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Infrared Multiple Photon Dissociation of Cyclobutanone

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The multiple photon dissociation of cyclobutanone was discussed on the basis of the observed relative significance of two reaction channels. Cyclobutanone was irradiated by a TEA CO_2 laser beam of 9.6 μm R(14) line in a parallel and a focussed geometry. The detected products were ethylene, ketene, and cyclopropane under parallel geometry irradiation. Propylene and acetylene were also produced in focussed geometry irradiation. The kind of the products as well as the effects of reaction conditions on their yields led to the conclusion that the dissociation proceeds along two channels, in one of which ethylene and ketene are produced and in the other cyclopropane and CO. The experimental results agreed almost with the result simulated by a statistical model calculation based on the hypothesis that the energy absorbed in cyclobutanone molecules is statistically distributed among all vibrational degrees-of-freedom.

During the last decade, there has been a lot of interest in the mechanism of chemical reactions induced by a strong infrared laser field through multiple photon excitation.1) A variety of polyatomic molecules are found to dissociate *via* the infrared multiple photon dissociation (MPD) even under a collisionless condition. The mechanism of MPD, at least its outline, is now well established, particularly for several pet molecules such as SF_6.2,3) In MPD of relatively simple polyatomic molecules, the energy pumped into a molecule by a laser field is more or less randomly distributed in all vibrational degrees-of-freedom before decomposition, and most of the excited molecules decompose along the lowest possible thermal decomposition channel. Sometimes, however, apparently unexpected processes from the hypothesis of energy randomization are reported, such as a direct formation of C_2 fragment from ethylene.4) Thus, more studies on variety of molecules are needed for full understanding of the MPD mechanism.

The events associated with MPD might be complex, particularly when the process is to be studied by means of conventional product analyses. The chemical reactions subsequent to MPD would be simplest for the case that the expected mode of dissociation involves only stable molecular products, thereby minimizing the possibilities of post-pulse chemical reactions. The thermal unimolecular dissociation process5–9) as well as single photon photochemistry10) is relatively well known for cyclobutanone. The thermal decomposition of this molecule occurs along two channels; the major one yields ethylene and ketene, and the minor one, cyclopropane and CO; *i.e.*,

cyclobutanone ⟶ ethylene + ketene (Ch 1)
⟶ cyclpropane + CO. (Ch 2)

These two channels seem to proceed in a concerted molecular elimination manner, though the detailed mechanism of the minor process is still open to debate. Provided that the decomposition of this molecule in MPD occurs along the above thermal channels, the dependency of the branching ratio as well as the yield of each channel on the laser energy would help understanding the inter- and intramolecular energy distributions of the excited molecules through multiple photon absorption. The branching ratio of the MPD reaction was studied very recently by Back and Back11) and also by Harrison *et al.*12) mainly as a function of pressure. Though these two data are quite contradictory to each other, both of them found that the branching ratio remained constant at pressures above 3 Torr, and concluded that the MPD at higher pressures was essentially the same as the thermal decomposition reaction. In the present paper, we will describe our experimental determination of the reaction yield as well as the branching ratio mainly against laser fluence at around 1 Torr. The result will be compared with calculations by a stochatic model for the excitation and reaction. Similar discussions on branching ratios were reported for several other molecules such as 1-bromo-2-fluoroethane,13) ethylchloride-2d_1,14) and 1-chloro-2-fluoroethylene.15)

Experimental

A grating tuned TEA laser (Lumonics Research Ltd. Type 102, multimode) was employed as the irradiation source. The laser medium was the mixture of He and CO_2 without adding N_2 and the ouput pulse was about 80 ns fwhm with no appreciable longer tail as measured with a photon drag detector (Rofin Ltd., Model 7425/7400). Shot-to-shot fluctuations in the pulse energy were within ±5%. The laser energy was selectively attenuated by polyethylene sheets and was monitored by an energy meter (Gentic, ED-500).

Two different ways of irradiation were adopted. (1) A cylindrical (2.6 cm inner diameter × 10 cm length) Pyrex cell sealed with NaCl windows at both ends was used for the following focussed gemetry irradiation. The CO_2 laser beam was focussed inside the cell by use of a Ge lens of a 25 cm focal length. The radial distribution of the laser intensity at the focal point was determined by scanning a pin hole (90 μm dia.) to be a near Gaussian with an effective diameter of 0.1 cm; thus the effective irradiation area at the focus was estimated to be 8×10^{-3} cm^2. (2) A disc type (2.6 cm inner diameter × 1 cm length) Pyrex cylinder sealed with two NaCl windows was employed for the following parallel geometry irradiation. The cell was placed between a 25 cm focal length Ge lens and its focal point, around 19 cm distant from the lens. The effective irradiation area was determined to be 0.36 cm^2 on the basis of the burnt area measurement on thermal paper by the laser irradiation. Within this area, the laser intensity was assumed to be constant. The field intensity or the fluence varied over 1.4 times between the two NaCl windows along the laser beam according to the geometric consideration. In both of the above geometries, precise determination of the effective area was difficult due to the multimode laser pattern. Errors introduced by the overall procedure might give a 40% uncertainty in the absolute value of the laser fluence, but much less than this for relative values.

Commercially obtained cyclobutanone of extra pure grade from Nakarai Kagaku Co. Ltd. was used after several freeze-thaw cycles. It proved to contain no detectable impurities identical to the irradiation products by gas-chromatography and infrared spectroscopy.

The gaseous materials were treated in a conventional vacuum line equipped with a MKS baratron pressure meter (170-6B/310BHS). Cyclobutanone was introduced into the irradiation cell manometrically. After the irradiation of a necessary number of laser shots (repetition rate was less than 0.3 Hz), the resultant gas mixture, or sometimes, a part of it, was transferred into a gas-sampler for a gas-chromatographic analysis. The products were analysed by use of a Shimadzu GC-4C gas-chromatograph with a flame ionization detector. The products (ethylene, acetylene, cyclopropane, and propylene) were identified in terms of their retention times by use of a Porapak Q and activated charcoal columns. Authentic samples were commercially obtained. Quantitative analyses were carried out with an activated charcoal column. Whether the products were totally recovered or not was checked with model mixture gases. The quantitative analyses were reliable within 10% for C_2 and C_3 hydrocarbons. Sometimes, the 10 cm irradiation cell itself was used as a sample cell for the double beam infrared spectrometer (Japan Spectroscopic Co. Ltd., IRA-1). The infrared spectra of cyclobutanone and the reaction mixture were thus obtained.

