AIP | The Journal of Chemical Physics

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Citation: The Journal of Chemical Physics **79**, 1312 (1983); doi: 10.1063/1.445885
View online: http://dx.doi.org/10.1063/1.445885
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/79/3?ver=pdfcov
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High vibrational overtone photochemistry of cyclobutene

Joseph M. Jasinski,[a] Joan K. Frisoli, and C. Bradley Moore

Department of Chemistry, University of California, and Materials and Molecular Research Division of the Lawrence Berkeley Laboratory, Berkeley, California 94720

(Received 17 January 1983; accepted 21 April 1983)

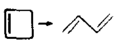
Direct single-photon excitation of high CH stretching overtone transitions has been used to induce the isomerization of cyclobutene to 1,3-butadiene. Values of the unimolecular isomerization rate constant $k(E)$ have been measured as a function of energy and overtone transition by studying the pressure dependence of the photoisomerization rate constant. The values of $k(E)$ depend on the total energy and do not show any observable dependence on the type of CH overtone transition excited. The values of $k(E)$ are in reasonable quantitative agreement with RRKM calculations.

INTRODUCTION

An important goal in understanding the unimolecular dynamics of highly vibrationally excited polyatomic molecules is to measure unimolecular reaction rate coefficients as a function of internal energy and site of initial excitation. Such studies have traditionally been carried out using chemical activation or electronic excitation followed by rapid internal conversion to prepare vibrationally excited reactants.[1] Recently it has become feasible to optically prepare vibrationally excited polyatomic molecules in the ground electronic state by exciting high overtone transitions of X–H stretching motions, where X is typically carbon, oxygen, or nitrogen.[2–4] The fact that this form of single-photon excitation can prepare molecules with a well defined total internal energy, combined with the possibility that the initial vibrational energy distribution may be significantly nonrandom has added a new dimension to the study of unimolecular reaction dynamics and the related questions of intramolecular vibrational relaxation and mode selective chemistry.

Thus far, kinetic studies of four reactions induced by overtone excitation have appeared. Berry and Reddy have used steady-state photolysis and Stern–Volmer analysis to measure the unimolecular rate coefficient as a function of energy $k(E)$ for the isomerization of methyl isocyanide[2,3] and allyl isocyanide.[4] Crim and co-workers have employed time-resolved techniques to measure $k(E)$ for the decomposition of tetramethyldioxetane[5,6] and *t*-butylhydroperoxide.[7] Zare and co-workers[8] have also studied *t*-butylhydroperoxide using steady-state photolysis. The results of most of these studies are in reasonable agreement with statistical unimolecular rate theories such as RRKM theory[1(d)] which assumes that energy randomization is rapid and complete prior to unimolecular reaction. Two exceptions have been noted. Zare and co-workers[8] present evidence that a small fraction of *t*-butylhydroperoxide molecules activated by excitation of the OH stretching overtone decompose prior to complete energy randomization and suggest a lower bound of $5.0\times10^{11}\ \mathrm{s}^{-1}$ for the rate of energy randomization. More remarkably, Berry and Reddy note[4] that allyl isocyanide exhibits small discrepancies from the predicted monotonic increase of $k(E)$ with E. They have attributed these discrepancies to a dependence of the rate coefficient on the particular type of C–H overtone transition excited. They have thus suggested that overtone excitation of allyl isocyanide produces a nonrandom initial energy distribution which persists and affects the observed reaction rate on a microsecond time scale. Since virtually all other experimental evidence implies that energy randomization in vibrationally excited medium size polyatomic molecules is complete on a much faster time scale,[1(b),1(c),9,10] these results are quite intriguing.

This paper describes studies of the overtone-induced isomerization of cyclobutene to 1, 3-butadiene Eq. (1). The reaction



(1)

is a prototypical example of a concerted electrocyclic ring opening as defined by Woodward and Hoffmann.[11] The reaction coordinate is very likely a simultaneous breaking of the carbon–carbon bond connecting the methylenic carbons and a rotation of the methylene groups to establish the π-electron system of the butadiene.[11,12]

There are a number of reasons for choosing to study cyclobutene. It is a small, structurally simple hydrocarbon with a completely assigned vibrational spectrum.[13] Its thermal isomerization to butadiene is clean and well studied. Reliable Arrhenius parameters for the thermal reactions are available[14] as are model RRKM calculations.[12,15] It has two distinctly different types of CH bonds which are expected to have well separated overtone transitions[16] and which may exhibit different coupling to the reaction coordinate.

Finally, many substituted cyclobutenes are known and have been studied thermally,[17] thus providing a large family of molecules with different structures, state densities, and C–H bond types which can be explored once the overtone photochemistry of the parent molecule is understood.

Values of $k(E)$ have been measured for reaction (1) for excitation of the methylenic and olefinic CH stretching overtones at $v=5$ and $v=6$ by measuring the pressure dependence of the phenomenological rate coefficient under steady state conditions. The results are in good agreement with expectations based on the as-

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[a] Present address: IBM, Thomas J. Watson Research Center, Yorktown Heights, New York, 10598.

