Kinetics of Primary Processes in the Pyrolysis of Cyclopentanes and Cyclohexanes

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Studies of the thermal unimolecular decomposition of cyclopentane, cyclohexane, vinylcyclopentane, and vinylcyclohexane have been carried out at temperatures in the range 900-1223 K using the technique of very low-pressure pyrolysis (VLPP). The results show that ring-opening isomerization to open-chain alkenes is the major primary process. Under the experimental conditions the alkenes undergo further decomposition via C-C bond fission and/or retro-ene processes. Application of RRKM theory shows that the VLPP data (falloff regime) are consistent with the following high-pressure rate expressions (at $\langle T \rangle$ = 1100 K) for reactant decay: $\log (k/s^{-1}) = (16.8 \pm 0.3) - (355 \pm 8)/\theta$ for cyclopentane, $\log (k/s^{-1}) = (16.9 \pm 0.3) - (355 \pm 8)/\theta$ $(361 \pm 8)/\theta$ for cyclohexane, log $(k/s^{-1}) = (16.0 \pm 0.3) - (304 \pm 8)/\theta$ for vinylcyclopentane, and log $(k/s^{-1}) = (16.0 \pm 0.3) - (304 \pm 8)/\theta$ for vinylcyclopentane, and log $(k/s^{-1}) = (16.0 \pm 0.3) - (304 \pm 8)/\theta$ for vinylcyclopentane, and log $(k/s^{-1}) = (16.0 \pm 0.3) - (304 \pm 8)/\theta$ for vinylcyclopentane, and log $(k/s^{-1}) = (16.0 \pm 0.3) - (304 \pm 8)/\theta$ for vinylcyclopentane, and log $(k/s^{-1}) = (16.0 \pm 0.3) - (304 \pm 8)/\theta$ for vinylcyclopentane, and log $(k/s^{-1}) = (16.0 \pm 0.3) - (304 \pm 8)/\theta$ for vinylcyclopentane, and log $(k/s^{-1}) = (16.0 \pm 0.3) - (304 \pm 8)/\theta$ for vinylcyclopentane, and log $(k/s^{-1}) = (16.0 \pm 0.3) - (304 \pm 8)/\theta$ for vinylcyclopentane, and log $(k/s^{-1}) = (16.0 \pm 0.3) - (304 \pm 8)/\theta$ for vinylcyclopentane, and log $(k/s^{-1}) = (16.0 \pm 0.3) - (304 \pm 8)/\theta$ for vinylcyclopentane, and log $(k/s^{-1}) = (16.0 \pm 0.3) - (304 \pm 8)/\theta$ for vinylcyclopentane, and log $(k/s^{-1}) = (16.0 \pm 0.3) - (304 \pm 8)/\theta$ for vinylcyclopentane, and log $(k/s^{-1}) = (16.0 \pm 0.3) - (304 \pm 8)/\theta$ for vinylcyclopentane, and log $(k/s^{-1}) = (16.0 \pm 0.3) - (304 \pm 8)/\theta$ for vinylcyclopentane, and log $(k/s^{-1}) = (16.0 \pm 0.3) - (304 \pm 8)/\theta$ for vinylcyclopentane, and log $(k/s^{-1}) = (16.0 \pm 0.3) - (304 \pm 8)/\theta$ for vinylcyclopentane, and log $(k/s^{-1}) = (16.0 \pm 0.3) - (304 \pm 8)/\theta$ for vinylcyclopentane, and log $(k/s^{-1}) = (16.0 \pm 0.3) - (304 \pm 8)/\theta$ for vinylcyclopentane, and log $(k/s^{-1}) = (16.0 \pm 0.3) - (304 \pm 8)/\theta$ for vinylcyclopentane, and log $(k/s^{-1}) = (16.0 \pm 0.3) - (304 \pm 8)/\theta$ for vinylcyclopentane, and log $(k/s^{-1}) = (16.0 \pm 0.3) - (304 \pm 0.3) -$ 0.3) - $(309 \pm 8)/\theta$ for vinylcyclohexane, where $\theta = 2.303RT$ kJ/mol. The A factors were based on known values for C-C bond fission in alkanes and alkenes. Comparison of the activation energies for the unsubstituted cycloalkanes with those for the vinyl-substituted cycloalkanes reveals that the effect of the vinyl substituent is close to the established value for the allyl resonance energy. This evidence supports the assumption of a biradical mechanism for the ring opening of medium-sized cycloalkanes. Decomposition of pent-1-ene (the open-chain isomer of cyclopentane) under VLPP conditions yields unimolecular rate constants for overall decay that are consistent with the high-pressure rate expressions $\log (k/s^{-1}) = (12.5 \pm 0.4) - (238)$ $\pm 10/\theta$ for retro-ene reaction and log $(k/s^{-1}) = (16.0 \pm 0.3) - (296 \oplus 10)/\theta$ for C-C fission. The A factors were assigned from estimates consistent with the results of a recent shock-tube study of the decomposition in the high-pressure regime. The Arrhenius parameters are consistent with previous data on the decomposition of monoolefins via C-C fission and retro-ene pathways.