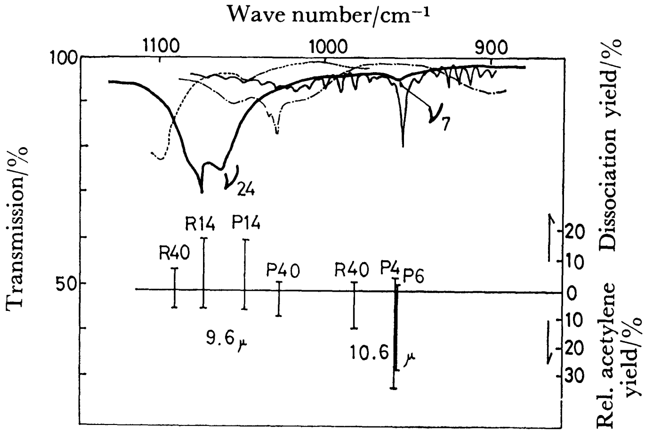

Fig. 1. Dissociation yield and relative acetylene yield with various laser lines, and the IR absorption spectra of cyclobutanone, ethylene, cyclopropane, and ketene. The dissociation yield is the consumed cyclobutanone per 100 shots divided by the initial cyclobutanone, and the relative acetylene yield is the fraction of acetylene among the summed yield of ethylene, acetylene, cyclopropane, and propylene. The irradiation was carried out in focussed gemoetry with 0.37—0.52 J incident laser pulses. The pressure of cyclobutanone was 1 Torr. The conventional IR absorption spectra were measured at 5 Torr (10 cm optical length) in the present work except for ketene. Its spectrum is from the Ref. 17.

Cyclobutanone (——), ethylene (——), cyclopropane (·–·–·), ketene (------).

Results

Product Analyses. The 9.6 μm R(14) line of the TEA CO_2 laser at 1075 cm^{-1} was usually employed in the present work. This line is approximately resonant with the Q branch of the cyclobutanone ν_{24} band (A type, rocking mode of the CH_2 groups, see Fig. 1),[16] which is the strongest absorption band in accord with the CO_2 laser lines. The linear absorption cross section was measured to be 3×10^{-19} cm^2 molecule^{-1} by means of a conventional infrared spectrometer with a 2 cm^{-1} slit width.

The identified products in focussed geometry irradiation were ethylene, cyclopropane, propylene, acetylene, and ketene. The products except ketene were quantitatively analysed gas-chromatographically. In the gas chromatograms with an activated charcoal column, three other peaks were found at the retention times corresponding to methane, ethane, and propane. One unidentified peak was also observed between the cyclopropane and the propylene peak. These products were, however, found to be very minor, less than 1% of the total products even under the strongest irradiation conditions. No other gas chromatographic peaks were recognized before the effusion of cyclobutanone. Ketene gave no gas chromatographic peak, probably because of its reaction with column materials. Thus it was identified by its characteristic infrared absorption peak at 2150 cm^{-1}.[17] Furthermore, the identification was confirmed by the fact that the infrared peaks disappeared when the reaction mixture was kept with 50 Torr methanol for 30 min,[18] and that the resultant production of methyl acetate was proved gas chromatographically.

In parallel geometry irradiation, ethylene and cyclopropane were almost the exclusive products found by gas chromatographic analyses; acetylene, propylene, and other minor products gave only trace gas chromatographic peaks if any.

If the MPD proceeds *via* the two reaction channels similar to the thermal decomposition, ethylene, cyclopropane, and ketene are the expected products. We did not try to detect one other expected product, CO, because of its low sensitivity for the gas chromatographic and infrared analyses. In agreement with the assumption that the major channel is Ch 1, the observed amount of ethylene was 80% or more of the decomposed cyclobutanone under various irradiation conditions. At the same time, the infrared peak intensity of the band assigned to ketene were found to be approximately proportional to the peak intensity at 950 cm^{-1} of the product ethylene. Cyclopropane must not be produced by a secondary reaction such as CH_2+ethylene→cyclopropane, in which CH_2 is supplied by MPD of ketene or other primary products, because the cyclopropane formed *via* the insertion of CH_2 to ethylene possesses too large internal energy to be stabilized under the present low pressure.[19] Acetylene and propylene, which are not primary products of the above two channels, were found only in focussed geometry irradiation. As will be discussed later, acetylene is formed through MPD of a primary product and propylene through isomerization of the energy-excess cyclopropane. Thus, we will assume that the MPD of cyclobutanone proceeds *via* the two dissociation channels which are the same as those in the thermal decomposition. The product ethylene or ethylene+acetylene represents an extent of the Ch 1 decomposition, while cyclopropane or cyclopropane+propylene does that of the Ch 2. The products and the reaction mechanism coincide with the results of Back and Back[11] and of Harrison *et al.*,[12] who irradiated cyclobutanone with the laser light of 1047 cm^{-1} P(20) and 1073 cm^{-1} R(12) lines, respectively.