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sumption of rapid and complete energy randomization prior to reaction over a pressure range of 1–700 Torr.

EXPERIMENTAL

General: Cyclobutene was prepared by the method of Cope *et al.*[18] and was purified by preparative gas chromatography followed by drying over 5 Å molecular sieves to remove trace quantities of water. The cyclobutene prepared in this manner was identified by its infrared spectrum which was identical to the published spectrum.[19]

All gas chromatography was performed on a Varian model 3700 gc. Preparative work employed a 3 ft ×1/4 in. stainless steel column packed with picric acid on Graphpac (Alltech) and a thermal conductivity detector. Analytical work employed a 5 ft×1/8 in. stainless steel column packed with picric acid on Graphpac and a flame ionization detector. Peak areas were determined using a Hewlett–Packard model 3390A reporting integrator.

All sample handling was done on a standard glass, grease, and mercury vacuum line. Cyclobutene was degassed by freeze–pump–thaw cycles. Pressure was measured with Validyne variable reluctance manometers. Interchangeable diaphragms were used to cover the pressure ranges 0–5, 0–50, 0–200, and 0–700 Torr with an estimated uncertainty of less than ± 5%.

The laser system used in both spectroscopic and photoisomerization studies was a Spectra Physics model 375 dye laser pumped by a Spectra Physics model UV-171-17 argon ion laser. The dye laser was tuned with a three-plate birefringent filter and had a nominal bandwidth of 1 cm^{-1}. Wavelength calibration of the dye laser was performed with a grating monochromator (Spex model 1700-II). Estimated uncertainty in wavelength calibration of the photoacoustic spectra is ± 5 cm^{-1}. All wavelength values are reported as vacuum wave numbers. The $v=6$ spectral region was covered using Rhodamine 6G, while the $v=5$ spectral region was covered using a mixture[20] of DCM and LD-700. Standard dye laser optics were used except for the output couplers which were coated (CVI Laser Corp.) to have less than 1% transmittance over the tuning range of a given dye. The dye laser output power was monitored with a Scientech model 36-0001 power meter.

High overtone spectra of cyclobutene were obtained using an intracavity dye laser photoacoustic spectrometer which has been described previously in detail.[16] Spectra were recorded at a total pressure of 50 Torr. No corrections to the spectra have been made for the photoacoustic background due to cell window absorption.

Absolute absorption cross sections for cyclobutene at $v=6$ were obtained from a spectrum of a 50/50 mixture of cyclobutene and methane recorded at a total pressure of 86 Torr. A value[21] of 2.23×10^{-25} cm^2 was used for the peak methane absorption cross section at 16 150 cm^{-1}.

Photoisomerization experiments were performed using a quartz and Pyrex photolysis cell to which quartz Brewster angle windows were affixed with glass transfer tape. The cell was fitted with Teflon stopcocks and was designed so that its contents could be directly injected into the gc by flushing with He carrier gas. The cell had a volume of 3.1 cm^3 and a length of 9.4 cm. Clean windows were essential for reproducible results. The cell windows were periodically cleaned by flaming in O_2 with a torch and were replaced several times during the course of the work.

In a typical experiment the cell was filled to a known pressure of cyclobutene and was placed inside the cavity of the dye laser. Dye laser alignment was then reoptimized as quickly as possible, primarily by adjusting the position of the output coupler. The dye laser output power was monitored continuously using the power meter and a strip chart recorder. The laser wavelength was checked and adjusted periodically during the course of a photolysis.

SPECTROSCOPY

The fourth and fifth CH overtone spectra of cyclobutene are presented in Fig. 1. Each spectrum consists of two well separated bands. High overtone spectra of XH containing molecules have generally been analyzed in terms of a local mode model which considers the XH bonds as a set of uncoupled anharmonic oscillators.[16,22,23] Thus, spectroscopic transitions are assigned as $0-v$ excitation of individual XH oscillators, where v is the vibrational quantum number of the oscillator. Such a picture has proven useful in explaining band positions, intensities, and isotopic substitution effects in high overtone spectra. This suggests that

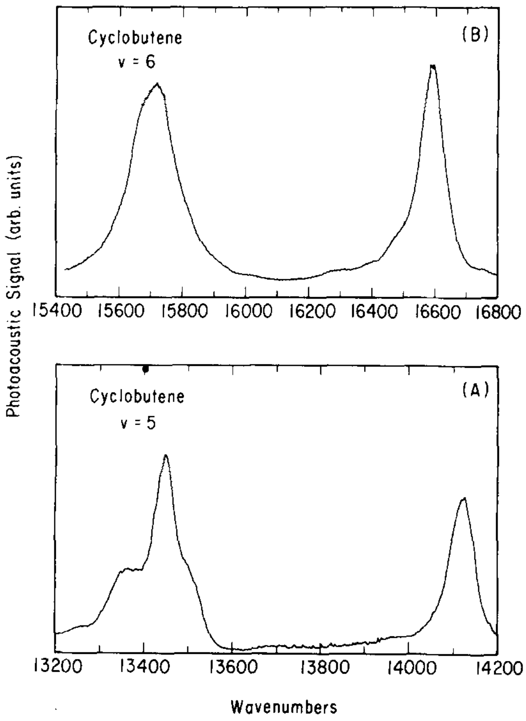

FIG. 1. (A) Fourth and (B) fifth CH overtone spectra of cyclobutene.

the concept of an XH local mode has some utility at least as a zero order spectroscopic state.