Introduction

Kinetic data on molecular elimination and rearrangement reactions are important in the establishment of a quantitative relationship between molecular structure and reactivity, and kinetic measurements on bond fission reactions lead to the determination of bond dissociation energies and free radical heats of formation.¹ Although the thermal ring-opening reactions of cyclopropanes and cyclobutanes have been exhaustively investigated little is known about similar primary processes in the higher cycloalkanes. These reactions are of considerable importance in high-temperature thermal cracking and combustion operations involving some hydrocarbon feedstocks. Although a number of studies of cycloalkane pyrrolysis have been reported²⁻⁴ these were mainly concerned with product distributions and yields at high conversion and free-radical chain processes. Kinetic data are lacking and little is known about the primary processes. As a step toward alleviating these deficiencies, $Tsang^{5,6}$ and Kalra et al.⁷ have carried out comparative rate single-pulse shock-tube studies of the pyrolysis of cyclopentane (CYP) and of cyclohexane (CYH). In both cases, the dominant primary process was found to be isomerization to the open-chain alkene, pent-1-ene (PEN) from CYP and hex-1-ene from CYH, followed by subsequent decomposition of these primary products under the experimental conditions. In the case of CYP a minor high-energy pathway leading to cyclopropane plus ethylene was also observed.⁵ Rate parameters were obtained which were consistent with a biradical mechanism for ring fragmentation.³

Kinetic studies of, for example, vinylcyclopentane (VCYP) and ethynylcyclopentane should provide further information on the mechanism and energetics of ring opening of higher cycloalkanes. Furthermore, with some substituents other primary pathways such as ring expansion and bond fission to form cyclic hydrocarbon radicals may become accessible under certain experimental conditions. We report here on studies of the thermal unimolecular decomposition of CYP, CYH, VCYP, and vinylcyclohexane (VCYH) at temperatures in the range 900-1223 K using the technique of very low-pressure pyrolysis (VLPP).^{8,9} In the course of these studies it became necessary to investigate the decomposition of pent-1-ene (PEN) under VLPP conditions and this work is also reported. Studies of the ethynylcycloalkanes will be reported on in due course.¹⁰

Experimental Section

The basic principles of the VLPP technique and its application to the study of thermal unimolecular reactions have been well documented.^{8,9} Essentially, the experimental method consists of allowing a steady-state flow of reactant to pass through a thermostated quartz reactor under very low-pressure conditions. In such an environment molecules undergo very few gas-gas collisions and energy transfer is predominantly via gas-wall collisions. Secondary reactions are eliminated and therefore the direct products of primary thermal excitation in unimolecular decomposition can be determined. Reactant and product species undergo molecular effusion from the VLPP reactor into a vacuum chamber for direct analysis by quadrupole mass spectrometry. Exit aperture diameters of the triple-aperture reactor were 1.07, 3.36, and 10.1 mm, giving Knudsen cell collision numbers Z of 21 460, 2177, and 260, respectively. The gas-wall collision frequency is given by

$$\omega_{\rm w} \,({\rm s}^{-1}) = 4.1 \times 10^3 (T/m)^{1/2}$$

where T is the temperature (K) and m the reactant molecular weight (amu).

All the reactants were from commercial sources: CYP from Koch-Light, CYH from Merck, VCYP from Aldrich, VCYH and PEN from Columbia. They were thoroughly degassed and vacuum distilled bulb-to-bulb prior to use. Carbon dioxide (J. T. Baker instrument grade) and carbon tetrafluoride (Matheson, CP) were used as internal standards for mass spectrometric analysis.