Effect of Irradiation Wavelength. Several preliminary experimental runs were carried out with various laser lines in focussed geometry. The kind of products did not change, but the dissociation yield and the relative yield of acetylene varied considerably as shown in Fig. 1. The dissociation yield is the highest at the 9.6 μm R(14) line among the examined laser lines, and decreases towards both sides of this line being approximately proportional to the linear absorption of cyclobutanone. The relatively high yield compared with the linear absorption at the 9.6 μm P(14) line may be reasonable, because the multiple photon absorption has the tendency to extend to the red compared with the single photon absorption.[1]

Ethylene[4,20,21] and cyclopropane[22] are known to give acetylene in high yields *via* CO_2 laser MPD. The high yield of acetylene in irradiation with the laser line of smaller wavenumber is understandable, because the primary products could absorb the laser lights of these wavenumber lines effectively. The absence of dissociation of ketene with 1080 cm^{-1} CO_2 laser irradiation is reported at a ketene pressure lower than 5 Torr. Only H_2 and CO with trace amount of acetylene is reported as gas phase products at higher ketene pressures.[23]

Thus we selected the 9.6 μm R(14) line as the most adequate for the present purpose to find out the dependence of the ratio of the two different channels on the irradiation conditions, because the dissociation yields were high and the interference by possible undesirable secondary reactions was small with this line. We confirmed, however, almost the same mechanism in the primary dissociation with other laser lines, including the 10.6 μm P(4) and P(6) lines which are resonant to the ν_7 ring mode band[16] of cyclobutanone.

Effect of the Number of Laser Shots. Figure 2 shows the dissociation yield as a function of the laser shot number in focussed geometry irradiation. Let $P_{\mathrm{CB(0)}}$ mean the initial pressure of cyclobutanone and $P_{\mathrm{CB(N)}}$, the pressure after N repetitive shots. log $[P_{\mathrm{CB(N)}}/P_{\mathrm{CB(0)}}]$ is plotted against the number of laser shots in Fig. 2 to show that a good proportionality exists between the two variables. The proportionality relation is readily derived, if the dissociation yield per one laser shot $W(=[P_{\mathrm{CB(N)}}-P_{\mathrm{CB(N-1)}}]/P_{\mathrm{CB(N-1)}})$, is independent of the consumption of cyclobutanone and the gas mixture becomes uniform before the subsequent laser shot. The following proportionality relation is equated,

$$\log(P_{\mathrm{CB(N)}}/P_{\mathrm{CB(0)}}) = N\cdot\log(1-W). \qquad (1)$$

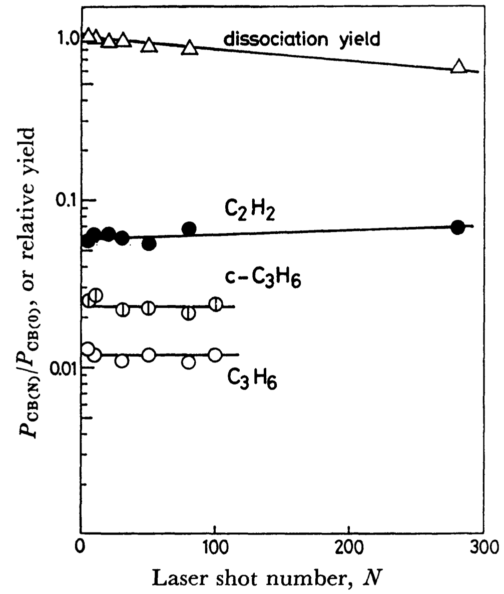

Fig. 2. Variations of dissociation yield and relative yields of acetylene, cyclopropane, and propylene with laser shot numbers. Cyclobutanone of 1.0—1.7 Torr was irradiated in focussed geometry with 0.46—0.47 J incident energy pulses.
△: $P_{\mathrm{CB(N)}}/P_{\mathrm{CB(0)}}$, ●: relative yield of acetylene, ⦶: relative yield of cyclopropane, ○: relative yield of propylene.

When the dissociation yield is kept small enough (for example less than 10%), Eq. 1 is approximated by the equation,

$$W = [(P_{\mathrm{CB(0)}} - P_{\mathrm{CB(N)}})/P_{\mathrm{CB(0)}}]/N, \qquad (2)$$

which makes it possible to obtain *W* by dividing the yield after *N* shots by number *N*.

The relative yields of acetylene, cyclopropane, and propylene against the number of laser shots are also shown in Fig. 2. The relative yields of cyclopropane and propylene are independent of the laser shot number as is expected from the proposed reaction mechanism if no appreciable secondary dissociation of these products occurs. The yield of acetylene shows a slight increase with the laser shot number. Most of acetylene is considered to be produced *via* some secondary dissociation of the primary products, probably ethylene, as will be described in the next section. The fact that the observed dependence of the acetylene yield on shot numbers is small implies that the secondary dissociation proceeds mainly during the same laser pulse when the primary products are still vibrationally hot.

Effect of Laser Energy in Focussed Geometry Irradiation. Figure 3 shows the effect of laser energy (which is proportional to laser fluence in the present work) upon the product yields. The total yield is proportional to the 3/2 power of the laser energy. In focussed geometry irradiation, the 3/2 power dependence could be explained based on a conical geometry of the laser beam incorporating saturation effects.[24] In this treatment, the volume inside of which the laser intensity exceeds a

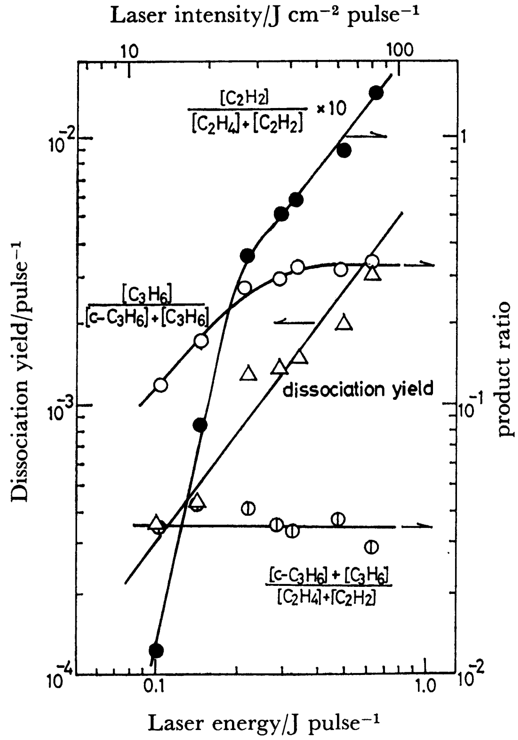

Fig. 3. The dependence of the dissociation yield, the fraction of acetylene, the branching ratio, and the degree of isomerization of the cyclopropane on the laser pulse energy in focussed geometry irradiation.
The laser energy (along the *absissa*) means the incident laser energy per pulse and the laser intensity means the field intensity which is defined as the energy of one pulse divided by the effectively irradiated area normal to the laser beam in the focal region.
△: Dissociation yield per pulse. The straight line shows the 3/2 power law, ●: ratio of acetylene *vs.* ethylene+acetylene (multiplied by 10), ⦶: ratio of cyclopropane+propylene *vs.* ethylene+acetylene, ○: ratio of propylene *vs.* cyclopropane+propylene.

