when the ligand atoms are arranged in a nearly collinear fashion, solution structural determinations such as those pertaining to the ligand fluxionality and kinetics, ligation of simple well-defined molecules to biological molecules in solution, etc. It is clear that such structural information involving the distant, normally nonbonding, shells can greatly facilitate either interpretation of the mode of binding of known ligands or identification of the unknown ligands. These applications will be subjects of future publications.

Acknowledgment. I am indebted to Dr. P. A. Lee (Bell Laboratories) for his generous assistance and consultations throughout the course of this work. I am also grateful to Dr. J. Rowe (Bell Laboratories) and Dr. C. J. Powell (NBS) for helpful discussions on electron mean free path. Thanks also go to Dr. B. M. Kincaid, A. Simons, and B. Chambers for their assistance in programming and Drs. J. Miller and S. Lippard for samples of **2** and **3**, respectively. The experimental EXAFS measurements were made at the Stanford Synchrotron Radiation Laboratory with the financial support of the National Science Foundation under Contract DMR 77-27489 in cooperation with the U.S. Department of Energy.

Supplementary Material Available: Tables I–IV contain scattering amplitude and phase functions for carbon and oxygen and the least-squares refined fitting parameters for AB and ABC fits. Figures A and B contain best AB fits and parameter correlations for **1**–**3** (15 pages). Ordering information is given on any current masthead page.

Infrared Multiphoton Photochemistry of Vinylcyclopropane. Variation of Yield and Branching Ratio with Experimental Parameters

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Abstract: The infrared photochemistry of vinylcyclopropane has been comprehensively investigated. Irradiation of vinylcyclopropane at relatively low pressures with the partially focused output of a CO_2 TEA laser leads to a mixture of the C_5 products cyclopentene, cyclopentadiene, 1,4-pentadiene, and *cis*- and *trans*-1,3-pentadiene. The composition of the product mixture as well as the total product yields are a sensitive function of experimental parameters. The effects of bath gas pressure, laser power, laser intensity, laser frequency, and number of pulses have been systematically examined. A simple physical picture of the multiphoton activation and resulting decomposition is developed. RRKM theory is employed to calculate energy-dependent unimolecular reaction rates. The model is quite successful in rationalizing these data, providing good evidence for the qualitative validity of a rate equation description of infrared multiphoton dissociation.

Dissociation of polyatomic molecules induced by multiphoton absorption in the infrared has a number of features that make it an attractive alternative to conventional activation methods for studying unimolecular reactions. It has been demonstrated that activation and dissociation can occur collisionlessly, over a microsecond or shorter timescale, and quite selectively for absorbing components in complex mixtures.[1-5] The general features of the mechanism by which individual molecules absorb the tens of photons required to reach dissociation thresholds are now fairly well understood. Models for this process commonly employ a rate equation approach.[6-9] It is postulated that activation occurs principally by sequential photon absorption. A partially activated molecule at any total internal energy may undergo further activation, deactivation, or chemical reaction with relative rates that are sensitive to reaction conditions. Much of the current interest in fundamental aspects of multiphoton activation comes from attempts to establish limits to the validity of such an approach and the specific form that rate constants of each of the three types should take.

It has been recognized for some time that reactant molecules that may decompose by more than one pathway can provide especially sensitive information relevant to these questions. Nevertheless, the number of studies which have investigated both yields and branching ratios as a function of systematic variation of reaction conditions have been relatively few.[10-15] Furthermore, in several cases one or both reaction pathways have yielded free radicals or other reactive fragments whose subsequent reactions complicate the analysis. We recently reported that multiphoton activation of vinylcyclopropane (vcp) leads to competitive isomerization reactions to four different, stable C_5H_8 products.[16] There

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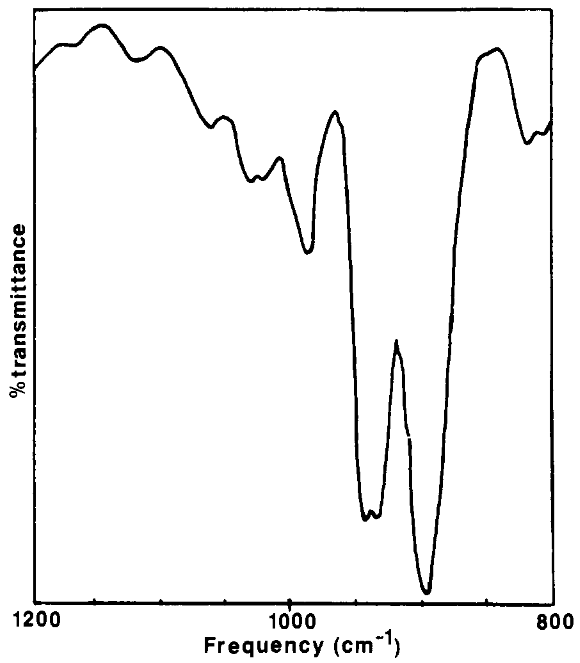


Figure 1. Infrared spectrum of 2.0 torr of vinylcyclopropane from 800–1200 cm^{-1} (Digilabs FTS-20).

are several features of this system that make it an especially attractive one for more thorough investigation.