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Results

Mass spectral analyses clearly showed that the major molecular products from the VLPP of CYP and CYH were ethylene and propylene, as was observed also by Tsang^{5,6} and Kalra et al.⁷ According to Tsang^{5,6} the major processes are



In the present work it was not possible to obtain absolute confirmation of the intermediate formation of the open-chain alkenes because CYP and PEN have essentially identical mass spectral cracking patterns, as do CYH and hex-1-ene. However, the results of a VLPP study of hex-1-ene¹¹ indicate that it should be completely decomposed (via retro-ene reaction and C–C bond fission) under the VLPP conditions for CYH. A VLPP study of PEN has not been carried out hitherto but RRKM calculations based on estimated rate parameters indicate that it too should be labile under the VLPP conditions used for CYP. In order to obtain confirmation of this, and also because the retro-ene decomposition of PEN is an important prototypical reaction, a separate VLPP study of PEN was deemed worthwhile (see below).

In the decomposition of PEN under VLPP conditions, the ethyl radicals from the bond fission pathway undergo rapid decomposition (relative to the rate of escape from the reactor) to ethylene and atomic hydrogen¹²

$$CH_3CH_2 \rightarrow H_2C=CH_2 + H$$

The allyl radicals are thermally stable under the experimental conditions, so either they escape from the reactor and reach the quadrupole ion source or they may abstract hydrogen atoms from the walls (inside or outside the reactor) to give propylene.¹³ Thus both retro-ene and bond fission pathways yield the same molecular products and hence may not be separated quantitatively using the present experimental technique. Nevertheless, rate constants may be obtained for overall reactant decay for comparison with calculations based on the sum of the individual pathways (also, if the kinetic parameters for one pathway are known or fixed, then information about the other pathway may be derived).¹⁴ Examination of the mass spectra at 70 eV of PEN both before and after decomposition confirmed the formation of propylene and ethylene. When the electron energy in the ion source was lowered to 9 eV (nominal) in order to examine parent peaks only, qualitative confirmation of the formation of allyl radicals was obtained.

By analogy with CYP and CYH, the ring opening of VCYP is expected to yield hepta-1,6-diene and hepta-1,3-diene

с-C₅H₉—C₂H₃ СH₂=CHCH₂CH₂CH₂CH₂CH=CH₂ CH₂=CHCH=CHCH₂CH₂CH₂CH₂CH₂CH₃

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 TABLE I: Temperature Range and Fractional Decomposition for the

 VLPP of Cycloalkanes and Pent-1-ene

	temp	f^a		
compd	range, K	Z = 21460	Z = 2177	Z = 260
CYP	1071-1221	0.04-0.65		
CYH	1070-1223	0.06-0.77		
VCYP	900-1219	0.03-0.92	0.06-0.90	0.06~0.50
VCYH	950-1209	0.06-0.96	0.09-0.79	0.07-0.49
PEN	926-1218	0.06-0.83	0.04-0.83	0.14-0.49

^a Fractional decomposition.

A previous VLPP study¹⁵ has shown that hepta-1,6-diene undergoes rapid retro-ene decomposition to propylene and buta-1,3-diene without competition from C-C fission

$$CH_2 = CHCH_2CH_2CH_2CH = CH_2 \rightarrow CH_3CH = CH_2 + CH_2 = CHCH = CH_2$$

Similarly, hepta-1,3-diene should undergo retro-ene decomposition to penta-1,4-diene and ethylene

$$CH_2 = CHCH = CHCH_2CH_2CH_3 \rightarrow CH_2 = CH_2 + H_2C = CHCH_2CH = CH_2$$

However, in this case because of the slower rate of the retro-ene pathway¹⁵ there is likely to be concurrent C-C bond fission

The mass spectrum of VCYP showed significant peaks at m/e 27, 28, 39, 41, 53, 54, 55, 67, 68, and 82. Examination of the mass spectra following pyrolysis confirmed the formation of buta-1,3-diene (m/e 50) and ethylene (m/e 25). However, because of the complex array of mass spectral peaks no attempt was made to obtain accurate quantitative measurements of product formation, only the overall rate of decomposition was measured. Within the limitations of the experimental system, no firm evidence could be found for the formation of ring expansion products such as cycloheptene or methylcyclohexene.