Within the context of the local mode model, the lower energy transition in each spectrum in Fig. 1 is assigned to the $0-v$ overtone of the methylenic CH stretch while the higher energy transition is assigned to the $0-v$ overtone of the olefinic CH stretch. This assignment is consistent with the IR spectrum of cyclobutene[13(a)] which shows normal mode fundamentals involving mainly olefinic CH stretching at 100–200 cm^{-1} higher energy than those for methylenic stretching. The assignment is also consistent with overtone spectral assignments for many other simple hydrocarbons which show the general trend that the overtone transition energies follow the same relative ordering as the fundamentals, with methylenic < methyl < olefinic.[16]

The peak absorption cross sections at $v=6$, based on calibration of the cyclobutene photoacoustic spectrum with methane, are $2.5\times10^{-25}\ \mathrm{cm}^2$ for the methylenic peak and $2.9\times10^{-25}\ \mathrm{cm}^2$ for the olefinic peak. The integrated absorption cross sections per C–H bond are $1.4\times10^{-23}\ \mathrm{cm}^2\,\mathrm{cm}^{-1}\,\mathrm{molecule}^{-1}$ for the methylenic peak and $2.0\times10^{-23}\ \mathrm{cm}^2\,\mathrm{cm}^{-1}\,\mathrm{molecule}^{-1}$ for the olefinic peak.

The shoulder to the low energy side of the $v=5$ methylenic transition has not been unambiguously assigned. Based on its position in the $v=5$ spectrum and its apparent disappearance at $v=6$, and assuming that this disappearance is due to complete overlap with the $v=6$ local mode transition, a possible assignment is as a combination band involving one less quantum of C–H stretch plus two quanta of an 1100 cm^{-1} vibration.[16(d)] Possible candidates are CH_2 twisting and ring breathing modes which appear at around 1100 cm^{-1} in the IR spectrum of cyclobutene.[13]

PHOTOISOMERIZATION KINETICS

Reddy and Berry have shown[2,3] that, under the asumption of a simple steady-state photoactivation and reaction mechanism

$$A \underset{k_s[M]}{\overset{k_a[\hbar\omega]}{\rightleftarrows}} A^* , \tag{2}$$

$$A^* \xrightarrow{k(E)} \text{product} , \tag{3}$$

the overall loss of reactant A follows the rate law:

$$-\frac{d[A]}{dt} = k[\hbar\omega][A] , \tag{4}$$

with the rate constant k given by

$$k = \frac{k_a k(E)}{k(E) + k_s[M]} . \tag{5}$$

In Eqs. (2)–(5), k_a is the rate constant for photon absorption ($k_a = \sigma c$, where σ is the absorption cross section and c is the speed of light), k_s is the rate constant for collisional deactivation of excited reactant molecules A^*, $[M]$ is the number density of the bath gas, $k(E)$ is the rate constant for conversion of A^* to product when A^* contains total internal energy E, and $[\hbar\omega]$ is the effective concentration of photons in the cell, given[3] by

$$[\hbar\omega] = (5.04\times10^{14}\,\lambda P Q)/cA_{\mathrm{eff}} . \tag{6}$$

In Eq. (6), λ is the photon wavelength in Å, P is the laser output power in W, Q is the ratio of the circulating intracavity laser power to the laser output power, c is the speed of light, and A_{eff} is the effective cross sectional area of the cell, defined as the cell volume divided by the cell length.

Inversion of Eq. (5) gives

$$k^{-1} = k_a^{-1} + \frac{k_s[M]}{k_a k(E)} . \tag{7}$$

Therefore, a plot of k^{-1} vs pressure (Stern–Volmer plot) should be linear with intercept k_a^{-1} and slope $k_s/k_a k(E)$. Once these quantities are known, the data can be further reduced by recognizing that k_a/k is just the inverse of the photochemical quantum yield

$$k_a/k = \frac{k_s[M] + k(E)}{k(E)} = \frac{1}{\text{quantum yield}} . \tag{8}$$

A plot of k_a/k vs pressure has slope $k_s/k(E)$ from which $k(E)$ may be extracted provided k_s can be measured or calculated. Implicit in writing Eq. (8) is the assumption that the quantum yield is one at zero pressure.

