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The isomerization of 1-methylcyclopropene: A multichannel unimolecular reaction induced by overtone excitation

J. E. Baggott and D. W. Law

Department of Chemistry, University of Reading, Whiteknights, P. O. Box 224, Reading RG6 2AD, United Kingdom

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The distribution of products resulting from the isomerization of gas phase 1-methylcyclopropene (**1**) induced by C–H stretch overtone excitation has been studied in a search for mode specific effects. Quantum yields for the disappearance of **1** have been determined as a function of the total pressure of a mixture of **1** and methylenecyclopropane and of the added bath gases SF₆ and Ar using a combination of intracavity dye laser photolysis and end product analysis by gas chromatography. These data, together with the ratios of the yields of the major isomerization products, are adequately reproduced by RRKM theory and a weak collisional energy transfer model: no evidence for mode specificity is obtained. The experimental data demonstrate the importance of inefficient collisional energy transfer but allow some conclusions to be drawn concerning the applicability of RRKM theory which are not strongly dependent upon the details of the energy transfer model.

INTRODUCTION

Unimolecular reactions induced by laser excitation of C–H or O–H stretching overtones have been studied in some detail over the last ten years in an effort to observe effects which can be ascribed to mode or bond specificity.^{1–6} The basis for optimism in this regard comes from the description of X–H bond stretching overtones (X = C, N, O, etc.) in terms of local modes.^{7–9} At high levels of vibrational excitation X–H stretching states show the characteristics (band positions and intensities) of single bond oscillators, even in the case where there is more than one symmetrically equivalent X–H bond present. The local mode model implies a degree of energy localization in the excited molecule which, if it persists on a time scale long compared to that of some molecular rearrangement, should invalidate the assumption of rapid energy redistribution implicit in the development of RRKM theory.¹⁰

To date, no unambiguous evidence for mode specificity is available from studies of reactions induced by local mode excitation. Lack of specificity is usually interpreted in terms of significant mixing of the local mode states with a number of other vibrational (normal) modes such that experimentally the energy localization implied by the local mode model is not realized. In some cases specific local mode–normal mode interactions may be observed in experimental spectra, and it is possible to analyze these in terms of a local mode/normal mode Fermi resonance model.^{9,11,12} In molecules containing C–H and C–D bonds there is some evidence for an harmonic resonance (C–H/C–D interbond coupling).¹³ As we continue to find evidence for local mode mixing the prospects for mode specificity diminish. Nevertheless, there are some high-energy X–H stretching overtones in some polyatomic molecules for which an interpretation in terms of unperturbed local modes would seem to be appropriate. Of course, this does not mean to say that local mode–normal mode coupling does not occur, merely that we have no evidence for it from experimental spectra.

In previous studies of the kinetics of unimolecular reactions induced by overtone excitation the search for mode specificity has been based on the suggestion that confinement of the excitation energy to one small part of a polyatomic molecule should lead either to an enhancement or a reduction of the reaction rate above or below that expected from the application of statistical theories (e.g., RRKM theory). Non-RRKM behavior is thus predicted; the reaction rate depending on the site of energy deposition (type of X–H bond excited).

In this paper we continue with this approach as a basis for searching for mode specificity but we examine in detail the unimolecular reaction of 1-methylcyclopropene (**1**) which has *three* uniquely defined isomerization channels, as indicated in Fig. 1.¹⁴ Although the isomerization mechanisms are not known with absolute certainty, there are good grounds for believing that each channel involves different 1,2 H shifts which occur in an initially formed biradical intermediate. Each channel may thus be assigned a distinct barrier height and set of transition state frequencies. The major product observed in thermal studies,¹⁴ but-2-yne (**2**), is formed from the biradical via a 1,2 H shift from ³C–⁴C and the minor products buta-1,3-diene (**3**) and buta-1,2-diene (**4**) are formed from 1,2 H shifts from ¹C–²C and from ³C–

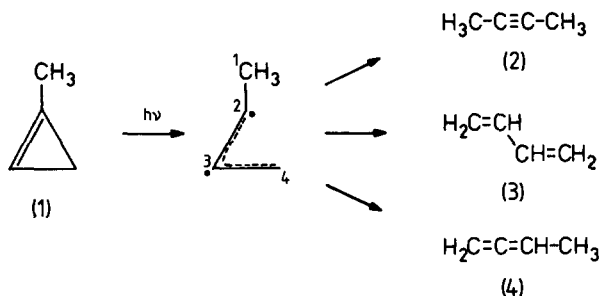


FIG. 1. Proposed mechanism for the three channel isomerization reaction of 1-methylcyclopropene induced by C–H stretch overtone excitation.

^{13}C , respectively. The product distribution is closely controlled by the relative values of the barrier heights and details of the transition state models: deviations from statistical behavior in any channel should be readily revealed in the product yields.