(1) The laser chemistry is rich but clean and relatively uncomplicated by secondary reactions.

(2) The unimolecular reactions of vcp have been previously studied by using both thermal[17] and chemical activation.[18] Arrhenius parameters for several competitive reaction pathways have been accurately determined. A comparison of chemical results from multiphoton activation with results from these better characterized activation methods can be directly informative in at least a qualitative way.

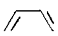
(3) Existing data in the high-energy (chemical activation) and low-energy (thermal activation) regions which bracket the energy regime accessible via multiphoton IR activation can be used to calibrate RRKM calculations on this system. This feature should make model calculations both more reliable and more informative.

We report here a more comprehensive look at the laser-induced chemistry of vcp. Experimental data on frequency, laser power, intensity, and pressure dependence of yields and branching ratio are reported. Model calculations using RRKM theory are employed to draw inferences about ensemble energy distributions in laser-activated vcp samples. Our results provide excellent evidence for the qualitative validity of a rate equation description that uses statistical theory to model chemical reaction rates. They also illustrate the ground rules under which applications of this activation method to studies of unimolecular organic reactions will be constrained to operate.

Results

The vapor-phase infrared spectrum of vinylcyclopropane is shown in Figure 1. In the bulk of the work described below, irradiation has been carried out at 935 cm^{-1} [P(28) 10 μm branch of CO_2 laser] within the profile of the strong absorption band centered at 940 cm^{-1}. This band appears to be associated with a deformation mode of the cyclopropane ring. The position of this band is unaffected by d_2 substitution at the terminal carbon of the vinyl group. In contrast, the bands at 900 and 990 cm^{-1} are strongly shifted to lower frequencies. These are assigned to the $=C(-H)_2$ out-of-plane and trans $(H-)C=C(-H)$ out-of-plane deformations of the vinyl group, respectively. Absorptions occur at similar frequencies (900, 990 cm^{-1}) in vinylcyclopentane and vinylcyclohexane.[19] In the larger cyclic molecules there is *no* comparable band at 940 cm^{-1}. The band at 1025 cm^{-1} is a group frequency characteristic of substituted cyclopropanes.[20] Like the 940-cm^{-1} band its position is unaffected by deuterium substitution on the vinyl group.

Table I. Product Distribution from Vinylcyclopropane Irradiated by CO_2 Laser under Standard Conditions Compared to Thermal and Chemcial Activation

activation method	% product distribution				
	pentadienes				
	1,4	1,3 trans	1,3 cis		
CO_2 laser activation: 250 pulses, 933 cm^{-1} (0.2 torr), 0.5 J/pulse = 2.5 J/cm^2 at front window; 4% N_2, 10% CO_2, and 86% He lasing gas mixture	9	4	4	36	48
chemical activation[a] CH_2: + 	21	28	23	26	2
thermal activation[b] (362.5 °C)	1.6	1.2	1.2	96	

[a] Reference 18. [b] Reference 17.

Table II. Relative Extents of Reaction of Ethyl Acetate/Vinylcyclopropane Mixtures as a Function of Laser Frequency[a]

P_{EtOAc}, torr	P_{vcp}, torr	irradiation freq, cm^{-1}	% EtOAc reacted/ % vcp reacted
0.10	0.10	1047	35 ± 3
0.10	0.10	937	0.03 ± 0.002

[a] 2.5 J/cm^3, "long" pulse (vide infra).

The set of reaction conditions shown in Table I has been chosen as a convenient starting point from which to examine the effect of systematic changes of the various adjustable parameters on product yield and branching ratio. The product distribution observed under these "standard" conditions as well as product distributions from other activation methods are also shown in Table I. The product mixture consists of the acyclic isomers of vinylcyclopropane (1,4-pentadiene and *cis*- and *trans*-1,3-pentadiene), the cyclic isomer (cyclopentene), and the dehydrogenation product, (cyclopentadiene). Presumably H_2 is present in amounts equivalent to cyclopentadiene, but it is not detected under these conditions. Error limits are one standard deviation from the mean of eight independent determinations. The sum of the yields of the five products shown accounts for 98% ± 2% of the vinylcyclopropane.[21] The fraction of the incident laser energy absorbed under these conditions is small (<10%), and no effort has been made to determine it accurately. The comparison among activation methods has been discussed in a previous report.[16]

The total yield and product distribution as a function of the number of laser pulses are shown in parts a and b, respectively, of Figure 2. Over this region the decay of starting material is nicely first order, and, as Figure 2b shows, the product ratio is invariant. All four major products, therefore, are primary products; this is, they are formed as a result of single laser pulses. None of these products shows appreciable reaction when irradiated alone at this frequency and laser power.