Again by analogy with CYP and CYH, the ring opening of VCYH is expected to yield octa-1,7-diene and octa-1,3-diene

H2C=CHCH2CH2CH2CH2CH=CH2

H2C=CHCH=CHCH2CH2CH2CH3

Both octadienes should yield propylene and penta-1,4-diene via retro-ene reaction

$$\begin{array}{c} H_2C = CHCH_2CH_2CH_2CH_2CH = CH_2 \rightarrow \\ CH_3CH = CH_2 + H_2C = CHCH_2CH = CH_2 \end{array}$$

$$\begin{array}{c} H_2C = CHCH = CHCH_2CH_2CH_2CH_3 \rightarrow \\ H_2C = CHCH_2CH = CH_2 + H_2C = CHCH_3 \end{array}$$

$$\begin{array}{c} H_2C = CHCH = CHCH_2CH_2CH_2CH_3 \rightarrow \\ CH_2 = CHCH = CHCH_2 + CH_2CH_2CH_3 \end{array}$$

In the VLPP experiments no attempt was made to completely unravel the complex mass spectra of the reaction mixture issuing from the reactor. However, there was sufficient evidence to at least confirm the formation of penta-1,4-diene and propylene as major products.

The unimolecular decompositions of VCYP, VCYH, and PEN were studied by using all three reactor apertures. However, because of the lower rate constants the pyrolyses of CYP and CYH were limited to only one reactor aperture (Z = 21460). CYP total disappearance was quantitatively monitored by its mass

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Figure 1. Unimolecular rate constants as a function of temperature for the VLPP of cyclopentane: points, experiment, for reactor collision numbers indicated; line, RRKM fit as described in text.



Figure 2. Unimolecular rate constants as a function of temperature for the VLPP of cyclohexane: points, experiment, for reactor collision numbers indicated; line, RRKM fit as described in text.

spectral peak at m/e 55 (fragment peak), CYH at m/e 56 (fragment), VCYP at m/e 81 (fragment), VCYH at m/e 110



Figure 3. Unimolecular rate constants as a function of temperature for the VLPP of vinylcyclopentane: points, experiment, for reactor collision numbers indicated; line, RRKM fit as described in text.

(parent), and PEN at m/e 55 (fragment). Either CO₂ (m/e 44) or CF₄ (m/e 69) was used as an internal standard. Table I shows the temperature ranges and the fractional extents of decomposition, f (as calculated from the mass-spectral peak intensities), for all compounds studied. Unimolecular rate constants were determined from the overall decay of each compound in the usual way^{8,9} from the expression

$$k_{\rm uni} = k_{\rm e}[f/(1-f)]$$

where k_e is the rate constant for escape through the reactor exit aperture. The unimolecularity of the reactions under VLPP conditions were confirmed in the usual way by checking that the variation of reactant flow rate (in the range where the contribution of gas-gas collisions to the activation of the reactant molecules is much less than the contribution of gas-wall collisions) and reactor exit aperture (hence collision number) had no effect on the observed rate constants.^{8,9} The experimental rate constants as a function of temperature are shown in Figures 1-5.

Since under VLPP conditions unimolecular reactions are in the falloff regime the experimental rate constants must be interpreted according to unimolecular reaction rate theory (e.g., RRKM theory)¹⁶ in order to determine the high-pressure rate parameters, A_{∞} and E_{∞} . Appropriate transition-state models are required for the application of RRKM theory, but the exact details are not important in determining the degree of falloff, only the values taken for A_{∞} and E_{∞} which the model is adjusted to fit.¹⁶ The transition state for the formation of ring fragmentation products was based on the assumption of a biradical mechanism. This is not critical, and it merely provides us with a procedure for estimating a set of transition-state frequencies.

King and Goddard¹⁷ have demonstrated that if cyclopentanes decompose via a biradical mechanism then ring opening to form the 1,5-biradical must be the rate-determining step. In such an

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Figure 4. Unimolecular rate constants as a function of temperature for the VLPP of vinylcyclohexane: points, experiment, for reactor collision numbers indicated; line, RRKM fit as described in text.



Figure 5. Unimolecular rate constants as a function of temperature for the VLPP of pent-1-ene: points, experiment, for the overall decomposition and reactor collision numbers indicated; lines, RRKM calculations showing C-C bond fission and retro-ene pathways and the fit to the data for the sum of these two pathways.