As we will describe in more detail below, the determination of the ratios of the product yields allows us to make observations which are less sensitive to the fact that in our steady-state experiments the collisional removal of the excitation energy is inefficient. This is an important advantage, and allows us to compare experimental data with the predictions of RRKM theory without the difficulties caused by our lack of knowledge concerning the details of intermolecular energy transfer. A full collisional master equation analysis is also presented, however, and the estimates of the energy transfer step sizes obtained by constraining the model to reproduce the experimental quantum yield data are compared with our previous determinations.¹⁵

EXPERIMENTAL

Synthesis of 1-methylcyclopropene

1 was prepared by the reaction of 3-chloro-2-methylpropene with sodium amide in dry tetrahydrofuran following established literature procedures¹⁴ and with gratefully received assistance from Dr. Gerhard Wacholz. Freshly prepared sodium amide was obtained from the reaction of sodium and liquid ammonia. The synthesis yielded a mixture of **1** (57%), methylenecyclopropane (**5**) (38%), **2** (3%), and **3** (2%). The minor impurities were removed by preparative gas chromatography but the major impurity could not be removed because of the similar retention characteristics of **1** and **5** under a variety of analysis conditions with different columns. Since **5** is not a product of the isomerization of thermally or overtone-excited **1** (as demonstrated in experiments described below) we decided instead to use it as an internal standard to check the mass balance at the end of every photolysis experiment. Thus, after purification the sample of **1** contained 61% of **1** and 39% of **5**. This sample was stored in liquid nitrogen at 77 K to prevent polymerization.

Overtone spectroscopy

The intracavity dye laser photoacoustic spectrometer used to determine overtone spectra of gas phase mixtures of **1** and **5** has been described in a previous publication.⁹ In Fig. 2 we show the overtone spectrum in the region covered by rhodamine 6G laser dye. The highest energy peak in Fig. 2 is readily assignable as the "olefinic" C–H $\nu = 6$ overtone band of **1**, and the bulk of the photolysis experiments were performed at the wavelength corresponding to the absorption maximum of this band. The two bands in midrange in Fig. 2 may be assigned as the olefinic and methylenic C–H $\nu = 6$ overtone bands of **5**. This was confirmed by the measurement of overtone spectra of pure samples of **5**.

The low energy bands, of which there are at least three discernible in Fig. 2, can thus all be assigned as C–H stretch $\nu = 6$ overtones belonging to **1**. However, assignment in terms of methylenic vs methyl C–H stretching is not

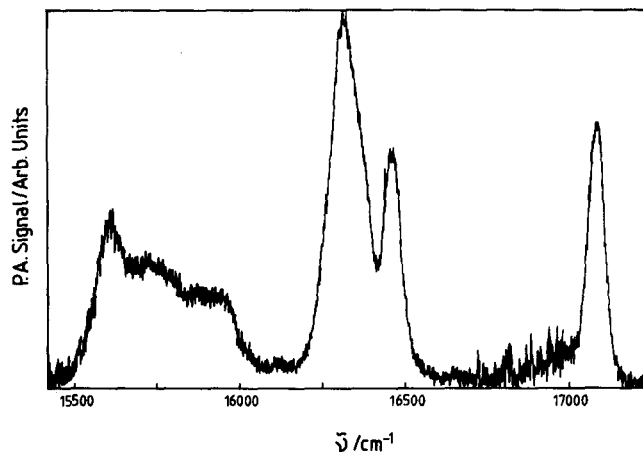


FIG. 2. Laser photoacoustic spectrum of a gas phase mixture of 1-methylcyclopropene and methylenecyclopropane. The total sample pressure was 200 Torr.

straightforward. The overtone spectrum of methylpropene in this region shows two strong bands at 15 628 and 15 978 cm^{-1} which have been assigned by Wong and Moore¹⁶ as overtones of the stretching vibrations of sterically inequivalent methyl C–H bonds. The methylenic C–H stretch $\nu = 6$ overtone of cyclobutene has been reported⁹ to have a maximum at 15 718 cm^{-1} and, given that the widths of the C–H overtones at this level of excitation are generally large, a fair amount of overlap between the methylenic and methyl C–H stretch overtone bands in **1** is expected. Tentative assignments of the three low energy bands shown in Fig. 2 are thus made on the basis of these comparisons. These assignments, together with those made above, are summarized in Table I.

