delta H_f^\circ$  for vinylcyclobutane, the transition structure for the interconversion is placed at  $71.2 \pm 0.5$  kcal/mol. Accounting for the differences in  $\Delta H_f^\circ$  values ( $24.9 \pm 0.5$  kcal/mol in Figure 5;  $24.8$  kcal/mol in an earlier estimation<sup>14</sup>) allows one to infer an activation energy for cyclohexene  $\rightarrow$  vinylcyclobutane of  $72.4$  kcal/mol (or  $72.3$  kcal/mol); the latter value was used in the successful modeling calculations for the decompositions and isomerizations of two deuterium-labeled cyclohexenes.<sup>14</sup> The two  $\Delta H_f^\circ$  values in close agreement imply that the transition structure does not have appreciable strain energy relative to the extended (*Z*)-2-hexen-1,6-diyl diradical;



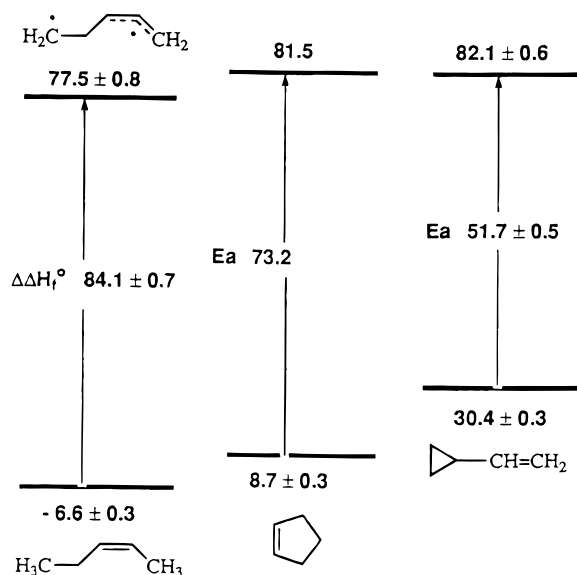
**Figure 5.** Thermochemical analysis of  $\Delta H_f^\circ$  of transition state for vinylcyclobutane  $\leftrightarrow$  cyclohexene interconversion. See text for explanation of how values were determined.

geometrically, it must be different, but it does not retain substantial ring strain or torsional strain.

The same inference was drawn earlier for transition structures for the interconversion of vinylcyclopentane with cycloheptene and of vinylcyclohexane with *cis*-cyclooctene, based on ground state  $\Delta H_f^\circ$  values and  $E_a$  parameters. The estimated transition state  $\Delta H_f^\circ$  values agreed within probable error limits with  $\Delta H_f^\circ$  values calculated for the corresponding extended (*Z*)-2-hepten-1,7-diyl and (*Z*)-2-octen-1,8-diyl diradicals.<sup>18</sup>

The activation energy for vinylcyclopropane  $\rightarrow$  cyclopentene obtained by connecting the present high-temperature shock-tube and lower temperature static-reactor data lies about 2 kcal/mol above the values obtained in earlier studies,<sup>2-4</sup> a modest but not insignificant upward revision. Extrapolated to 1200 K, the rate constant for vinylcyclopropane  $\rightarrow$  cyclopentene is  $k = 7.7 \times 10^4$  s<sup>-1</sup>. Since the reverse rate constant at 1200 K has been found<sup>8</sup> to be  $2.3 \times 10^2$  s<sup>-1</sup>,  $\log K_p = 2.5$ , in agreement with estimations based on thermochemical data for the two isomers.<sup>9</sup>