From solution of rate law (4), k is given phenomenologically by

$$k = \frac{-\ln(A/A_0)}{[\hbar\omega]t} , \tag{9}$$

where A_0 is the concentration of reactant at $t=0$ and A is the concentration of reactant at time t. Experimentally, A/A_0 is determined from the ratio of the areas of the gc peaks for butadiene and cyclobutene. The quantity $[\hbar\omega]t$ is determined by integrating the strip chart record of the laser output power with a planimeter.

The activation energy for the thermal isomerization of cyclobutene[14(c)] to butadiene is 32.9 kcal mol^{-1} (11 500 cm^{-1}). Thus, the critical energy for isomerization is well below the available energy when cyclobutene is activated by overtone absorption using any of the overtone transitions shown in Fig. 1. The only observed photoproduct when cyclobutene was irradiated at any of these transitions was 1, 3-butadiene which was identified by its gc retention time and by coinjection of an authentic sample of butadiene (Matheson) with a photolyzed sample of cyclobutene.

Before attempting to use the data analysis presented above to measure values of $k(E)$, a number of checks were performed to test the validity of the analysis and to check for any possible experimental artifacts. Equation (9) was tested by carrying out a series of photolyses at 1 Torr total pressure for varying amounts of time. Data for this experiment at 15 706 cm^{-1} are shown in Fig. 2 as a plot of $-\ln(A/A_0)$ vs the laser fluence ($[\hbar\omega]t$). The data are well fit by a straight line with an intercept of zero to at least 50% conversion. A similar experiment was performed at 16 602 cm^{-1}. Again the data gave a linear plot of $-\ln(A/A_0)$ vs fluence. Since 16 602 cm^{-1} also corresponds to an overtone absorption

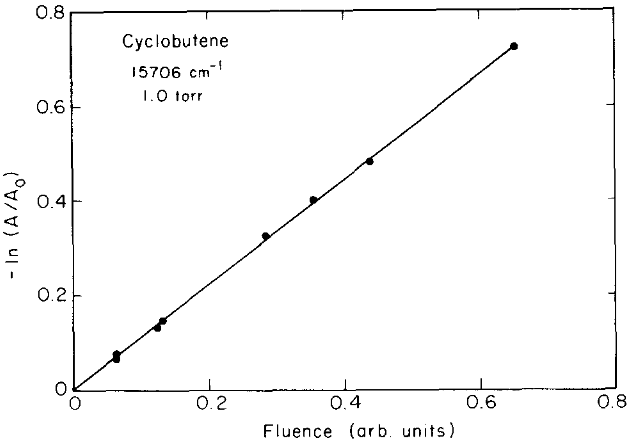

FIG. 2. Plot of $-\ln(A/A_0)$ vs laser fluence for irradiation of 1.0 Torr of cyclobutene at 15 706 cm^{-1}. The line is a linear least squares fit to the data. The highest experimental point represents 50% conversion.

of 1, 3-butadiene, the linearity of the data to 60% conversion demonstrates that overtone induced isomerization of butadiene back to cyclobutene is not important under the experimental conditions. The value of k obtained from Eq. (9) is independent of laser intensity. This was demonstrated by photolyzing 1 Torr of cyclobutene at 15 706 cm^{-1} with intracavity laser powers of 100, 40, and 20 W. The maximum variation of k from the mean value for these three experiments was 8%. Samples of cyclobutene which were allowed to stand in the photolysis cell did not show a significant amount of thermal and/or heterogeneously catalyzed isomerization (0.17% isomerization in 15 h at a pressure of 1 Torr at room temperature). Finally, values of k at 1 Torr followed the overtone absorption band shapes for all four transitions. This indicates that there was no significant production of butadiene via mechanisms other than overtone absorption (for example,surface enhanced photochemistry or multiphoton effects). Taken together, these control experiments leave little doubt that the results reported below are due to single-photon overtone photochemistry and that under the experimental and analytical conditions employed Eq. (9) is valid over a wide range of conversions, photon fluxes, and photolysis times.

Values of $k(E)$ were obtained by measuring k as a function of pressure at fixed wavelength. At each pressure k was obtained from a single photolysis by applying Eq. 9. At several wavelengths data were acquired over an extended period of time (several months) using different samples of cyclobutene. During this period the laser alignment and cell windows were changed several times. Some early experiments were performed using samples of cyclobutene which contained 20% butadiene prior to photolysis. Appropriate corrections were made in calculating k when these samples were used. Most of the data were obtained using cyclobutene samples that contained $\ll 0.1\%$ butadiene prior to photolysis. No systematic variations in k with photolysis time, laser intensity, sample history, or percent conversion were evident. Depending on the cyclobutene pressure, laser wavelength, and laser power, photolysis times ranged from 10 min to 2 h. Yields ranged from 5%–60% and were typically 10%–20%. Typical intracavity laser powers were 50–100 W for $v=6$ photolyses and 20–30 W for $v=5$ photolyses.