In order to determine reliable quantum yields for product formation (see below) we found it necessary to obtain an estimate of the absorption cross section of the olefinic C–H overtone of **1** at 17 090 cm^{-1} . This was done by recording the photoacoustic spectrum of the mixture of **1** and **5** to which an equal pressure of cyclobutene had been added. The olefinic C–H $\nu = 6$ overtone of cyclobutene has a maximum at 16 601 cm^{-1} with an absorption cross section of $3.2 \times 10^{-25} \text{ cm}^2$ (measured relative to the $\nu = 6$ C–H stretch overtone of CH_4).¹⁵ The relative peak heights of the olefinic C–H overtones of **1** and of cyclobutene were determined by computer deconvolution of the overlapping bands present in the spectrum of the mixture. Lorentzian band profiles were

TABLE I. Positions and assignments of the overtone bands of 1-methylcyclopropene (**1**) and methylenecyclopropane (**5**) in the region 15 500–17 500 cm^{-1} .

Band position/ cm^{-1}	Assignment
15 619	– CH_3 , $\nu = 6$ 1
15 735	$>\text{CH}_2$, $\nu = 6$ 1
15 935	– CH_3 , $\nu = 6$ 1
16 337	$>\text{CH}_2$, $\nu = 6$ 5
16 471	$=\text{CH}_2$, $\nu = 6$ 5
17 090	$>\text{CH}$, $\nu = 6$ 1

assumed. The absorption cross section of the C–H stretch overtone of **1** at $17\,090\text{ cm}^{-1}$ was thus determined to be $3.9 \times 10^{-25}\text{ cm}^2$.

Photolysis and end product analysis

Timed photolyses of the mixture of **1** and **5** were performed using an intracavity dye laser arrangement. For the bulk of the experiments the laser radiation was tuned to the maximum of the olefinic C–H overtone feature at $17\,090\text{ cm}^{-1}$. Some experiments were performed with the laser tuned to the methyl C–H overtone feature at $15\,619\text{ cm}^{-1}$. The experimental arrangement has been described previously.¹⁵ The mixture of **1** and **5** was found to be stable to the isomerization of **1** for typical photolysis periods (between 1–3 h). Samples left at room temperature overnight were found to be slightly richer in **5** but produced no products characteristic of the laser-induced isomerization of **1**, indicating a surface-induced conversion from **1** to **5** over long periods. Photolysis experiments performed with the dye laser tuned off resonance or tuned to an overtone absorption feature assigned as belonging to a C–H bond of **5** (Table I) produced no observable isomerization products.

Photolysis products were analyzed by gas chromatography. A $6\text{ ft} \times 1/8\text{ in.}$ stainless steel column of picric acid on Graphpak (Alltech Associates) was found to give good separation of the reactants and products. Typical retention times were: **5**, 1.95 min, **1**, 2.15 min, **4**, 3.00 min, **2**, 5.00 min, and **3**, 5.85 min with a He carrier gas flow rate of 30 ml/min and a column temperature of 30°C . Peak areas were determined by electronic integration.

RESULTS AND DISCUSSION

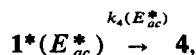
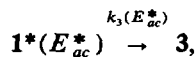
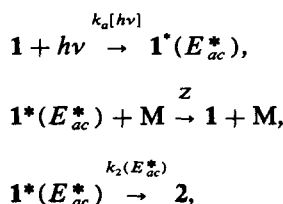
Steady-state kinetics

A phenomenological rate constant characterising the disappearance of **1** as a result of isomerization induced by overtone excitation may be defined as

$$k_{\text{obs}} = -\frac{\ln(A/A_0)}{pt}, \quad (1)$$

where p is the photolysis laser power measured extracavity and t is the photolysis time. The relationship between the extracavity and intracavity laser powers is given in Ref. 15. A is the peak area of **1** as obtained from g.c. analysis and A_0 is the sum of the peak areas of **1** and of the isomerization products **2**, **3**, and **4**, taken to be a measure of the initial concentration of **1**. For each photolysis experiment the mass balance was checked by comparison of A_0 with the peak area of **5** and was found to be in agreement to within 0.6% with the known proportion of **1** and **5** in the unreacted mixture.

By analogy with previous studies of overtone-excited reactions, we may write a simplified reaction scheme as follows:



where the asterisk denotes overtone excitation and M may be any collider molecule (**1**, **5**, or some added bath gas molecule). E_{ac}^* is the initial excitation energy which may be taken as the photon energy $h\nu$ plus the room temperature vibrational energy $\langle E_{\text{vib}} \rangle$. A steady-state analysis of this scheme gives

$$-\frac{d[\mathbf{1}]}{dt} = k[\mathbf{1}][h\nu], \quad (2)$$

where

$$k = \frac{k_a \sum_{n=2}^4 k_n(E_{ac}^*)}{\sum_{n=2}^4 k_n(E_{ac}^*) + Z} = pk_{\text{obs}} \quad (3)$$

and Z is the total collision frequency, obtained as the product of the Lennard-Jones collision rate constant and the pressure of each collider gas present, i.e., **1**, **5**, and any added bath gas where appropriate. This last equation can be rearranged to give

$$\Phi_i^{-1} = k_a/k = 1 + Z / \sum_{n=2}^4 k_n(E_{ac}^*) \quad (4)$$

which indicates, as before,^{2,15} that we should expect the reciprocal quantum yield for the total loss of **1** (all channels) to be linearly related to the collision frequency (and hence the total pressure). This result has been achieved with the assumption of unit efficiency for the deactivation of **1*** by the collider molecule M (strong collision assumption). Collisional energy transfer is generally much less efficient than this.¹⁵ We will return to this point below.