The results of cophotolysis experiments of mixtures of vinylcyclopropane and ethyl acetate are shown in Table II. The

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(21) The sum of the integrated areas of product gas chromatography peaks in the irradiated sample compared to nonirradiated standard. Areas are not corrected for differences in detector response.

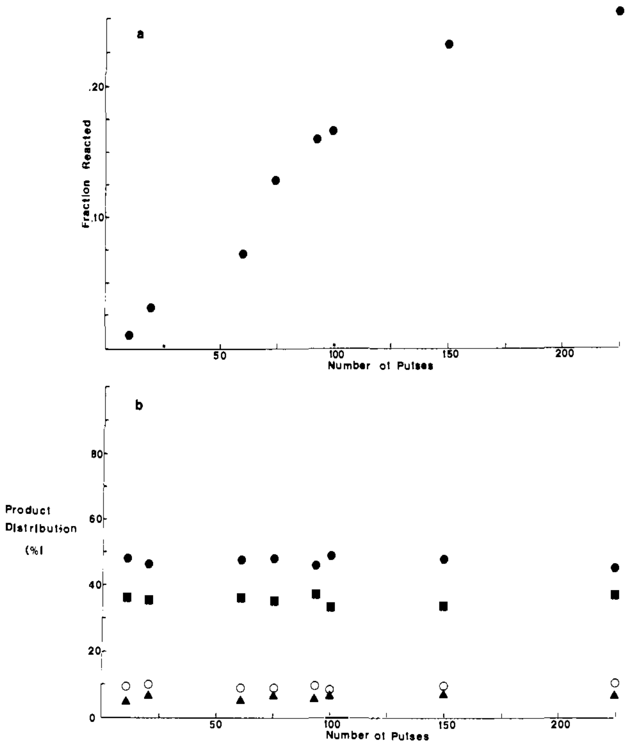


Figure 2. (a) Total product yield vs. number of laser pulses. For standard conditions, see Table I. (b) Product ratio vs. number of laser pulses: ●, cyclopentadiene; ■, cyclopentene; ○, 1,4-pentadiene; ▲, 1,3-pentadiene.

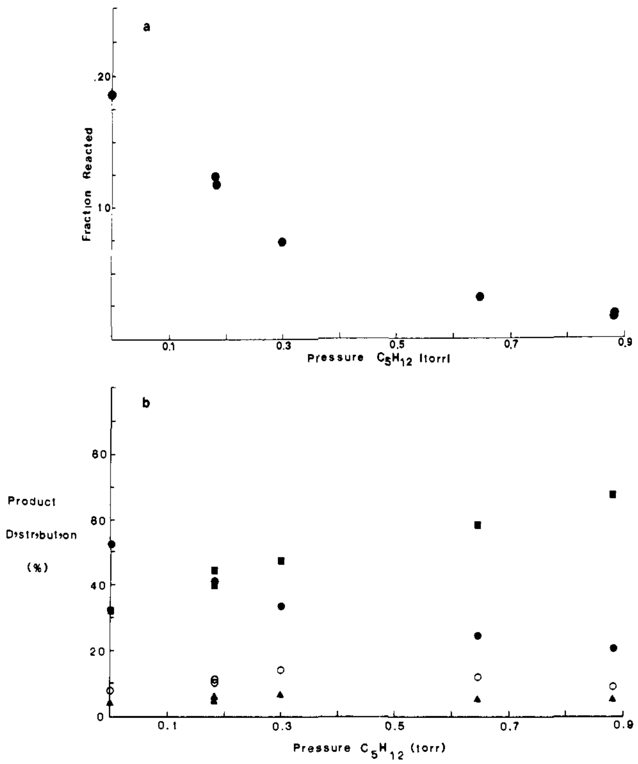
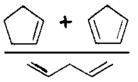
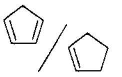


Figure 3. (a) Total product yield after 250 pulses vs. pressure of pentane (bath gas) (3.0 J/cm^2/pulse, 0.2 torr of vcp). (b) Product ratio vs. pressure of pentane. Symbols are as those in Figure 2.