Values of the slope and intercept of Stern–Volmer plots were calculated from a weighted linear least squares fit to the data. The weighting factor for each value of $1/k$ was k. As a result low pressure data points, which have smaller error limits in the reciprocal plots, are weighted most heavily. Values of $k_s/k(E)$ were calculated from the slopes and intercepts using Eq. (8). Error limits for $k_s/k(E)$, and thus for $k(E)$ were assigned graphically by using the least squares intercept and drawing the worst straight line which might possibly be consistent with the data. This error analysis results in error limits which are approximately a factor of 2 larger than those calculated using unweighted least squares fits and considering the standard deviations in slope and intercept.

Note that values of $k_s/k(E)$ in units of Torr^{-1} may be obtained from the Stern–Volmer analysis regardless of the absolute calibration used to measure $[\hbar\omega]t$, provided that this calibration is the same for all points obtained at a given wavelength. All the units implied for $[\hbar\omega]$ in Eq. (6) are contained in k_a. In particular, uncertainties in values of Q, A_{eff}, or the laser power meter calibration do not affect $k_s/k(E)$, but only affect values of the absorption cross section calculated from k_a. The only quantities which contribute to errors in $k_s/k(E)$ are the pressure, the ratio of A/A_0, and the integrated relative laser output power. Pressure readings are estimated to be reliable to ± 5%. Ratios of A/A_0 determined by replicate gc analyses of the same sample were generally reproducible to within 1%–2% of the value of A/A_0. The major source of scatter in the data appears to be due to uncertainty in values of $[\hbar\omega]t$ from run to run. This scatter is probably due to small changes in Q and/or in power meter readings as a function of exact laser alignment and could probably be reduced significantly by mounting the photolysis cell permanently in the laser cavity. The problem was most severe at the lowest energy transition studied (~ 13 400 cm^{-1}) since the laser output was smallest there (6–10 mW), due to the high reflectivity of the output coupler, and since rapid alignment and tweaking of the laser once the cell was put in place was more difficult in this region.

The validity of the data analysis given above and of the assumption that the quantum yield is one at zero pressure can be further checked by a comparison of the absorption cross sections determined spectroscopically with those determined from the intercepts of the Stern–Volmer plots. In order to do this, a value of Q in Eq. (6) must be obtained at each wavelength of interest. While Q can be obtained from the transmission spectrum of the dye laser output coupler,[2,3] this technique proved unsuitable in our case since the output couplers used transmitted less than 1% and sometimes as little as 0.1% at wavelengths of interest. Thus measurements of the transmission were unreliable.

For this reason, Q was determined experimentally for at least one wavelength in each overtone band studied by comparing photoisomerization rates for intra- and extracavity photolysis of cyclobutene under otherwise identical conditions. The ratio of the two rate constants gives Q directly. Once Q was established in this fashion at several wavelengths, relative values of Q at nearby wavelengths were determined by simultaneously measuring the laser output power and the signal from a photodiode which monitored light reflected off an intracavity Brewster window in a manner similar to that used to obtain the normalization signal for the photoacoustic spectra.[16(a),16(c)] Values of Q obtained at each wavelength used for $k(E)$ measurements are 13 346 cm^{-1}, 3013; 13 420 cm^{-1}, 3188; 13 446 cm^{-1}, 3052; 13 500 cm^{-1}, 2859; 14 096 cm^{-1}, 309; 14 120 cm^{-1}, 276; 15 706 cm^{-1}, 864; 16 602 cm^{-1}, 629. Values at 13 446, 14 096, 15 706, and 16 602 cm^{-1} were determined by cyclobutene photolysis, the remaining values were determined using the photodiode technique. Values at 13 346, 13 420, and 13 500 cm^{-1} were calculated relative to that for 13 446 cm^{-1}, the value at 14 120 cm^{-1} is relative to that at 14 096 cm^{-1}. The estimated uncertainty of Q values is ± 20%. As defined above Q is simply a proportionality constant relating the intracavity laser power to the laser output power and may be arbitrarily large. It should not be confused with the cavity quality factor for an optical resonator. The Q defined above is approximately equal to the cavity quality factor only if cavity losses due to output coupler transmission outweigh all other cavity losses. This is not likely to be true for the highly reflecting output couplers used in the present work.

RESULTS

The rate of overtone induced isomerization of cyclobutene was investigated at eight wavelengths. Values of $k(E)$ were obtained near the peak of each transition shown in Fig. 1 as well as at several wavelengths across the $v = 5$ methylenic peak to see if there was any significant variation in $k(E)$ for irradiation on the shoulder compared to the main peak. Reduced data for wavelengths near the peak of each transition are shown as plots of 1/(quantum yield) vs pressure in Fig. 3 for $v = 5$ and in Fig. 4 for $v = 6$. In addition to the data shown, four other wavelengths were investigated. At each of these wavelengths the Stern–Volmer plots were linear over the pressure range studied and down to the lowest quantum yields studied. These wavelengths, pressure ranges, and quantum yield ranges were 13 346 cm^{-1}, 0.3–51 Torr, quantum yield 0.99 – 0.05; 13 420 cm^{-1}, 0.1–60 Torr, quantum yield 0.93 – 0.05; 13 500 cm^{-1}, 0.1–51 Torr, quantum yield 0.95 – 0.05; and 14 096 cm^{-1}, 0.5–60 Torr, quantum yield 0.84 – 0.1.