In order to determine experimental quantum yields it was necessary to obtain an estimate for the excitation rate constant k_a . Such information is available from the intercept of a plot of k_{obs}^{-1} vs Z but we preferred to estimate k_a from the measured absorption cross section for two reasons: (i) the intercept of a plot of k_{obs}^{-1} vs Z was relatively poorly determined because of the large gradient and (ii) the master equation calculations led us to expect a fair amount of curvature in the low pressure region of such a plot: extrapolation of the data in a linear fit would have overestimated the magnitude of k_a .

The methods for obtaining an estimate of the excitation rate constant from the absorption cross section have been described in Ref. 15. In fact, we define a slightly modified excitation rate constant k'_a , given by $\sigma[h\nu]/p$ where σ is the absorption cross section, $[h\nu]$ is the photon density in the reaction cell, and p is the extracavity laser power. The ratio k'_a/k_{obs} gives the reciprocal quantum yield directly.

In Fig. 3 we show the results of experiments performed on mixtures of **1** and **5** at a photolysis wavelength of $17\,090\text{ cm}^{-1}$ in the form of a plot of reciprocal quantum yield vs collision frequency Z . The collision frequencies were determined using the bimolecular Lennard-Jones collision rate constant estimated for cyclobutene¹⁷ and the total pressure. Within the experimental scatter of the data, the linear relationship between the reciprocal quantum yield and the colli-

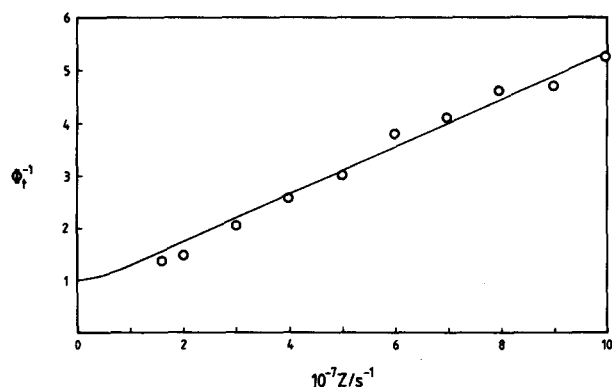


FIG. 3. Variation of the reciprocal quantum yield for the total loss of 1-methylcyclopropene in mixtures with methylenecyclopropane as a function of collision frequency following excitation at $17\,090\text{ cm}^{-1}$. The bold line has been obtained by numerical solution of the collisional master equation with $\langle\Delta E\rangle = -730\text{ cm}^{-1}$ for the two gases.

sion frequency seems to be established. The bold line in this figure shows the fit to the data obtained by assuming RRKM theory and a weak collisional energy transfer model with an energy transfer step size, $\langle\Delta E\rangle$, of -730 cm^{-1} . We used the exponential-down model in all our collisional master equation calculations and $\langle\Delta E\rangle$ represents the energy transferred in a single collision from the vibrationally excited reactant to the collider molecule averaged over all energy up and down transitions. The reader is referred to our previous study¹⁵ for further details and discussion. The value of $\langle\Delta E\rangle$ was obtained by numerical solution of the collisional master equation, i.e., by varying $\langle\Delta E\rangle$ to give the best fit to the experimental data. Note in Fig. 3 that the predicted curvature at low pressures is quite distinct in this system.

We also studied the overtone-excited isomerization of 1 as a function of the pressure of the added bath gases SF_6 and Ar in order to obtain energy transfer information for comparison with our earlier work on cyclobutene.¹⁵ These data are shown in Fig. 4. As in Fig. 3 the bold lines represent fits to the data obtained by allowing the energy transfer step