When one considers the thermochemical aspect of the vinylcyclopropane interconversion with cyclopentene following the simple model used above, the scheme shown in Figure 6 is obtained. The  $\Delta H_f^\circ$  values for (*Z*)-2-pentene,<sup>19</sup> cyclopentene,<sup>24</sup> and vinylcyclopropane<sup>20,25</sup> are known, thus defining reference energies. Estimates for  $\Delta H_f^\circ$  of the transition structure for the interconversion are 81.5 kcal/mol (from previously published shock-tube kinetic studies<sup>8</sup>) and  $82.1 \pm 0.6$  kcal/mol (from the present work), values that are entirely consistent. The energy of the (*Z*)-2-penten-1,5-diyl diradical, however, is placed at  $77.5 \pm 0.7$  kcal/mol, a value noticeably below the energy of the transition structure. One may infer that the transition structure for the vinylcyclopropane to cyclopentene rearrangement still retains some of the strain energy associated with the cyclic reactant and product; the allylic unit of the transition structure may not be fully planar, and other torsional strain factors may still be at play. The residual strain energy, taken to be  $(82.1 \pm 0.6) - (77.5 \pm 0.7) = 4.6 \pm 0.9$  kcal/mol, is significantly larger than zero, both formally and in contrast to the absence of any similar strain energy term in the thermochemical analyses of the related interconversions of vinylcyclobutane, vinylcyclopentane,<sup>18</sup> and vinylcyclohexane<sup>18</sup> with the corresponding isomeric cycloalkenes.



**Figure 6.** Thermochemical analysis of  $\Delta H_f^\circ$  of transition state for vinylcyclopropane  $\leftrightarrow$  cyclopentene interconversion. See text for explanation of values.

That the allyl units of transition structures for vinylcyclopropane to cyclopentene rearrangements are substantially twisted out of planarity has been hypothesized to account for remarkably large secondary deuterium kinetic isotope effects at the 2'-carbon of the vinyl group;  $k_H/k_D = 1.17 \pm 0.02$  at 338 °C for 2',2'- $d_2$ -labeled vinylcyclopropane, a fact taken as an indication of torsional distortion.<sup>26,27</sup> This interpretation of the  $k_H/k_D$  data and the different patterns of thermochemical relationships displayed in Figures 5 and 6 suggest that  $k_H/k_D$  effects for isomerization of vinylcyclobutane-2',2'- $d_2$  to cyclohexene-3,3- $d_2$  will turn out to be far more modest than those seen for superficially analogous vinylcyclopropane and substituted vinylcyclopropane isomerizations.

## Conclusions

Accurate rate constants measured over large temperature ranges provide more reliable Arrhenius parameters than can be secured from rate constant data obtained over modest temperature ranges. By combining static-reactor-based kinetic data and shock-tube kinetic results, the present work has essentially reproduced the Arrhenius activation parameters obtained by Pottinger and Frey<sup>10</sup> and by Micka<sup>11</sup> for the thermal fragmentation and isomerization reactions of vinylcyclobutane at relatively low temperatures and demonstrated that they give a reliable basis for calculating rate constants even when applied at much higher temperatures. This confirmation of Arrhenius parameters for the reactions vinylcyclobutane  $\rightarrow$  all products, vinylcyclobutane  $\rightarrow$  ethene + 1,3-butadiene, and vinylcyclobutane  $\rightarrow$  cyclohexene to within combined experimental uncertainties extends the temperature range of demonstrated reliability for rate constants calculated with these parameters. Computer modeling based on these parameters strengthens the case for a nondirect and stereochemically nonconservative path leading from cyclohexene to ethene plus 1,3-butadiene by way of vinylcyclobutane.<sup>14</sup> Rate constants secured for the vinylcyclopropane to cyclopentene isomerization over a wide temperature range, 577–1054 K, provided a revised  $E_a$  for the isomerization of vinylcyclopropane to cyclopentene,  $51.7 \pm 0.5$  kcal/mol rather than the  $E_a = 49.6$ – $49.7$  kcal/mol reported by earlier investigators. This new  $E_a$  value and thermochemical considerations suggest that the transition structure for the isomerization has some  $4.6 \pm 0.9$  kcal/mol of strain energy, while the transition structure for the

formally analogous vinylcyclobutane to cyclohexene process is essentially strain free. Other lines of experimentation and theoretical definitions of geometries and energies for the transition structures associated with these isomerizations will be required before this kinetically and thermochemically based inference may be properly tested.

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