certain value increases proportional to the 3/2 power of the incident laser energy. If the dissociation yield is effectively described by the relation $W=\alpha(I/I_{th})^n$ with a large n when $I<I_{th}$ and is constant α when $I\geq I_{th}$, the 3/2 power law holds over a broad intensity range, masking the effect of the order n of the process. The experimental finding in Fig. 3 is understandable in this context.

The ratio of acetylene *vs.* the sum of ethylene and acetylene increases proportional to the power of 3/2 or higher of the laser energy. This fact shows that acetylene is not a primary reaction product from cyclobutanone. Most of acetylene must be produced through MPD of some primary products during the same laser pulse. A theoretical model calculation will show in Discussion that the dissociation of cyclobutanone is complete far before the end of the laser pulse of a large power, and thus it is possible that the primary products absorb enough laser energy within the same laser pulse to dissociate. Under stronger irradiation conditions with a focussed geometry, visible luminescence was observed at the focal region. This suggests that radicals such as C_2 and CH_x are produced *via* some secondary MPD of primary products and may be intermediates for production of acetylene and other minor hydrocarbon species. Most of the acetylene should come from ethylene and/or ketene, which are the primary products capable of yielding a considerable amount of acetylene *via* the subsequent multiple photon absorption. The yield of acetylene under irradiation of a stronger laser pulse exceeds considerably the yield of C_3 hydrocarbons, which is almost independent of the laser energy. This shows that the C_3 hydrocarbons could not be the main primary product to yield acetylene. It is not determined conclusively which is the main primary product to produce acetylene, ethylene or ketene. Though ketene is reported not to produce acetylene through the MPD at 1080 cm^{-1},[23] the possibility may not be denied that the primary ketene, when it is still hot, could be the starting material for some secondary MPD. In spite of this, we prefer a view that the primary hot ethylene is the main precursor, judging from the fact that the relative acetylene yield decreased with increasing the irradiation wavenumber, roughly in agreement with the change of the linear absorption of ethylene, but reverse to that of ketene (see Fig. 1). The possibility that the primarily produced ethylene dissociates directly to yield acetylene without absorbing subsequent laser photons is considered to be very small on the basis of energetics.

It is important to note that the ratio of the sum of cyclopropane and propylene *vs.* that of ethylene and acetylene is independent of the laser energy. This is probably caused by the fact that, in focussed geometry irradiation, most of the dissociation occurs in the region where the laser intensity is equal to or slightly exceeds I_{th} in the context of the previous explanation of the geometric effect. Moreover, the later theoretical model calculation shows that the branching ratio does not strongly depend on the laser intensity so long as it is strong enough. The slight decrease in the experimental plots with increasing laser energy may mean some occurrence of secondary dissociations of the C_3 hydrocarbons.

The ratio of propylene *vs.* the sum of cyclopropane and propylene increases with the laser energy to a certain plateau value as shown in Fig. 3. This behaviour is consistent with the hypothesis that most of propylene is produced *via* unimolecular isomerization of the primary product cyclopropane.[25] The energetical threshold for the isomerization is much higher than those for Ch 1 and Ch 2 (see Discussion, Fig. 8). Thus the increase of the ratio until a certain plateau value does not conflict with the observed constancy in the branching ratio over the examined laser energy range. The fact that the certain plateau value is reached indicates that most of propylene is not produced *via* secondary MPD of primary products. If so, the ratio should increase with the laser energy similarly to the yield of acetylene.

Pressure Effects in Focussed and in Parallel Geometry Irradiations. Figure 4 shows the effect of the cyclobutanone pressure on the dissociation yield, the branching ratio, and also the degree of the isomerization of the primary product cyclopropane. The yield is pressure dependent, which may mean that the dissocia-