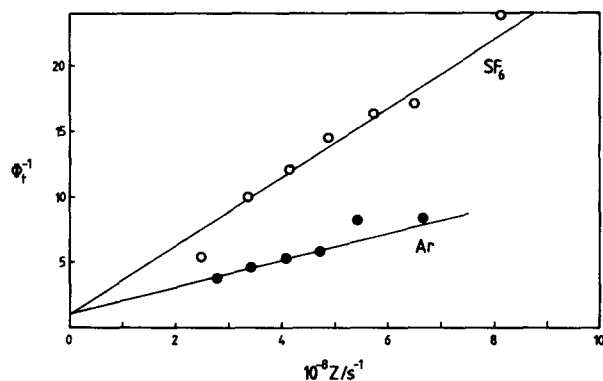


FIG. 4. Variation of the reciprocal quantum yield for the total loss of 1-methylcyclopropene in the presence of methylenecyclopropane and an excess of (○) SF_6 and (●) Ar as a function of the total collision frequency following excitation at $17\,090\text{ cm}^{-1}$. The bold lines represent the master equation calculations with $\langle\Delta E\rangle = -470$ and -150 cm^{-1} for SF_6 and Ar, respectively.

sizes to vary. In calculating Z for these gases we have used the same bimolecular Lennard-Jones collision rate constants estimated for cyclobutene- SF_6 and cyclobutene-Ar collision partners.^{15,17} In these experiments the partial pressure of 1 and 5 was fixed at 1 Torr and the bath gas pressures allowed to vary in the range 15–50 Torr.

The simple one-step deactivation mechanism given above suggests that the ratio of the yields of the major products 3 and 2 should be independent of pressure and given by the ratio of the energy-specific rate constants at the initial excitation energy $k_3(E_{ac}^*)$ and $k_2(E_{ac}^*)$:

$$y_3/y_2 = k_3(E_{ac}^*)/k_2(E_{ac}^*). \quad (5)$$

In Fig. 5 the ratio of the yields of 3 and 2 obtained from the photolysis of mixtures of 1 and 5 is plotted as a function of collision frequency. Again, within the experimental scatter the data do appear to be largely independent of pressure but, as we will see below, the value of the ratio calculated from Eq. (5) overestimates somewhat the value obtained from experiment. This discrepancy is indicative of the fact that, even in the presence of C_4 hydrocarbons, intermolecular energy transfer has less than unit efficiency.

RRKM calculations

Calculations of the energy specific rate constants $k_n(E^*)$, $n=2-4$, were performed using RRKM theory. The high pressure Arrhenius parameters for the three isomerization channels reported by Hopf *et al.*¹⁴ were used to fix the transition state frequencies and barrier heights. No attempt was made to allow for the fact that these reactions proceed through a biradical intermediate or to correlate the vibrational frequencies of the transition states with those of the reactant or products, largely because the vibrational frequencies of 1 had to be estimated. The estimated frequencies of 1 and of the three transition states are supplied in the Appendix. The high pressure thermal data on which the RRKM models are based are summarized in Tabel II, together with the estimated barrier heights for the three channels. Sums of harmonic states of the transition states were obtained using the Beyer-Swinehart algorithm¹⁸ and the

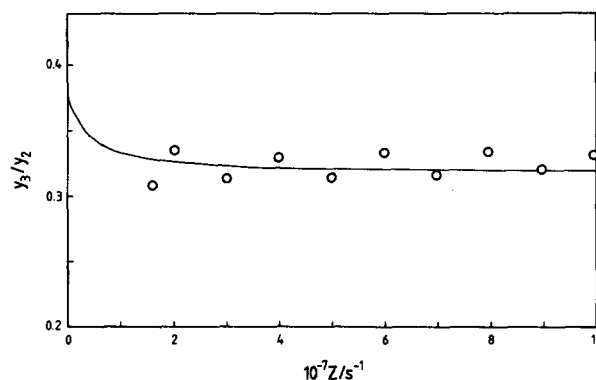


FIG. 5. Variation of the ratio of the yields of the isomerization products buta-1,3-diene and but-2-yne in the presence of methylenecyclopropane as a function of the total collision frequency.

TABLE II. High pressure Arrhenius parameters^a and barrier heights for the three isomerization channels of 1-methylcyclopropene.

Product	$\log(A/s^{-1})$	$E_a/kJ\ mol^{-1}$	E_0/cm^{-1}
$CH_3-C\equiv C-CH_3$ (2)	12.72 ± 0.15	158 ± 1.5	13 158
$CH_3-CH=CH-CH_2$ (3)	13.48 ± 0.31	177 ± 3	14 661
$CH_2=C=CH\cdot CH_3$ (4)	13.49 ± 0.66	183 ± 6	14 949

^a From Ref. 14.

densities of states of the energized reactant molecule were obtained using the Whitten-Rabinovitch algorithm.¹⁹

The $k_n(E^*)$ vs E^* curves for each channel are shown in Fig. 6. If we assume an excitation energy for the initially excited reactant $E_{ac}^* = h\nu + \langle E_{vib} \rangle$, where $h\nu$ is the photon energy and $\langle E_{vib} \rangle$ is the mean vibrational energy of the reactant molecule at room temperature (determined from the vibration frequencies to be $343\ cm^{-1}$) we may use Eq. (5) to calculate $y_3/y_2 = 0.377$ compared to the experimental value 0.323 ± 0.010 (Fig. 5). The difference between these figures is well outside the experimental uncertainty and, as stated above, we understand this difference to be due to inefficient collisional energy transfer.