Arrhenius parameters for thermal unimolecular reaction of ethyl acetate are log $k_{\mathrm{uni}} = 12.5 - 47.8/2.3RT$[22] and for vinylcyclopropane log $k_{\mathrm{uni}} = 13.5 - 49.6/2.3RT$.[17] Uniform thermal activation of a mixture of these two compounds would lead to essentially equivalent extents of reaction at any temperature. As shown in Table II, the relative extent of reaction under laser activation conditions is strongly dependent on the irradiation frequency. At each frequency decomposition of the absorbing molecule predominates. Ethyl acetate absorbs strongly at 1047 cm^{-1} and decomposes to CH_3COOH and ethylene.[23] Both the frequency dependence of the selectivity of reaction and the magnitude of selectivity at either frequency make it clear that most chemical reaction precedes energy equilibration with the bath. Together the results of Figure 2 and Table II demonstrate that product ratios analyzed after 250 pulses represent the sum of 250 essentially equivalent one-pulse experiments. Each of these one-pulse experiments may be best described as a homogeneous, multiphoton-activated, unimolecular reaction. The single pulse yield under these conditions is approximately 1% of the vinylcyclopropane molecules within the irradiated volume.

Figures 3–5 and Table II illustrate how yields and product ratios change with the following experimental parameters: (i) bath gas (pentane) pressure (Figure 3a,b); (ii) energy per pulse (Figure 4a,b); (iii) laser frequency (Figure 5a,b); (iv) laser intensity (Table III). Energy per pulse is changed by varying the power supply voltage or by attenuation with a preabsorbing cell of 1,1,1-trifluoroethanol. Laser intensity is varied by changing the gas composition in the laser. Short-pulse conditions are 13% CO_2 and 87% He (single spike ~150-ns fwhm). Long-pulse conditions are 10% CO_2, 4% N_2, and 86% He (spike + tail to 1 μs). In each case the product ratio is plotted as percent of the total product mixture. Subsequent discussion will focus on three aspects of this data: (1) the total yield, (2) the ratio of (cyclopentene + cyclopentadiene) to 1,4-pentadiene, henceforth referred to as the branching ratio, and (3) the ratio of cyclopentadiene to cyclopentene, which will be called the successive reaction ratio.

Table III. Yields and Product Distributions from Vinylcyclopropane Irradiation High[a] and Low[b] Laser Intensity

irradiation condns		yield/ 500 pulses	
0.2 torr, 0.86 J/cm^2, short pulse	7.70 ± 0.15	0.258 ± 0.006	1.07 ± 0.05
0.2 torr, 0.86 J/cm^2, long pulse	8.09 ± 0.15	0.122 ± 0.008	0.75 ± 0.05

[a] Short pulse, 87% He and 13% CO_2. [b] Long pulse, 86% He, 10% CO_2 and 4% N_2.

Discussion

A potential energy profile for the ground-state reactions of vinylcyclopropane is shown in Figure 6. The pathways to the 1,3-pentadienes have been omitted for simplification. The heats of formation of 1,4-pentadiene, vinylcyclopropane, and cyclopentadiene were calculated by the group additivity method.[24] The barrier heights were obtained from known Arrhenius parameters for thermal activation of each of the three relevant reactions. A simplified model for the dynamics of the infrared multiphoton-activated reaction is indicated by the arrows above the surface. Up arrows represent photon absorption or activation steps, down arrows deactivation steps, and horizontal arrows chemical reaction. The multiphoton process involves sequential absorption of 10.6 micron photons until dissociation intervenes. At each step along the way further activation k_u, deactivation k_d, and—above threshold—unimolecular reaction k_1 or k_2 compete. The yields, branching ratios, and successive reaction ratios will be discussed below in terms of these relative rates. Inferences will be drawn from this data about the approximate magnitudes of $k_u(E)$, $k_d(E)$,

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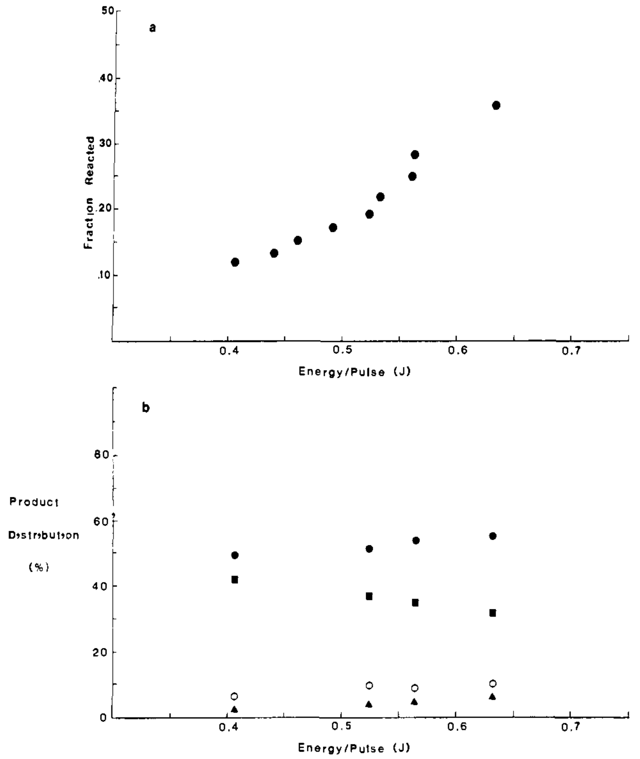

Figure 4. (a) Total product yield after 250 pulses vs. energy per pulse. Standard conditions, see Table I. (b) Product ratio vs. energy per pulse. Symbols are as those in Figure 2.

and $k_r(E)$ and what experimental parameters influence those magnitudes.