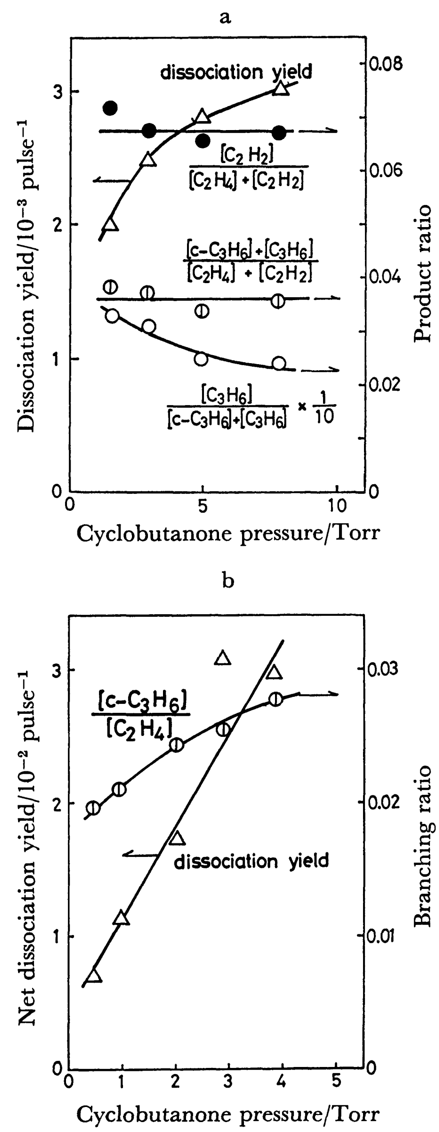

Fig. 4. The dependences of dissociation yield, the branching ratio, and the degree of isomerization of the cyclopropane on the pressure of cyclobutanone in focussed (4a) and in parallel (4b) geometry irradiations. 4a) △: Dissociation yield per pulse, ●: ratio of acetylene *vs.* ethylene+acetylene, ⦶: ratio of cyclopropane +propylene *vs.* ethylene+acetylene, ○: ratio of propylene *vs.* cyclopropane+propylene (multiplied by 1/10). The incident energy per pulse was 0.47 J.
4b) △: Dissociation yield per pulse in the effectively irradiated volume (=net dissociation yield), ⦶: ratio of cyclopropane *vs.* ethylene. The incident laser intensity was 6.0 J cm^{-2} pulse^{-1}.

tion partly proceeds collision free and is partly supported by a certain kind of collisional events. It is difficult to extrapolate the dissociation yield to zero pressure to find out the percentage of the contribution of collision free dissociation without doubt, but it seems to be less than 50% even under 1 Torr of cyclobutanone. The branching ratio is pressure dependent in the parallel geometry irradiations. The dependence in the present experiments are in agreement with the observation by Harrison *et al.*,[12] but reverse to the result by Back and Back.[11] The increase in the branching ratio with increasing the pressure suggests that the collisional events result in producing cyclobutanone molecules with a relatively larger internal energy. In focussed geometry irradiation, the pressure effects are rather small, as is expected from the geometric consideration explained in the previous section. The fraction of propylene among C_3 products decreases with increasing pressure. This is due to the collisional stabilization of the primary hot cyclopropane.

In practice, full analysis of collisional effects is very difficult.[26] There must be many factors to be discussed such as rotational relaxation, redistribution of the energies of laser excited molecules, retardation of the diffusion loss of active species, collisional deactivation, and so forth. The data under lower pressures are thus desirable in order to elucidate the MPD mechanism, so long as a detection technique allows. However, our subsequent discussions are limited to the data taken at around 1 Torr due to the detectivity of the present analytical method.

Laser Intensity Effect on Product Yields in Parallel Geometry Irradiation. As has been already described, the exclusive products in parallel geometry irradiation are ethylene (Ch 1) and cyclopropane (Ch 2). The laser intensity dependence of the ethylene yield is plotted in Fig. 5. In these experiments, the yield is corrected for the fact that the effectively irradiated volume

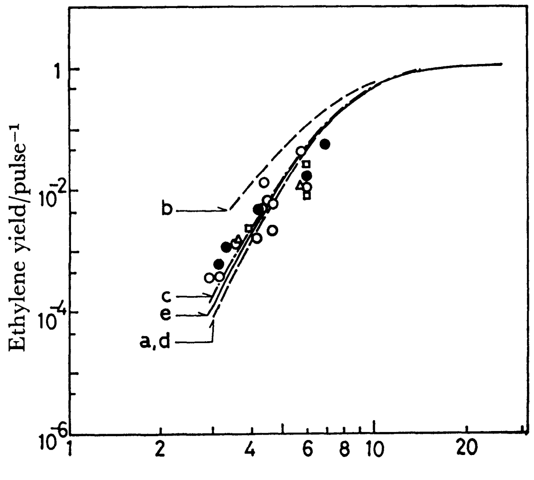

Fig. 5. Yield of ethylene *vs.* laser intensity in parallel geometry irradiation. Experimental data were from experiments with 2 (●), 1 (○), 0.5 (□), and 0.25 Torr (△) cyclobutanone. The yield means the yield per pulse in the effectively irradiated volume. The laser intensity means the incident energy of one pulse divided by the effectively irradiated area. The curves show model calculation results.
a: Calculations with $s=27$ for 1 Torr cyclobutanone. The effective dissociation threshold is at $n=18$ for Ch 1, and $n=21$ for Ch 2, b: calculations with $s=6$. The other conditions are the same as a, c: calculations for 0.25 Torr cyclobutanone. Other conditions are the same as a, d: calculations with $s=27$ for 1 Torr cyclobutanone. The effective dissociation threshold is at $n=18$ for Ch 1, and at $n=20$ for Ch2, e: revised relationship calculated by incorporating the inhomogeneity effect of the field intensity along the laser beam. The data are from curve a.

($0.36\ \mathrm{cm}^3$) is much smaller than the total cell volume ($6.77\ \mathrm{cm}^3$). The yield increases apparently proportional to around 7 power of the laser intensity. This trend is qualitatively in agreement with that observed by Back and Back[11] at 9.5 Torr pressure. The dissociation yield in the present experiment is, however, considerably smaller comparing at the same fluence. This is partly because of the pressure difference between the two experiments. At the same time, the P(20) line might be more efficient than the present R(14) line.

The ratio of the yield of cyclopropane over that of ethylene, which is the branching ratio of the two channels, is plotted against the laser intensity in Fig. 6. The range of the branching ratio (=[cyclopropane+propylene]/[ethylene+acetylene]) from focussed geometry irradiation is also indicated in the figure by hatching.

The experimental results in Figs. 5 and 6 are open to theoretical discussions on the basis of statistics in Discussion. The curves drawn in the figures show such theoretically predicted relationships.