TABLE II: Arrhenius Parameters for the Unimolecular **Decomposition of Cycloalkanes**

compd	$\log \left(A_{\infty}/\mathrm{s}^{-1}\right)$	$E_{\infty}, \text{kJ/mol}$	ref
СҮР	16.8	355	this work
	16.1	355	5
CYH	16.9	361	this work
	16.7	369	6
VCYP	16.0	304	this work
VCYH	16.0	309	this work

event the observed rate constant $k_{obsd} = k_{\alpha}/2$, where k_{α} is the rate constant for ring opening. This means that the observed A factor should be one-half that for ring opening, where the latter should be the same as that for C-C fission in the open-chain analogue. It is known that the A factors for alkane bond fission¹⁸ yield $10^{16.4}$ s^{-1} per reaction path and those for alkene bond fission¹⁹ yield $10^{16.0}$ s^{-1} per reaction path (allylic C-C bond fission). On this basis, after taking into account reaction path degeneracies the A factors (in s⁻¹) have been assigned as follows: CYP ($10^{16.8}$), CYH ($10^{16.9}$), VCYP and VCYH (10^{16.0}). The suggested A factor for CYP is somewhat higher than the value of $10^{16.1}$ s⁻¹ found by Tsang.⁵ However, Tsang's value seems too low for C-C bond fission and Kalra et al.⁷ have pointed out that there is a ~ 40 °C temperature discrepancy between their results and Tsang's study (Tsang's temperatures are too high). Correction of Tsang's temperatures by 40 °C would result in an upward adjustment of the A factor deduced from his data to $10^{16.7}$ s⁻¹.

In conjunction with his shock-tube study of CYP, Tsang⁵ also carried out a separate study of PEN decomposition. As with VLPP, the shock-tube technique did not differentiate quantitatively between the retro-ene and bond fission processes so only the overall rate was obtained. However, assuming A factors of $10^{12.5}$ s⁻¹ for retro-ene and 10^{16.0} s⁻¹ for bond fission, and making estimates of the proportions of propylene and ethylene arising from the molecular and bond fission pathways, Tsang obtained the rate expressions log $(k/s^{-1}) \simeq 12.5 - 240/\theta$ for retro-ene and log (k/s^{-1}) $\simeq 16.0 - 298/\theta$ for bond fission. These A factors are in keeping with previous data for allylic bond fission¹⁹ and retro-ene decomposition of monoolefins,¹¹ therefore they have been adopted here for the interpretation of the VLPP data.

Details of the molecular and transition-state parameters employed in the RRKM calculations are given in the Appendix. A temperature-dependent nonunit gas-wall collision efficiency was included in the calculations where appropriate. Previous studies^{20,21} have shown that the gas-wall collision efficiency, β_w , is not only less than unity at high temperatures but it decreases with increasing temperature. As outlined in a recent formulation²² a suitable empirical functional form is

$$\beta_{\rm w}(T) = \min\{1, 0.64 \tanh^{-1}(T/T')\}$$

where min means minimum value and T' (essentially the temperature above which β_w begins to fall below unity) is a function of the molecular weight, potential well depth, and dipole moment of the reactant. Application of this expression shows that, of the molecules in the present study, CYP and PEN (because of their low molecular weights) are the only ones for which $\beta_w < 1$ over the temperature range of the experiments; the values are 0.95 at 1000 K falling to 0.63 at 1200 K for CYP, and 0.61 at 900 K falling to 0.45 at 1200 K for PEN. The RRKM fits to the experimental data are shown in Figures 1-5 and the rate parameters for the cycloalkanes are summarized in Table II. In the case of PEN, the VLPP data are consistent with the Arrhenius parameters given by log $(k/s^{-1}) = 12.5 - 238/\theta$ for retro-ene and

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Pyrolysis of Cyclopentanes and Cyclohexanes

log $(k/s^{-1}) = 16.0 - 296/\theta$ for C-C fission, where the fit to the experimental data was obtained for the sum of the two pathways, taking into account two competing unimolecular reactions in the falloff regime.¹¹ The uncertainties in A_{∞} are taken to be $10^{\pm 0.3}$ s⁻¹ for ring opening and bond fission, as suggested by Tsang.¹³ and $10^{\pm 0.4}$ s⁻¹ for retro-ene, as shown by an analysis of all previous data.^{11,15} The uncertainties in the activation energies ($\pm 8-10$ kJ/mol) were determined by the scatter of experimental data, together with the stated uncertainties in A_{∞} .