At any energy, E, above threshold, the branching ratio may be defined as the ratio of unimolecular rate constants for the competing decay channels (i.e., $B = k_1(E)/k_2(E)$, Figure 6). The experimentally observed branching ratio β is a summation over all populated energies above threshold, $\beta = \sum_{E=n_0h\nu}^{nh\nu} N(E)k_1(E)/k_2(E)$. The grain size of the summation is the photon energy $h\nu$. $N(E)$ is the number of molecules reacting at E, (not the number reaching that level). n_0 is the number of photons of frequency ν required to reach threshold. n is an upper limit to the number of photons absorbed above which the reacting population $N(E)$ becomes insignificant. If it is assumed that statistical unimolecular rate theory can be applied to multiphoton-activated molecules, as most studies have concluded,[25] then $k_1(E)/k_2(E)$ as a function of E may be calculated. The best fit to β for any assumed population distribution function $N(E)$ may then be determined. For example, with the assumption that $N(E)$ is a delta function (all molecules react at an equivalent total energy), the best fit to the observed branching ratio under "standard" conditions using RRKM theory gives $\bar{E} = 72$ kcal/mol or approximately eight photons in excess of the decomposition threshold (Figure 7). It has been suggested that reactions occur from an ensemble energy distribution that may be described by a uniform vibrational temperature,[26] $N(E) \alpha \rho(E)e^{-E/kT}(k_1(E) + k_2(E))/(k_1(E) + k_2(E) + k_{\text{collision}})$ where $\rho(E)$ is the vibrational state density at energy E.[27] The best fit to this assumed energy distribution yields $T_{\text{vib}} \cong 1350$ K (Figure 8). These descriptions of the extent of activation in vinylcyclopropane decomposition, $\bar{E}$ or T_{vib}, are similar to those obtained in other systems.[1]

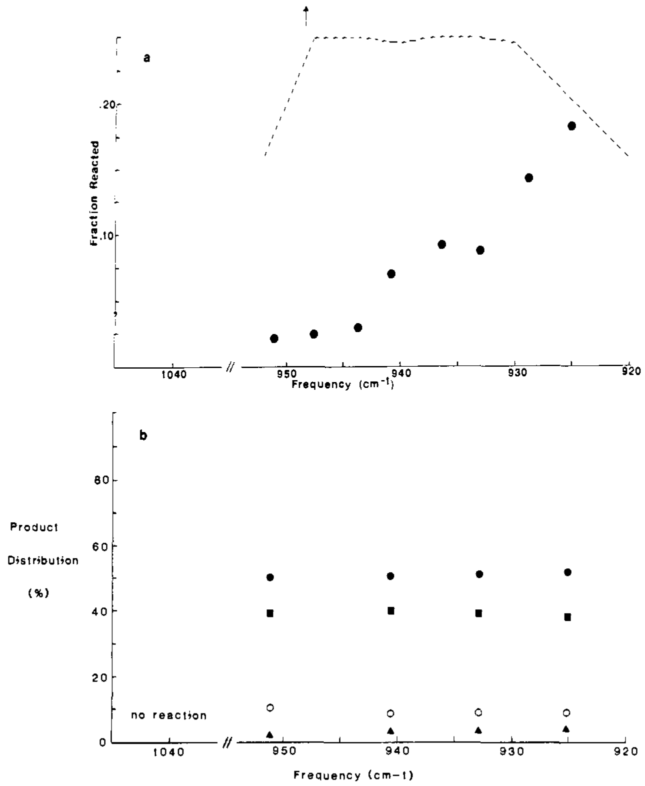

Figure 5. (a) Total product yield after 100 pulses vs. irradiation frequency. Dotted line represents relative absorbance for single photon absorption. Absorbance increases in the direction shown by the arrow. For standard conditions, see Table I. (b) Product ratio vs. irradiation frequency. Symbols are as those in Figure 2.

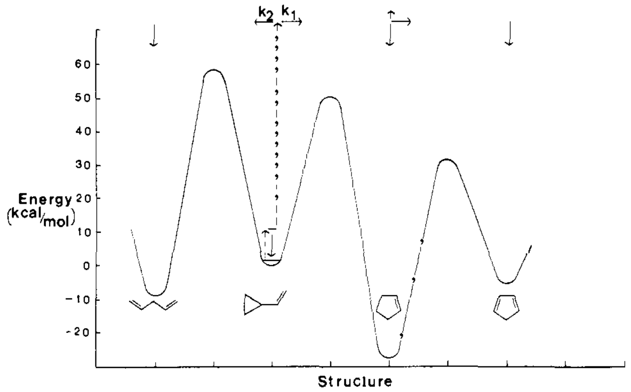

Figure 6. Potential energy diagram for vinylcyclopropane, 1,4-pentadiene, cyclopentene, and cyclopentadiene + H_2.