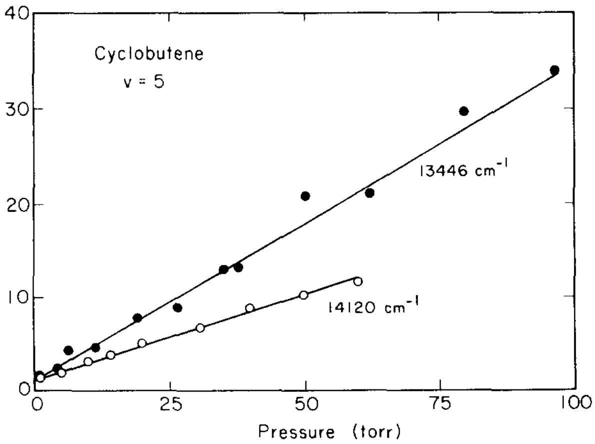

FIG. 3. Reduced Stern–Volmer data for cyclobutene photolysis at 13 446 and 14 120 cm^{-1}. Most of the low pressure data (0–5 Torr) is not shown. The lines are weighted least squares fits to the data. The intercept is 1.0 by definition [see Eq. (8)].

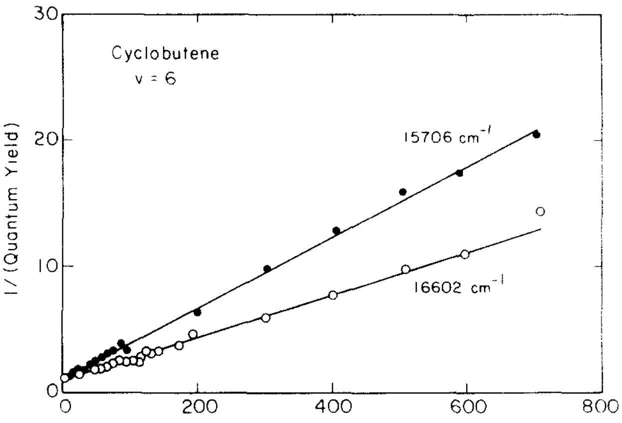

FIG. 4. Reduced Stern–Volmer data for cyclobutene photolysis at 15 706 and 16 602 cm^{-1}. Most of the low pressure data (0–100 Torr) is not shown. The lines are weighted least squares fits to the data. The intercept is 1.0 by definition [see Eq. (8)].

Values of $k(E)$ derived from these data are shown in Table I. These values were calculated from the ratio

TABLE I. Cyclobutene → butadiene CH overtone isomerization rates.

Wavelength (cm^{-1})	Spectroscopic assignment	$k(E)/10^8$ (s^{-1})	$\sigma/10^{-24}$ (cm^2)[a]	$\sigma/10^{-24}$ (cm^2)[b]
13 346	Combination band[c]	0.35 ± 0.08	1.5	1.3
13 420	0–5 methylenic	0.43 ± 0.06	2.0	2.1
13 446	0–5 methylenic	0.40 ± 0.05	3.1	3.1
13 500	0–5 methylenic	0.35 ± 0.07	1.5	1.5
14 096	0–5 olefinic	0.91 ± 0.14	2.4	1.9
14 120	0–5 olefinic	0.74 ± 0.18	3.5	2.5
15 706	0–6 methylenic	4.9 ± 0.6	0.30	0.25
16 602	0–6 olefinic	8.2 ± 1.1	0.31	0.29

[a] Optical cross section calculated from Stern–Volmer incercepts.

[b] Optical cross section from photoacoustic spectra. $v = 5$ values are relative to the cross section at 13 446 cm^{-1} which has been set equal to 3.1×10^{-24} cm^2, the value derived from the Stern–Volmer intercept. $v = 6$ values are absolute.

[c] Unassigned. Intensity borrowed from 0–5 methylenic.