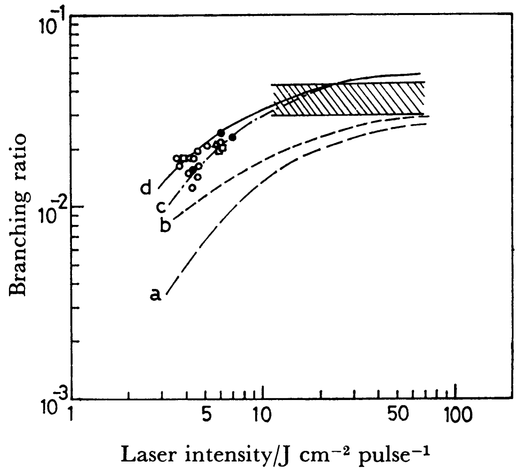

Fig. 6. The branching ratio *vs.* laser intensity. The branching ratio is the ratio of cyclopropane+propylene *vs.* ethylene+acetylene. The experimental results are plotted for 2 (●), 1 (○), 0.5 (□), and 0.25 Torr (△) cyclobutanone pressures. The hatching shows the range from focussed geometry irradiation. In this case, the laser intensity is that one at focal point. The curves show model calculation results. a, b, c, and d have the same meaning as those described in the figure caption of Fig. 5.

Discussion

Model Calculation of MPD Process. There have been reported a lot of theoretical treatments of multiple photon absorption and dissociation of polyatomic molecules. This complex process is analysed[2,3,27–34] based on a rather phenomenological view point by classifying the process into three regions: the first one is a coherent interaction region until some photons are absorbed, the second is an incoherent quasicontinuum region, and the third is a region where dissociation competes with absorption of laser photons. In the first region, the laser power is the deciding factor, and in the second, the laser fluence. In most polyatomic molecules, the dissociation yield as well as other observed phenomena are found to be dependent on the laser fluence, not on the laser power.[31] Thus the absorption of the laser photons in the second quasicontinuum region and the dissociation mechanism are considered to determine almost completely the total MPD process.

In this paper, the MPD process of cyclobutanone will be simulated on the method described by Black *et al.*,[31] whose validity has been proved in the analysis of the MPD of SF_6. We will expand their way to the case of the present two channels dissociation. The first coherent absorption region is neglected. In the quasicontinuum region, the energy pumped into a molecule by the laser field is assumed to be randomly distributed among all available internal degrees-of-freedom, owing to a very fast intramolecular energy migration. Molecules above the threshold of dissociation decompose at RRKM rates. The formulation is as follows.

The probability W_n of being in the state having the energy $n\hbar\omega$ above the starting level is described by use of the following rate equations,

$$\begin{aligned}\mathrm{d}W_n/\mathrm{d}t = {} & K_n^{\mathrm{a}}IW_{n-1} + K_n^{\mathrm{e}}IW_{n+1} - (K_{n+1}^{\mathrm{a}} + K_{n-1}^{\mathrm{e}})IW_n \\ & - K_n^{\mathrm{d1}}W_n - K_n^{\mathrm{d2}}W_n, \end{aligned} \tag{3}$$

where K_n^{a} and K_n^{e} are absorption and stimulated-emission coefficients into that group, K_n^{d1} and K_n^{d2} are the dissociation rate constants along the two dissociation channels, and I is the laser intensity. The absorption and stimulated-emission coefficients in Eq. 3 represent up and down transitions. Assuming that the transition rates are governed by Fermi's Golden rule, the ratio of transition rates is given by the ratio of density of final states,

$$K_n^{\mathrm{e}}/K_{n+1}^{\mathrm{a}} = \rho_n/\rho_{n+1}, \tag{4}$$

where ρ_n is the density of vibrational states at a vibrational energy of $n\hbar\omega$ above the starting state. The net absorption cross section σ_n is equated as,

$$\sigma_n = (K_{n+1}^{\mathrm{a}} - K_{n-1}^{\mathrm{e}})\hbar\omega. \tag{5}$$

In this treatment, the possible collisional effect on the distribution is neglected. In fact under stronger irradiation, the dissociation proceeds very rapidly and may not be interfered by collisional events seriously. But in weak irradiation, the dissociation occurs mainly after the laser pulse with a relatively slow rate. Dissociation must compete with some sort of collisional deactivation, and not every molecule with an energy in excess of the dissociation energy may react. The fractional dissociation from level n after the laser pulse is assumed to be written as,

$$f_n^{\mathrm{i}} = K_n^{\mathrm{di}}/(\sum_{\mathrm{i}} K_n^{\mathrm{di}} + D) \quad (\mathrm{i} = 1, 2), \tag{6}$$

where D is the collisional deactivation rate constant with which K_n^{di} competes. The total fraction yield F^{i} after the laser pulse is the convolution of the fractional deactivation with the distribution function $W_{n(\mathrm{f})}$ at the end of the laser pulse,

$$F^{\mathrm{i}} = \sum_n f_n^{\mathrm{i}}\, W_{n(\mathrm{f})}. \tag{7}$$

These values should be added to the dissociation yields during the laser pulse.

According to the above procedure, the calculation was carried out with a Gear package for ordinary differential equations.[35] The necessary factors are selected as follows. (1) The time profile for the laser pulse was assumed to be an isoscales triangle of 80 ns fwhm. (2) The internal energy was quantized by $\hbar\omega$ of the adopted laser line, which is 3.07 kcal mol^{-1}. (3) ρ_n was calculated mostly by a RRK formula with $s=27$, the total number of the degrees-of-freedom of internal motion. Sometimes different s values were adopted. The density was once calculated according to the Whitten-Rabinovitch method[36] by adopting the internal vibrational frequencies summarized by E. K. C. Lee *et al.*[37] The result fairly agreed with calculations based on a RRK formula with $s=27$. (4) The net absorption cross section σ_n was assumed to be a constant independent of the internal energy. The value was selected so as to result in a fair agreement between the calculated and experimental results. The selected value was 4.5×10^{-20} cm^2 molecule^{-1}, which was about an order of magnitude smaller than the linear absorption cross section. Because the MPD process is described by the product $\sigma_n \times I$ as the first approximation, but not by the individual σ_n or I, the possible experimental error in the estimation of the laser intensity up to 40% may result in the estimation error in σ_n up to the same amount. (5) The RRKM dissociation rates were taken from the work of E. K. C. Lee *et al.*[37] The values were from their OSA and MP models respectively. No serious differences were expected by selecting other models. In accordance with the artificial quantization of the internal energy of cyclobutanone, the effective threshold for the two channels were selected at $n=18\,(K^{\mathrm{d1}}_{18}=3\times10^6\ \mathrm{s}^{-1})$, and $n=21\,(K^{\mathrm{d2}}_{21}=3\times10^5\ \mathrm{s}^{-1})$, respectively. (6) The collisional stabilization rate constant D was selected as 1.1×10^7 s^{-1} based on the collision diameter of 5.07 A for cyclobutanone.[38]