Effects of weak collisions

Using the RRKM estimates of the energy specific rate constants described above, we performed master equation calculations to determine the best values of the energy transfer step sizes $\langle \Delta E \rangle$ for collisions of 1^* with mixtures of **1** and **5** and with SF_6 and Ar. An exponential-down model was used and the procedures used in a previous study¹⁵ were followed with the exception that a delta function at $E_{ac}^* = h\nu + \langle E_{vib} \rangle$ was adopted as the initial excitation function. The results of fitting the experimental quantum yield data as shown in Figs. 3 and 4 and are summarized in Table III. Quite good fits to the data could be achieved with energy transfer step sizes which are in good accord with more direct determinations²⁰ but which are somewhat larger than our previous estimates¹⁵ in absolute terms. These observations support the general conclusion that RRKM theory when combined with a model for weak intermolecular energy

transfer is adequate to explain the experimental data.

The differences between the energy transfer step sizes reported here and those given in our earlier paper¹⁵ are significant. This is intriguing, since the experimental techniques and methods of analysis are virtually identical. The present results are in much better agreement with those of a number of different previous studies which have made use of a variety of techniques. Of course, the results of Table III might be reflecting some real difference in the abilities of the bath gases to deactivate vibrationally excited 1-methylcyclopropene compared to vibrationally excited cyclobutene, but the reliability of the method of obtaining the $\langle \Delta E \rangle$ values from the data probably does not warrant such a comparison. For example, we experienced difficulties of analysis as a consequence of the low yields of products obtained from **1** (which were, in retrospect, due to the smaller energy-specific rate constants associated with the isomerization of **1** compared to cyclobutene). In the experiments involving SF_6 and Ar the gas analysis was performed at the very limits of the detection sensitivity of the flame ionization detector, and this is reflected in the scatter of the data shown in Fig. 4.

As discussed previously¹⁵ the master equation analysis is very sensitive to the RRKM model parameters used (barrier heights, transition state frequencies) which, in turn, depend upon the reliability of the high pressure thermal rate data used to constrain them. However, we feel that the greatest uncertainty involves the use of spectroscopically determined absorption cross sections to estimate the excitation rate constants, k'_a .

In the absence of more certain information on k'_a we are left in the rather unsatisfactory position of not knowing whether differences in the $\langle \Delta E \rangle$ values reflect some real difference in the nature of the deactivation of the vibrationally excited reactant or some deficiency in the RRKM models (and thus possible non-RRKM behavior). However, in the present multichannel isomerization there is another comparison we can make which, as we will demonstrate, is critically dependent upon the choice of RRKM parameters but much less sensitive to details of the energy transfer model.

The product yield ratio

In Fig. 5 we show how the ratio of the yields of the major products **3** and **2** vary with collision frequency. Within the scatter of the data the ratio y_3/y_2 is independent of pressure, as expected on the basis of the single collision deactivation

TABLE III. Energy transfer step sizes determined from numerical solutions of the collisional master equation.

Collider molecule	$-\langle \Delta E \rangle/cm^{-1}$		
	Ref. 15 ^a	Ref. 20 ^b	This work
1/5	444 ^c	995 ^d	730
SF_6	308	644	470
Ar	29	198	150

^a Deactivation of vibrationally excited cyclobutene, $E_{ac}^* = 16\ 850\ cm^{-1}$.

^b Deactivation of vibrationally excited azulene, $E_{ac}^* = 17\ 500\ cm^{-1}$.

^c Value for cyclobutene.

^d Value for *n*-butane.

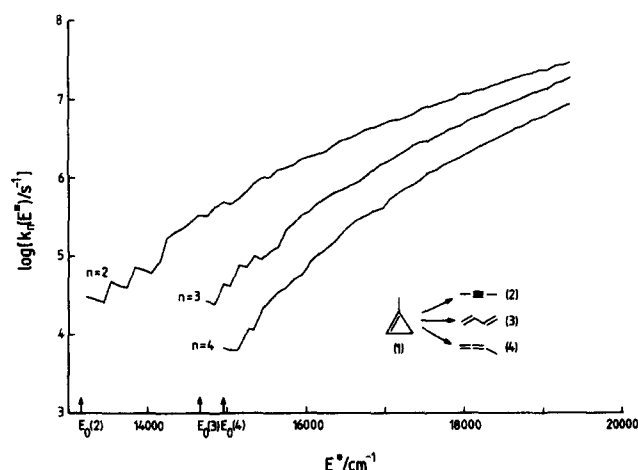


FIG. 6. Results of RRKM calculations for the energy-specific rate constants $k_n(E^*)$ for each of the three isomerization channels.