Discussion

The results for CYP and CYH are in general agreement with the work of Tsang^{5,6} and Kalra et al.⁷ The intermediate formation of the open-chain isomers, PEN from CYP and hex-1-ene from CYH, was not observed under VLPP conditions but this may be ascribed to rapid and complete secondary decomposition of these compounds. This was confirmed by separate VLPP studies of PEN and hex-1-ene.¹¹ The dominant end products from CYP and CYH are the same in both VLPP and shock-tube experiments and the rate parameters are in good agreement (see Table II).

The reaction products and rate parameters obtained in the present and previous studies suggest similar mechanisms for the decomposition of CYP, CYH, VCYP, and VCYH. The results are readily interpretable in terms of a biradical mechanism for ring fragmentation, e.g., for CYP

CH3CH=CH2 + H2C=CH2

where the overall observed rate constant for reactant decay is given by

$$k_{\rm obsd} = \frac{k_{\rm a}k_{\rm c}}{k_{\rm b} + k_{\rm c}}$$

Generation of 1,5-biradicals via the photolysis of cyclohexanones shows that disproportionation occurs readily.^{23,24} Tsang⁵ has argued that, because the disproportionation-to-combination ratio for n-propyl radicals has been measured as 0.16, then, for CYP pyrolysis, $k_b > k_c$ and hence $k_{obsd} = k_a k_c / k_b = k_c K_{a,b}$. However, as mentioned in the Results, King and Goddard¹⁷ have pointed out that there is ample evidence for disproportionation-to-combination ratios from 1,5-biradicals that are much higher than for the reactions between two monoalkyl radicals, at least at moderate temperatures (303-453 K).^{23,24} Under high-temperature pyrolysis conditions a reasonable assumption is $k_b \approx k_c$ and the biradical mechanism then yields $k_{obsd} = k_a/2$. Examination of the results in Table II shows that the rate parameters are similar to those for C-C bond fission in open-chain alkanes and alkenes. The difference in activation energies between CYP and VCYP (51 kJ/mol) and between CYH and VCYH (52 kJ/mol) is in both cases close to the established value of 50 kJ/mol for the allyl resonance energy.¹³ Also, using thermochemcial and group additivity data¹ we may calculate $\Delta H^{o}_{a,b}$. In each case it was found that the energy required to form the biradical (e.g., for CYP $\Delta H^{\circ}_{ab}(1100 \text{ K}) = 326 \text{ kJ/mol})$ is less than the observed activation energy, which means that a biradical is energetically feasible.

If, on the other hand, we follow Tsang's approach⁵ to the biradical mechanism and assume $k_{obsd} = k_c K_{a,b}$ with k_c/k_b given by the disproportionation-to-combination ratio for *n*-propyl radicals then the observed A factor should be $0.16A_a$ (at least for CYP) instead of $0.5A_{\alpha}$ as above. The assigned A factors would then be $10^{0.5}$ s⁻¹ less than the values shown in Table II. Refitting of

TABLE III: RRKM Parameters

- frequencies,^a cm⁻¹
- reactant: 2965 (5), 2875 (5), 1470 (5), 1275 (4), 1160 (4), 1030 (3), 1050, 1000, 985, 949, 896, 886, 858, 827, 770, 617, 545, 283 complex: 2965 (5), 2875 (5), 1470 (5), 1275 (4), 1160 (4), 1050, 1030 (3), 985, 949, 896, 886, 858, 283, 210, 196, 157, 140

CYP

- $10^{40}I_r$ (g cm²) = 11.0 (reactant and complex)
- $10^{120} I_{A\bar{A}\bar{B}} I_C (g \text{ cm}^2)^3 = 0.3507 \times 10^7 \text{ (reactant)}, 0.1736 \times 10^8 \text{ (complex)}$