It is important to note that $\bar{E}$ and/or T_{vib} are phenomenological descriptions of the energy distribution only. The best fit to any functional form for $N(E)$ could be determined equivalently. The delta or Boltzman distributions are two easily visualized, convenient functions. In fact, the energy distribution among reacting molecules is determined by dynamic competition among up, down, and over rate constants at each energy level and cannot be extracted unambiguously from experiments of this kind. Nevertheless, interpretation of product ratios in terms of one of these simplified energy distributions leads to considerable insight into the major effects of experimental parameters on up, down, and over rate constants and the amount of control the experimentalist can expect to be able to exert over the ultimate chemical result of IR multiphoton activation experiments.

The ratio of cyclopentadiene to cyclopentene (the successive reaction ratio) can be understood in this way. The isomerization of vinylcyclopropane to cyclopentene is exothermic by 27 kcal/mol. Therefore, the nascent cyclopentene at the instant of its formation contains approximately 99 kcal/mol of internal energy in excess

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[27] $(k_1(E) + k_2(E))/(k_1(E) + k_2(E) + k_{\text{collison}})$ is a weighting factor that recognizes that at these pressures, not all activated reactants decompose. $k_{\text{collision}}$ represents the collisional deactivation rate. Strong collisions are assumed. The distribution is truncated at $E = 100$ kcal/mol.

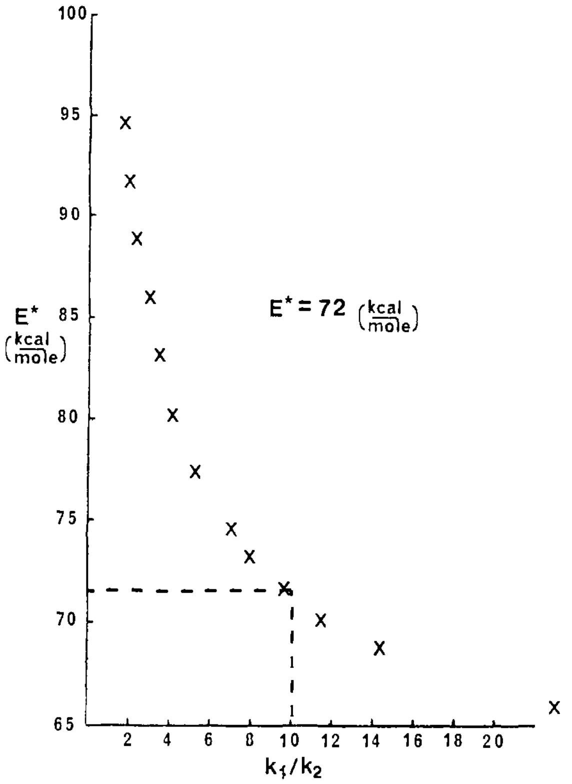

Figure 7. Total accumulated energy vs. RRKM calculated ratio of unimolecular rate constants k_1 (vcp → cyclopentane)/k_2 (vcp → 1,4-pentadiene).

of its ground state. (Figure 6, $\bar{E}$ (72 kcal/mol) + ΔH (27 kcal/mol)). This is more than sufficient to overcome the 59 kcal/mol barrier to dehydrogenation.[28] Unimolecular reaction of "hot" cyclopentene will then compete with collisional deactivation yielding both the primary product cyclopentene and a secondary product cyclopentadiene during single laser pulses.

Again, RRKM theory may be employed to model this unimolecular process. The calculated rate constant for the cyclopentene → cyclopentadiene reaction at this total energy is $9.1 \times 10^5\ \mathrm{s}^{-1}$. The collision rate constant at this pressure is approximately $2.4 \times 10^6\ \mathrm{s}^{-1}$. Therefore, assuming every collision renders the "hot" cyclopentene unreactive (strong collision assumption), one expects a successive reaction ratio of ~0.38. The observed value is ~1.4. It is not surprising that the calculated value is low. It is well-established that the strong collision assumption is not valid even for large collision partners.[29] If a stepwise deactivation model with 6-kcal/mol stepsize increments is employed instead,[30] the calculated ratio increases to 0.49. Using the vibrational temperature model for reacting vinylcyclopropane and following the level populations in the cyclopentene produced combined with the 6-kcal/mol stepsize increments for deactivation give a successive reaction ratio of 0.72. The continuing high value of the observed ratio may imply that some amount of absorption by the "hot" cyclopentene occurs over the tail of the laser pulse during which it was formed. The extent of such activation required to fit the experimental data is relatively small. Absorption of one photon on average will boost the calculated ratios by the factor of 2 required to reproduce the experimental value of 1.4.