Comparison between the Calculated and Experimental Results. Figure 7 shows the time evolution of the dissociation yields. In this figure, no collision effect is taken into account even after the laser pulse. One important fact is that almost all molecules are dissociated shortly after the beginning of the laser pulse under a such intense irradiation as is met in focussed geometry irradiation. It is then understandable that the secondary multiple photon dissociation of the primary product occurs. Another fact to note is that the dissociation continues long after the end of the laser pulse, particularly under weaker irradiations.

Figure 8 shows the calculated dissociation yields from various levels above the dissociation energy during the laser pulse and also after the laser pulse. The average energy of the distribution of the yield is about 65 kcal mol^{-1} for Ch 1 dissociation under 4.7 J cm^{-2} pulse^{-1} irradiation, and is high as 85 kcal mol^{-1} for Ch 1 under 67 J cm^{-2} pulse^{-1} irradiation.

As has been already described in Results, the yield of Ch 1 as well as the branching ratio depend somewhat on the cyclobutanone pressure even at 1 Torr or less.

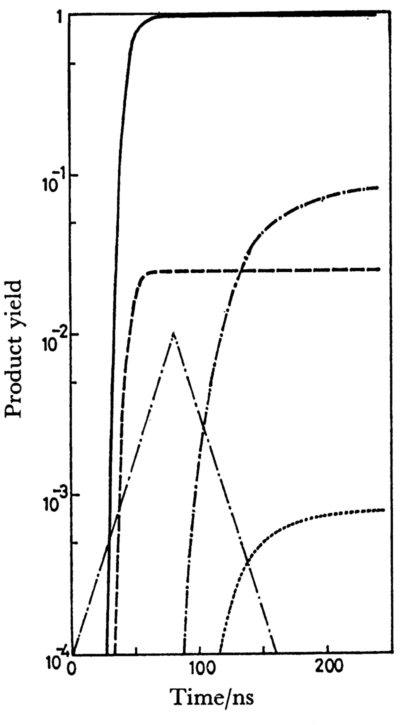

Fig. 7. Calculated time evolution of products of Ch 1 and Ch 2 under irradiations of several laser intensity. The isoscales triangle shows the time evolution of the model laser pulse (linear scale). Calculations were carried out by assuming $s=27$, and the absorption cross section$=4.5\times10^{-20}$ cm^2 molecule^{-1}, and by using the RRKM specific rates. The effective dissociation threshold is at $n=18$ (Ch 1) and at $n=21$ (Ch 2). Laser intensity, 67 J cm^{-2} pulse^{-1} (——; Ch 1, ----; Ch 2), or 6.7 J cm^{-2} pulse^{-1} (·—·—·; Ch 1, ------; Ch 2).

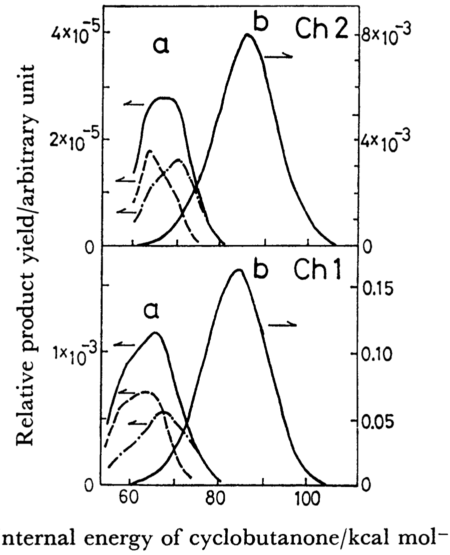

Fig. 8. The calculated dissociation yields from various levels above the dissociation energy.

a shows the results under a 4.7 J cm^{-2} pulse^{-1} irradiation. ·—·—·: The yields during the pulse, ----; the yields after the pulse, ——: the summation.

b shows the results under a 67 J cm^{-2} pulse^{-1} irradiation. In this case, dissociation is complete during the laser pulse.

The pressure of cyclobutanone was 1 Torr. $s=27$, and the RRKM specific rates with the threshold for Ch 1 at $n=18$, and that for Ch 2 at $n=20$ were adopted.

This might correspond to the gradual change from the intrinsic MPD at a lower pressure to the thermal reaction at a higher pressure as are suggested by previous researchers.[11,12] The present model calculation does not take into account the collisional events rigorously. It is worthy to note that Eq. 3 is originally derived for collision-free MPD, and the vibrational-translational energy transfer is disregarded. When the absorption cross section σ_n is assumed to be independent of n, the analytic solution of Eq. 3 with neglecting the dissociation process turns out to be a thermal distribution,

$$W_n = (1/Q)\exp(-n\hbar\omega/kT)(n+s-1)!/[n!(s-1)!]. \tag{8}$$

Here, the state density is estimated by a RRK type calculation, and Q is an appropriate partition function. In the actual MPD, the distribution may be somewhat different from the one in Eq. 8 because of the effect of the dissociation process. Anyhow in this case of the constant σ_n, collisions are expected not to affect the distribution seriously. When the cross section σ_n is different in each energy state, the distribution reached by the absorption of laser photons might be quite different from the thermal one, and may change to a large extent through collisions towards the thermal distribution. That is, the collisional events play an important role. We have not any information about the individual σ_n values, and assumed a constant cross section. We consider that the treatment on the basis of Eq. 3 with the constant σ_n is valid as a zeroth approximation, and the following comparison between the present experimental results at around 1 Torr and the model calculations should be taken rather qualitatively.