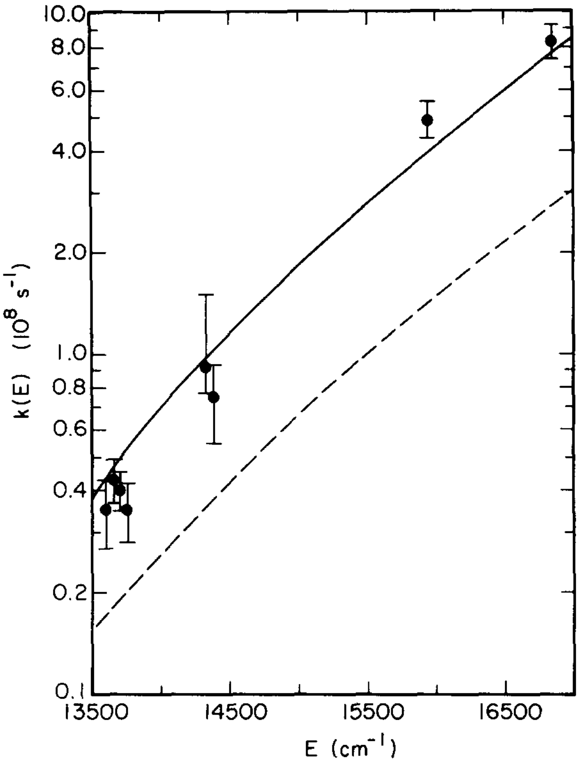

FIG. 5. Plot of experimental values of $k(E)$ vs E. E has been defined as the photon energy plus the average thermal energy (246 cm^{-1}). The dotted line is the result of an RRKM calculation by Frey (Ref. 12). The solid line is the result of an RRKM calculation discussed in the text.

$k_s/k(E)$ using a value of 1.38×10^7 s^{-1} $Torr^{-1}$ for k_s. This assumes that collisional deactivation proceeds at the hard sphere collision rate and that the collision diameter[24] is 5.3 Å. Also shown in Table I are absorption cross sections calculated from Stern–Volmer intercepts. The values calculated from the intercepts at 15 706 and 16 602 cm^{-1} agree with those measured spectroscopically from the methane calibrated $v=6$ spectrum to within 20%, which is within the combined uncertainty of the two measurements. The relative values of the absorption cross sections calculated from the $v=5$ data agree with the relative spectroscopic intensities to better than 10% for wavelengths within a given band and to within 30% between the methylenic and olefinic bands. This is again within the combined uncertainty of the measurements. The $P=0$ quantum yields are thus measured to be unity within the experimental error.

The values of $k(E)$ are plotted vs E in Fig. 5. In this case E has been defined as the photon energy plus the average thermal vibrational energy of cyclobutene (247 cm^{-1} at 298 K). The dotted line in Fig. 5 is a plot of $k(E)$ values calculated from RRKM theory by Frey.[12] The experimental values are systematically larger than the calculated values by a factor of 2 at low energies and by a factor of 3 at higher energies. The solid line, which more nearly fits the data, is the result of an RRKM calculation (see Appendix I) using Frey's parameters[12] for cyclobutene but a looser transition state. The parameters used by Frey (dotted line) give high pressure Arrhenius parameters which exactly reproduce the thermal rate constant at 150 °C. The parameters used to generate the solid line give high pressure Arrhenius parameters which overestimate the experimental thermal rate constant by a factor of 1.6 at 150 °C.

A rather interesting experimental result is that while values of k follow the absorption cross sections for the overtone transitions, as discussed above, k does not drop to the dark reaction limit when samples of cyclobutene are photolyzed "off resonance." This result suggests that further study of off resonance quantum yields at wavelengths very far removed from CH overtone transitions may provide quantitative information on the "continuum absorption" which has been suggested by spectroscopic studies,[23,25] but which has proven difficult to quantitate owing to the photoacoustic background signal produced by cell window absorption.

DISCUSSION

The measured high overtone photochemical isomerization quantum yields conform to the simple kinetic scheme of Eqs. (2) and (3) over a substantial range of pressures and photon energies. The values of $k(E)$ obtained from this analysis are in qualitative agreement with predictions based on the assumption of complete energy randomization on the time scale of the experiment. Were there any significant nonrandom component to the reaction it should appear either as curvature at the high pressure end of the Stern–Volmer plots[8] or as a nonmonotonic dependence[4] of $k(E)$ on E.

The time scale during which an excited molecule may react is defined by the nature of the experiment as the average time between deactivating collisions. Since there is no evidence for nonrandom reaction at pressures up to 700 Torr of cyclobutene, an upper limit of 100 ps may be set for the time required for complete energy redistribution.[26]

The $v=5$ methylenic band has a low frequency shoulder which must involve significant excitation of a hydrogen bending or C–C stretching vibration. Although such modes are likely to be involved in the reaction coordinate, no significant variation in $k(E)$ was observed as a function of laser frequency. There is no evidence for differences in $k(E)$ (other than scaling with the energy of the transition) for excitation of olefinic as opposed to methylenic CH overtones.