Changes in yield and product distribution with experimental conditions serve to illustrate the degree of experimental control that can be exerted over the rates of up and down transitions. Increasing bath gas pressure causes sharp decreases in yield and successive reaction ratio without substantially changing the branching ratio. This observation appears not to be unique to our system or conditions.[31,32] It is tempting to think about the yield change in terms of a decrease in the effective temperature or average energy of a steady-state distribution of reactant molecules as pressure increases. The constant branching ratio, however, seems inconsistent with this analysis. A change of an order of magnitude in the yields resulting from lower average energy of decomposing molecules should be accompanied by a change of about a factor of 2 in the branching ratio in favor of the lower threshold pathway.

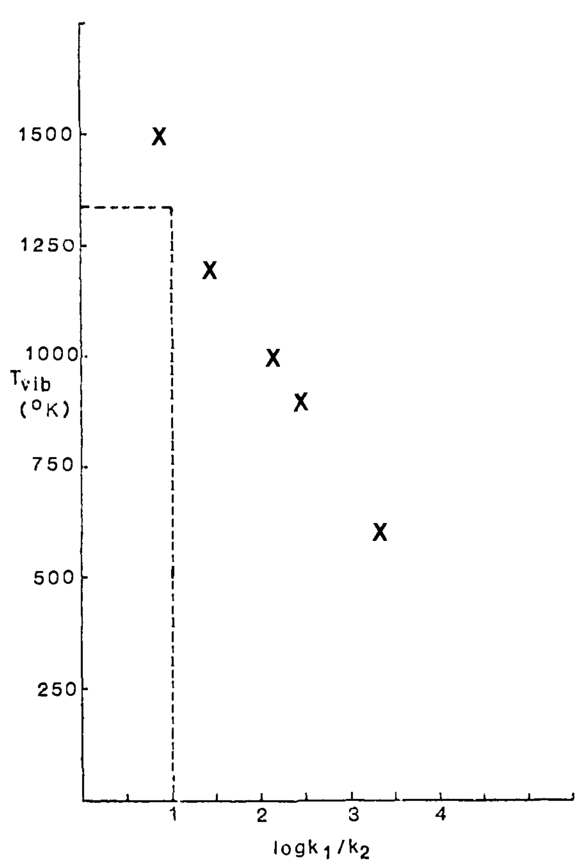

Figure 8. Effective vibrational temperature vs. log of RRKM calculated ratio of unimolecular rate constants k_1 (vcp → cyclopentane)/k_2 (vcp → 1,4-pentadiene).

It is possible that a substantial amount of reaction may be occurring after the laser pulse. Such a situation would be analogous to chemical activation, in which a distribution of activated molecules prepared by an exothermic reaction either decomposes to product or is collisionally stabilized. In fact, in the decomposition of chemically activated vinylcyclopropane prepared by addition of methylene to butadiene, pressure increases sufficient to alter the yield of products by an order of magnitude seem to have little influence on the branching ratio.[33] The analogy between chemical activation pressure dependence and that observed here may be misleading, however, since it implicitly requires that the energy distribution among the ensemble of reactant molecules present at the end of the laser pulse be pressure independent.

A simplified, but qualitatively attractive, mechanism that can accommodate these data would be as follows. The slow step in the activation process occurs at relatively low energies. It may be the result of a bottleneck to accessing the quasi-continuum as

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(33) See ref 18.

has often been suggested.[34] Once the bottleneck has been crossed, further activation to levels above threshold is rapid. Yields decrease because the steady-state population of partially activated molecules waiting to cross the bottleneck is diminished. Branching ratios are unaffected, however, because the pumping rate in the threshold region is still much faster than collisions.[35] The successive reaction ratio falls as expected, since the collisional deactivation rate has been changed without changing the (energy-dependent) unimolecular decomposition rate of "hot" cyclopentene. Figure 5a shows that the total yield maximizes at frequencies at least 10 cm^{-1} to the low-energy side of the single photon absorption maximum. This observation has been made in a number of other systems and has been offered as evidence for a low energy bottleneck.[36] Figure 5b demonstrates that yield changes over this frequency range are not accompanied by any substantial change in the product distribution.