 $E_0 = 340.2 \text{ kJ/mol}, I^{\dagger}/I = 1.97$, reaction path degeneracy = 5

VCYP

- frequencies, cm⁻¹
- reactant: 3080 (2), 3000, 2950 (6), 2868 (3), 1642, 1452 (5), 1335 (3), 1245 (5), 1138, 1093, 1020, 1007, 985 (2), 920, 909 (3), 893, 847, 800, 790, 760, 718, 610, 600 (2), 530, 400, 300, 140, 80 complex: 3080 (2), 3000, 2950 (6), 2868 (3), 1642, 1452 (5),
- 1335 (3), 1245 (5), 1138, 1093, 1020, 985 (2), 920, 909 (3), 893,
- 847, 800, 790, 718, 600 (2), 350, 300, 171, 140, 137, 119, 90
- $10^{40}I_r$ (g cm²) = 29.0 (reactant and complex)
- $10^{120}I_{A}I_{B}I_{C}$ (g cm²)³ = 0.3385 × 10⁸ (reactant), 0.1508 × 10⁹ (complex)
- $E_0 = 290.8 \text{ kJ/mol}, I^{\dagger}/I = 1.99$, reaction path degeneracy = 2

CYH

- frequencies, cm⁻¹ reactant: 2900 (12), 1449 (6), 1357 (6), 1262 (3), 1155 (3), 1060 (2), 1057, 1027 (2), 903 (2), 863, 802 (2), 782 (2), 523 (2), 426, 383, 248 (2)
 - complex: 2900 (12), 1449 (6), 1357 (6), 1262 (3), 1155 (3), 1060 (2), 1057, 1027, 903 (2), 863, 802 (2), 523, 426, 383, 248, 195 (2), 130, 60
- $10^{120} I_A I_B I_C (g \text{ cm}^2)^3 = 0.2398 \times 10^8 (\text{reactant}), 0.8240 \times 10^8 (\text{complex})$
- $E_0 = 347.3 \text{ kJ/mol}, I^{\dagger}/I = 1.25$, reaction path degeneracy = 6

VCYH

- frequencies, cm⁻¹ reactant: 3080 (2), 3000, 2898 (11), 1642, 1442 (6), 1358 (5), 1275 (5), 1157 (2), 1060 (2), 1027 (2), 985 (2), 950, 920, 909 (2), 863, 802 (2), 782 (2), 700, 629 (2), 450, 400 (2), 300 (3), 190 (2), 90
- complex: 3080 (2), 3000, 2898 (11), 1642, 1442 (6), 1358 (5), 1275 (5), 1157 (2), 1060 (2), 1027, 985 (2), 950, 920, 909 (2), 863, 802 (2), 782, 700, 629 (2), 400, 300, 189 (2), 108, 96, 46
- $10^{120}I_A I_B I_C (g \text{ cm}^2)^3 = 0.2184 \times 10^9 \text{ (reactant)}, 0.9647 \times 10^9 \text{ (complex)}$
- $E_0 = 298.3 \text{ kJ/mol}, I^{\dagger}/I = 1.3$, reaction path degeneracy = 2

PEN

frequencies, cm⁻¹ reactant: 3080 (2), 300, 2962 (3), 2880 (4), 1642, 1456 (5), 1379 (3), 1279 (2), 1146 (2), 1053 (2), 991, 920, 912, 868, 800, 766,

- 728, 628, 417, 335, 190, 160, 100, 90
- complex 1, retro-ene: 3080 (2), 3000, 2962 (3), 2880 (4), 2200,
- 1456 (4), 1379 (3), 1279 (2), 1300 (3), 1146, 1000 (4), 991, 912, 766, 728, 628, 500, 425 (2), 400 (2), 100
- complex **2**, C–C fission: 3080 (2), 3000, 2962 (3), 2880 (4), 1642, 1456 (5), 1379 (3), 1279 (2), 1146 (2), 1068, 991, 920, 912, 868, 800, 628, 417, 350, 220, 210, 190, 95, 45
- $10^{120}I_A I_B I_C \text{ (g cm}^2)^3 = 0.6686 \times 10^7 \text{ (reactant)}, 0.1086 \times 10^8$
- (complex 1, retro-ene), 0.4624×10^8 (complex 2, C-C fission)
- $E_0 = 237.1 \text{ kJ/mol}$ (retro-ene), 289.8 kJ/mol (C-C fission)
- $I^{\dagger}/I = 2.21$ (C-C fission), reaction path degeneracy = 3 (retro-ene), 1 (C-C fission)

^a Degeneracies in parentheses.

the experimental data using these new A factors did not lead to any significant change in the shape of the RRKM fitted curves shown in Figures 1-5. The activation energies were found to be on average 7.5 kJ/mol less than the values listed in Table II. This is within the estimated uncertainties and in each case the observed activation energy is still greater than the energy required to form the biradical. Thus both extremes of the biradical mechanism give reasonable answers.