Frey's calculated RRKM values of $k(E)$ fit thermal isomerization data ($\langle E\rangle \sim 13\,600$ cm^{-1} for molecules isomerizing at 150 °C), but are a factor of 2 smaller than the "measured" $k(E)$ for $E=13\,700$ cm^{-1} and a factor of 3 smaller for $E=16\,800$ cm^{-1}, Fig. 5. This may reflect a progressively greater deviation from the strong collision assumption as E increases. More energy must be removed from the molecule for a given fractional change in $k(E)$ as E increases. It is interesting to note that Frey's RRKM calculation[12] does not fit the thermal falloff behavior for cyclobutene and can only be made to do so by assuming that the collisional deactivation efficiency is about 0.3 times the gas kinetic collision rate rather than equal to the gas kinetic rate. Reducing k_s by a factor of 3 in the present case would result in values of $k(E)$ three times smaller than those reported and would lead to nearly quantitative agreement with Frey's calculated values. Alternatively, a modest change in estimated transition state frequencies (Appendix) fits the high overtone $k(E)$'s, but gives a rate 1.6 times too large for the thermal data. Given the simplicity of the models used and the number of adjustable parameters, one may conclude only that all data are consistent with the RRKM hypothesis of complete energy randomization.

The introduction and discussion of this paper have tacitly considered cyclobutene to be prepared with a nonrandom vibrational energy distribution by optical excitation. However, the nature of the vibrational state or states prepared by excitation of a high overtone with a cw dye laser is not known.

Most current models are based on spectroscopic studies of benzene.[25,27] These models[23,28,29] describe overtone transitions in terms of a zero order, XH local mode, overtone state which is coupled to a bath composed of all other zero order vibrational states. The strength of coupling between the local mode state, which carries the oscillator strength from the ground state, and the bath modes determines the width and band shape of the observed overtone transition and hence the "lifetime" of the zero order local mode state. Preparation of a completely local mode state requires coherent excitation over the entire transition width, e.g., a 50 fs transform-limited laser pulse for a typical width of 100 cm^{-1}.[1(c)] This requirement has not yet been met in any study of overtone induced photochemistry. The Lorentzian line shapes observed for benzene are consistent with but do not demonstrate a model in which all bath states are equally coupled and dephasing leads to complete energy randomization with an exponential decay time of 50 fs. However, the initial dephasing must be with respect to those zero order states which are most strongly coupled to the local mode and are therefore responsible for the overall transition width. Less strongly coupled modes become excited less rapidly. For the trihalomethanes structured overtone spectra show that energy exchange among several states occurs on an ~20 fs time scale while for the remaining bath states the time scales are longer than 100 fs.[16(c)-16(e)]

Given that cw irradiation with a narrow bandwidth laser cannot prepare a local mode state, it is necessary to consider what sort of vibrational excitation is introduced when a molecule is activated in this manner. In order to fully answer this question it is necessary to know the energy eigenstates of the true molecular Hamiltonian. Which nuclear motions are excited, and to what degree, is determined by which eigenfunctions are optically coupled to the ground state and how strongly. Unfortunately, not enough is known about realistic vibrational wave functions even for relatively simple polyatomics at high levels of vibrational excitation.[30] The limiting case that all energy eigenstates near a given energy are equally coupled to the ground state by optical selection rules seems intuitively rather unlikely. It seems more probable that the majority of states do not involve significant CH stretching. If so, laser excitation within an overtone absorption band results in excitation of nuclear motions which involve much more than a statistical amount of CH stretching and of those nuclear motions which are close in space to, or nearly resonant in frequency with, CH stretching motions. If this is the case, then the fact that no effects attributable to reaction of cyclobutene from a nonrandom vibrational energy distribution have been observed is best attributed to a lack of stronger coupling of the initially excited nuclear motions to the reaction coordinate than to other vibrational motions.

CONCLUSION

The overtone induced isomerization of cyclobutene to butadiene has been studied over a substantial range of internal energy and pressure. A simple Stern–Volmer analysis adequately describes the observed pressure dependence of the overall forward reaction rate constant over the pressure range 1–700 Torr. The unimolecular reaction rate constant increases monotonically with increasing internal energy in a manner consistent with RRKM predictions on time scales as short as 100 ps. No evidence has been found for any dependence of the unimolecular rate constant on the initially prepared vibrational energy distribution. Assuming that optical excitation does prepare a significantly nonrandom vibrational state distribution, the results are best attributed to a lack of strong selective coupling of the initially excited nuclear motions to the reaction coordinate.

ACKNOWLEDGMENTS

We thank Dr. Hai-Lung Dai and Dr. James S. Wong for discussions and assistance in the early stages of these experiments. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U. S. Department of Energy under Contract Number DE-AC03-76SF00098.

APPENDIX

RRKM calculations were performed using a standard computer program available from QCPE.[31] The parameters used were those suggested by Frey[12] for cyclobutene and his complex "C" for the transition state, except that five transition state frequencies were lowered from 660 to 450 cm^{-1}. This leads to calculated high pressure Arrhenius parameters of $A_\infty = 10^{13.76}$ s^{-1} and $E_\infty = 33.15$ kcal mol^{-1}. These Arrhenius parameters give a thermal rate constant of 3.7×10^4 s^{-1} at 150 °C compared to the published experimental value[14(b)] of 2.3×10^4 s^{-1}. State sums and densities were evaluated using the Whitten–Rabinovitch algorithm.

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