There has been considerable discussion about the comparative importance of fluence and intensity effects in multiphoton activation.[37] Figure 4 and Table III show that substantial changes in both yield and product distribution accompany changes in either laser intensity or fluence. At higher intensity or higher fluence the yields increase and the product distribution changes in favor of the acyclic isomers and cyclopentadiene at the expense of cyclopentene. Thus, the branching ratio undergoes a modest shift in favor of the higher threshold pathway. The successive reaction ratio, which is more sensitive to changes in $\bar{E}$ since $k(E)$ is being probed directly rather than a ratio of $k_1(E)/k_2(E)$, shows larger changes. The direction of change implies greater average energies at either high intensity or increased fluence. These results quite clearly demonstrate that laser intensity has a significant influence on the amount of energy reacting molecules may acquire. As was the case in the bath gas experiments, yield increases and product distribution changes cannot be simultaneously explained on the basis of a single energy distribution function for the entire irradiated sample whose average value changes in response to some parameter change. A bimodal distribution provides a more satisfactory model. A change in instantaneous laser intensity brought on by either shortening the pulse or increasing the energy has two effects. It alters the relative populations below and above the bottleneck, and it modifies the average energy of the excited population.

Experimental Section

The radiation source for these experiments was a grating-tuned Lumonics TEA CO_2 laser operated at 0.5 Hz. The beam was focused with a 15-in. ZnSe lens, and the cell was centered 5 cm beyond the focal point. Typical output was approximately 0.5 J/pulse, leading to a fluence of $\sim$2.5 J/cm^2 at the front window of the cell. Standard photolysis conditions are described in Table I. Laser power was monitored with a Scientech (Model 38-0102) volume-absorbing calorimeter. The temporal profile of the laser pulse was monitored with a Laser Precision kT-1510, pyroelectric detector. An Optical Engineering 16A spectrum analyzer was used to determine the laser frequency.

Reactions were carried out in cylindrical Pyrex cells 5 cm × 2 cm (i.d.) fitted with polished KCl or NaCl windows. The cell was filled to known pressures of materials ranging from 0.02 to 10 torr on a vacuum line equipped with an MKS-Baratron 220 capacitance manometer. Following irradiation, analysis was carried out by gas chromatography (10% β,-β'-oxydipropionitrite on Chromasorb G, 20 ft, 30 mL/min) or GC mass spectroscopy, in both cases by direct gas injection. Vinyl cyclopropane was prepared by the method of Kirmse et al. and purified by preparative gas chromatography prior to use.[38]

Energy-dependent unimolecular rate constants were calculated from the RRKM expression $k(E) = L^{\ddagger}\ (Q_1{}^{+}/Q_1)\ (\sum P(E^{+}{}_{vr})/hN^{*}(E^{*}))$.[39] Sums and densities of states were obtained by the direct count method of Stein and Rabinovitch.[40] Parameters for the calculations are shown below. They are essentially the same as those of ref 18. Activated complex frequencies were chosen to fit thermal A factors by a suitable modification of reactant or product frequencies. Relative rates of the competitive decomposition pathways calculated in this manner are in excellent agreement with experimental chemical activation and thermal activation data at the appropriate energies. vcp → cyclopentene: $E_0 = 16\,850\ cm^{-1}$; vcp frequencies (cm^{-1}) 3050 (8), 1625, 1425 (3), 1300 (2), 1050 (2), 1000 (8), 900, 800 (2), 700 (2), 425, 310 (2), internal rotor $I_r = 4.5$ amu Å^2/molecule; activated complex frequencies (cm^{-1}) 3050 (8), 1425 (3), 1300 (4), 1050 (2), 1000 (6), 900, 800 (2), 700 (2), 675, 225, 112 (2) vcp → 1,4 pentadiene: $E_0 = 19\,050\ cm^{-1}$; activated complex frequencies (cm^{-1}) 3050 (8), 1425 (3), 1300 (4), 1050, 1000 (4), 900, 800 (2), 700 (2), 500, 340 (2), 310 (2), 258, 100. cyclopentene → cyclopentadiene + H_2: $E_0 = 20\,171\ cm^{-1}$; cyclopentene frequencies[41] (cm^{-1}) 3000 (8), 1600, 1425 (4), 1300 (3), 1200 (4), 1050 (3), 950 (2), 900 (2), 800, 700, 650, 600, 400, 200, activated complex frequencies (cm^{-1}) 3000 (6), 1600 (4), 1425 (4), 1300 (4), 1200 (4), 1050 (3), 950 (2), 900 (1), 800 (2), 650, 600 (2).

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(34) Reference 1, p 381 and references therein.

(35) Rough estimates of these unimolecular rate constants may be made as follows: $k_{up} = \sigma I/h\omega \sim 2 \times 10^7\ s^{-1}$ where σ is the absorption crosssection for the 0–1 transition at 940 cm^{-1}, I is the laser intensity, and $h\omega$ is the photon energy. $k_{down} \sim k_{collision} \sim 2 \times 10^6\ s^{-1}$ and $k_{reaction}(E) = \sum$RRKM rate constants at 72 kcal/mol for vpc → cyclopentene, 1,4-pentadiene, and *cis*- and *trans*-1,3-pentadiene $\sim 1.3 \times 10^6\ s^{-1}$.

(36) Reference 2 and references therein.

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