scheme presented above, but experimentally the value is substantially lower than that expected from such a scheme. The bold line in Fig. 5 is the ratio as derived from the master equation calculations using the value of $\langle \Delta E \rangle$ which provides the best fit to the quantum yield data (Fig. 3 and Table III). The agreement is very good, and demonstrates that weak collisional energy transfer is important in this system and that at high pressures the ratio will tend to become independent of pressure. However, the predicted ratio is not very sensitive to the choice of energy transfer step size over a range of "reasonable" values. For example, a value for $\langle \Delta E \rangle$ of -500 cm^{-1} gives a high pressure limit for y_3/y_2 of 0.313, i.e., just within one standard deviation of the data of Fig. 5. The predicted ratio rises to 0.337 with a value for $\langle \Delta E \rangle$ of -1500 cm^{-1} . This is an important result: the ratio y_3/y_2 is determined directly from the g. c. analysis and is not affected by uncertainties in the excitation rate constant, k'_a , unlike the quantum yield data of Figs. 3 and 4. The ratio does not contain much useful information on the size of $-\langle \Delta E \rangle$ (except that it must be within the limits $500\text{--}1500 \text{ cm}^{-1}$) but it does depend critically on the relative barrier heights and the shapes of the $k_n(E^*)$ curves. The experimental y_3/y_2 ratio thus reflects both the reliability of the high pressure thermal rate data and the applicability of RRKM theory to both of these isomerization channels.

We can illustrate this last point qualitatively by reference to the simple stepladder model for energy transfer discussed in our earlier paper.¹⁵ In this simple stochastic treatment energy is removed in fixed steps and the distribution contracted on each collision. If we begin with a delta-function excitation then the energy distribution remains a delta function as the energy is reduced in fixed intervals. The size of the energy transfer step dictates how many collisions will be required to reduce the energy to a level below the threshold for a particular isomerization channel. At each level on this ladder of energies, E_i^* , the probability that the excited molecule will experience a deactivation step rather than reaction through channel n is given by $Z/[Z + k_n(E_i^*)]$ where Z is the total collision frequency. The probability of collisional stabilization is therefore

$$\frac{S}{S + D_n} = \prod_{i=1}^T \left[\frac{Z}{Z + k_n(E_i^*)} \right], \quad (6)$$

where S is the number of molecules stabilized by collisions and D_n is the number which decompose through channel n . We define T to be the number of collisions required to reduce the energy of the excited molecule below the lowest of the three barrier heights, i.e., that for isomerization to 2. Equation (6) can be rearranged to give

$$\frac{D_n}{S} = \frac{1}{Z^T} \prod_{i=1}^T [Z + k_n(E_i^*)] - 1. \quad (7)$$

At high pressures, $Z \gg k_n(E_i^*)$ and Eq. (7) simplifies to²¹

$$\frac{D_n}{S} = \frac{1}{Z} \sum_{i=1}^T k_n(E_i^*). \quad (8)$$

Thus, the ratio of the product yields may be expressed as

$$y_3/y_2 = D_3/D_2 = \frac{\sum_{i=1}^T k_3(E_i^*)}{\sum_{i=1}^T k_2(E_i^*)}. \quad (9)$$

We can see in Eq. (9) that the ratio becomes independent of pressure but will now depend critically upon both the relative barrier heights, which will determine not only the number of terms in each summation but also the magnitudes of the terms, and on the curvature in the $k_n(E^*)$ vs E^* curves. Both of these properties are fixed by the high pressure thermal rate data upon which the RRKM models are based: the barrier heights are fixed by the measured activation energies and the high energy limiting values of the energy specific rate constants are fixed by the measured A factors.

In the strong collision limit, $T = 1$ and Eq. (5) is reproduced from Eq. (9). In the limit of very inefficient energy transfer T is large and the sums can be approximated as integrals.²² Under these latter circumstances the ratio y_3/y_2 would become completely independent of the energy transfer step size and would be determined by the areas under the $k_n(E^*)$ vs E^* curves.

This is still an approximate treatment, since it does not allow the excitation energy to spread among the available energy levels during the deexcitation process. Nevertheless, the treatment does explain in a qualitative fashion why the y_3/y_2 ratio should be a good guide to the applicability of RRKM theory, dependent only on a choice of "reasonable" energy transfer step sizes and independent of those experimental factors which are not easy to determine with accuracy. We therefore take the agreement between the master equation calculations and the experimental data in Fig. 5 to indicate that RRKM theory provides a very good description of the kinetics of the overtone-excited isomerization of 1.