Tsang⁵ observed that in the decomposition of CYP there was a very minor high-energy pathway leading to the formation of cyclopropane plus ethylene with Arrhenius parameters of A_{∞} =

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 $10^{16.3}$ s⁻¹ and $E_{\infty} = 398$ kJ/mol. Under the shock-tube conditions, cyclopropane isomerized to propylene, the same product that arises from the subsequent decomposition of PEN. It would be impossible to detect the cyclopropane pathway with the VLPP technique. Cyclopropane and propylene have almost identical mass spectral cracking patterns and, moreover, RRKM calculations based on the above rate parameters show that this pathway would be too slow to compete under VLPP conditions. It is interesting to note that Tsang⁶ did not observe the analogous reaction in the shock-tube decomposition of CYH.

The decomposition of PEN to propylene and ethylene is the most simple retro-ene reaction. However, reliable kinetic data have been difficult to obtain because the rate of this reaction is slow enough for its temperature of accessibility to be in the range where the bond fission pathway is competitive or dominant and hence under conventional experimental conditions the primary steps become masked by subsequent radical-chain processes. Richard and Back²⁵ avoided these experimental problems by studying the reaction in the ene addition direction and by combining their results with the appropriate thermochemical data they obtained log $(k/s^{-1}) = 12.5 - 240/\theta$ for the retro-ene process. The VLPP results are in accord with this work and also with the shock-tube study by Tsang.⁵ In addition, the rate parameters for the C-C fission pathway are consistent with previous results for allylic bond fission.¹⁹ It is interesting to note that, over the common temperature range (1000-1200 K) of the VLPP and shock-tube studies, the bond fission pathway is dominant in the high-pressure limit whereas the retro-ene pathway is dominant under VLPP conditions. This is a further demonstration that "falloff" can drastically alter the balance between competitive pathways in unimolecular decomposition.^{11,14}

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Appendix

Molecular and Activated Complex Models. Complete vibrational frequency assignments of CYP^{26-28} and CYH^{29} have been reported in the literature. The assignments of VCYP and VCYH were based on those of CYP and CYH, respectively, combined with the terminal olefin frequencies as in alk-1-enes.³⁰ The vibrational frequencies of PEN were based on those of *n*-pentane³¹ and the terminal olefin frequencies.³⁰ The pseudorotation moment of inertia of CYP was taken from Tanner and Weber³² and that of VCYP was estimated from the values for CYP and methylcyclopentane.²⁸ The external moments of inertia were calculated by using normal bond lengths and angles³³ or, in some instances, structural parameters as measured for specific molecules.^{32,34} The calculated molecular entropies at 300 K agree with the experimental values³⁵ or, where these have not been measured, the values estimated by using group additivity data.^{1,36}

A vibrational transition-state model was assumed for ring opening of the cycloalkanes. The appropriate C-C bond stretch was chosen as the reaction coordinate, and this bond was lengthened to 2.5 times the ground-state distance. The frequencies of the four bending modes associated with the fission of this bond were lowered in the activated complex. In the cases of VCYP and VCYH, resonance stiffening was included by increasing the frequencies of the C-C=C bends.

In the C-C fission activated complex for PEN, the C_3-C_4 stretch was taken as the reaction coordinate, the rotational barrier about this bond was reduced to zero, and the frequencies of two methylene rocks, one C-C-C bend, and one C-C-C= bend were lowered from their molecular values. In addition, the torsion about C_2-C_3 was changed to a propylene three-electron torsion¹ in order to account for allyl resonance stiffening. The frequencies of the six-membered ring transition state for retro-ene decomposition were chosen according to the O'Neal-Benson rules.³⁷ Basically the three hindered internal rotations, together with some of the low-frequency bending modes (mainly skeletal) of PEN, were replaced by higher frequency out-of-plane ring bending modes. The hindered internal rotation about C_3-C_4 was taken as the reaction coordinate, and the torsion about C=C was replaced by a three-electron torsion.

The frequency assignments and other parameters for the RRKM calculations are summarized in Table III.

Registry No. CYP, 287-92-3; CYH, 110-82-7; VCYP, 3742-34-5; VCYH, 695-12-5; PEN, 109-67-1.

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