Excitation of the methyl C-H stretch overtone

We also performed some photolysis experiments on mixtures of 1 and 5 at an energy of $15\,619 \text{ cm}^{-1}$, corresponding to the absorption maximum of the band which has been tentatively assigned as a methyl C-H stretch $\nu = 6$ overtone of 1 (Table I). Due to the smaller energy-specific rate constants (Fig. 6) the product yields were significantly smaller than those obtained at the higher energy excitation and therefore somewhat less reliable. The experimental product ratio y_3/y_2 was found to be 0.206 ± 0.016 compared to the value 0.173 predicted by the master equation analysis based on the best-fit $\langle \Delta E \rangle$ value given in Table III. This difference implies an enhancement of the overtone-induced reaction in favor of buta-1,3-diene, a product of the 1,2 H shift from $^1\text{C}-^2\text{C}$ and therefore consistent with the notion of localized C-H bond excitation giving rise to non-RRKM behavior. However, the difference between these values, 0.033, is only just outside two standard deviations of the experimental ratio and may reflect not only experimental uncertainties but also inadequacies in the master equation calculations when performed at energies close to threshold. Note that the ratio predicted using the strong collision assumption is 0.141 and thus the effects of inefficient collisional energy transfer are to raise the predicted yield of 3 compared to 2. These values are extremely sensitive to the curvature in the $k(E^*)$ curves: details of which are much less reliably predicted by RRKM theory close to threshold (cf. Fig. 6). Consequently, we do not believe the difference between experimental and calcu-

lated product yield ratios to be significant.

Within the limits of experimental uncertainty, the data at both excitation energies would seem to support the conclusion that the application of RRKM theory is appropriate. We certainly do not see a domination of one unimolecular reaction channel over the others which depends upon the identity of the excited C–H bond.

CONCLUDING REMARKS

Many earlier steady-state studies of overtone-excited unimolecular reactions were based on a simple Stern–Volmer analysis in which the strong collision assumption was made. In recent years a number of papers have appeared which have demonstrated the importance of inefficient intermolecular energy transfer in such systems and which have warned of the neglect of these effects.^{15,23–26} However, the factors which control the energy transfer efficiency are not well understood. In this study we have demonstrated that a multichannel unimolecular reaction induced by overtone excitation can provide a much more rigorous test of the applicability of RRKM theory and, consequently, the presence or absence of mode specific effects. By making use of the ratios of the yields of different product channels, which are much less sensitive to details of the energy transfer model than are the quantum yields themselves, the accuracy of the RRKM models can be properly assessed. Our studies fully support the high pressure thermal rate data of Hopf *et al.*,¹⁴ the applicability of unsophisticated RRKM estimates of the energy-specific rate constants, and the absence of mode specificity in this system.

There remains the question of how the findings of studies such as this one can be reconciled with the local mode model. To obtain an answer we must examine closely (i) details of the initial state preparation and (ii) mixing of vibrational modes which may result in the short-time loss of any initial state specificity. These are problems of a largely spectroscopic nature which we are addressing in both low and high resolution spectroscopic studies in our laboratory.

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APPENDIX

The following vibrational frequencies (and degeneracies) were used in the RRKM calculations.

Energized molecule: 3000 (2), 2950, 2900 (2), 2850, 1650, 1550, 1450 (2), 1400 (2), 1100, 1050 (2), 1000 (2), 900 (2), 750, 700, 600, 400, 200.

These frequencies were estimated by reference to the vibrational spectra of cyclopropene [Eggers *et al.*, *J. Chem. Phys.* **47**, 946(1967)] and of propene [Herzberg, *Infrared*

and Raman Spectra (Van Nostrand Reinhold, New York, 1945)]. We are grateful to Professor Ian Mills for some additional advice.

1* → 2 transition state: 3000 (5), 1600 (2), 1450 (3), 1100 (4), 1050 (5), 1000 (2), 600, 300.

This reaction has a path degeneracy of 1 and a barrier height of 13 158 cm⁻¹. The transition state frequencies give a high pressure *A* factor of 5.28 × 10¹² s⁻¹. In accordance with the idea of the reaction proceeding via a 1,2 H shift a C–H stretch vibration has been chosen as the reaction coordinate.

1* → 3 transition state: 3000 (5), 1600 (2), 1450 (3), 1100 (4), 1050 (5), 1000, 950, 450, 200.

This reaction has a path degeneracy of 3 and a barrier height of 14 661 cm⁻¹. The transition state frequencies give a high pressure *A* factor of 3.05 × 10¹³ s⁻¹.

1* → 4 transition state: 3000 (5), 1600 (2), 1450 (3), 1100 (5), 1050, 1000 (3), 500 (2), 400, 200.

This reaction has a path degeneracy of 1 and a barrier height of 14 949 cm⁻¹. The transition state frequencies give a high pressure *A* factor of 3.09 × 10¹³ s⁻¹.

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