The curves drawn in Fig. 5 show the yield of Ch 1 *vs.* the laser intensity. Curve b shows the result with $s=6$ for the state density calculation. As has been stated in Experimental, the field intensity varies over 1.4 times along the laser beam between the two NaCl windows even in parallel geometry irradiation. The curve e is estimated from the data in the curve a with taking into account the inhomogeneous distribution of the field intensity. This curve should be compared with the experimental results directly. The agreement between the experimental and calculated results is good, though the theoretically predicted pressure effect is overwhelmed by the data scattering. Unfortunately, we could explain the experimental results by an alternative choice of a larger absorption cross section with a smaller s value. Thus it is impossible to decide whether the vibrational freedom is all available or not by the analysis of this kind, unless the absorption cross section is exactly known.

The curves in Fig. 6 show the dependence of the branching ratio on the laser intensity. The inhomogeneity in the field intensity does not affect the theoretical curves to any appreciable extent. The calculation could not reproduce the experimental results, even by selecting a very small s value. Thus a faster dissociation along Ch 2 than that is predicted by the previous model must be assumed in order to reproduce the experimental results. This was achieved by lowering the effective threshold energy of Ch 2 by one unit, thus from $n=21$ to $n=20$. The results are shown in the figure. The experimental results both from parallel and focussed geometry irradiations seem to be relatively well reproduced. The change in the effective threshold must not be taken so serious, because of the unrealistic, but unavoidable, quantization of energy in the present model calculation, and also because of some ambiguity in the set of the RRKM calculation. The latter is caused by the fact that the thermal decomposition experiments of cyclobutanone by previous researchers are limited to a rather small temperature range with a very small yield of Ch 2 (about 0.5%).[5-9] At the same time, the theoretical curves are affected by the way of estimation of the collisional deactivation rate constant, D, under weaker irradiation. The change of the energy threshold of Ch 2 does not affect the curves in Fig. 5 to any appreciable extent.

Isomerization of the Primarily Produced Cyclopropane. If the cyclopropane possesses an excess internal energy of more than 63 kcal mol^{-1} immediately after its production, the unimolecular process to form propylene starts to compete with the collisional stabilization.[25] The energy content of the cyclopropane may be estimated by the following relation on the assumption that the excess energy along the dissociation is equally divided to all degrees-of-freedom,

$$\varepsilon_{\mathrm{CP}} = (\varepsilon_{\mathrm{CB}} - Q_{\mathrm{endo}}) \times (3M-6)/(3N-6), \tag{9}$$

where $\varepsilon_{\mathrm{CB}}$ is the internal energy of cyclobutanone dissociating along Ch 2 and Q_{endo}, the endothermisity of Ch 2 (6.8 kcal mol^{-1} at 298 K[25]). N and M are the number of atoms in cyclobutanone and cyclopropane, respectively. The specific isomerization rates were taken from the work of Lin and Laidler,[39] and the strong collision was assumed with adopting the collisional deactivation rate constant as $1.1\times10^7\ \mathrm{s^{-1}\ Torr^{-1}}$ from the collision diameters, 5.07 Å for cyclobutanone[38] and 4.17 Å for cyclopropane.[39]

The calculated fraction of isomerization is plotted

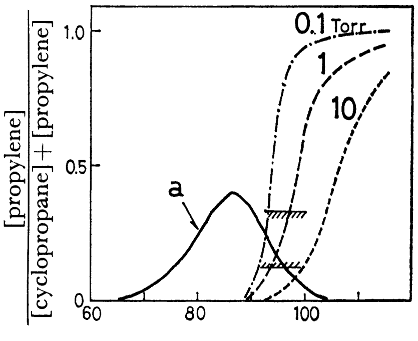

Fig. 9. The calculated degree of isomerization of the primary cyclopropane against the interanal energy of the dissociating cyclobutanone along Ch 2.
The cyclobutanone pressures of 0.1 (–·–·–), 1 (––––), and 10 Torr (------) were employed. The hatching shows the range of the experimental results. The bold line of a mountain shape is the dissociation yield distribution against the internal energy of the dissociating cyclobutanone under 67 J cm^{-2} pulse^{-1} irradiation. This is taken from Fig. 8.

against the internal energy of cyclobutanone in Fig. 9. The experimental fraction is about 0.3 in focussed geometry irradiation, which leads to the conclusion that the average internal energy of the dissociating cyclobutanone is around 95 kcal mol^{-1}, with the aid of the curve in Fig. 9. This average values seems to be somewhat higher than the average energy content of the dissociating cyclobutanone obtained in the previous model calculation under 67 J cm^{-2} pulse^{-1} irradiation, but the difference is not so large. It is also understandable that no propylene is observed in parallel geometry irradiation, where the energy of the dissociating cyclobutanone along Ch 2 is estimated to be lower than 80 kcal mol^{-1} as is shown in Fig. 8. Thus the degree of the cyclopropane isomerization does not contradict the hypothesis of the statistical molecular energy distribution in the MPD process.

The possibility of the unimolecular formation of acetylene from the primary hot ethylene without absorbing any subsequent laser photon is denied, because the process requires more than an excess energy of 70 kcal mol^{-1} [40,41] in ethylene. As an average, the ethylene possesses only a 36 kcal mol^{-1} excess energy after its formation from the cyclobutanone of 100 kcal mol^{-1} internal energy, according to the analogous estimation procedure to Eq. 9. No thermal unimolecular dissociation is known for ketene.

TABLE 1. BRANCHING RATIOS UNDER VARIOUS EXCITATION METHODS

Excitation	Ch 2/Ch1	Ref.
Pyrolysis at 350 °C	*ca.* 0.005	6
IR-MPD		
parallel ($\simeq$1 Torr)	0.015—0.03	this work
focus ($\simeq$1 Torr)	0.03—0.045	
IR-MPD		
parallel (>3 Torr)	*ca.* 0.01	11
parallel (>3 Torr)	*ca.* 0.033	12
Triplet sensitization	>*ca.* 100	42
Direct photolysis at		
334.3 nm	3.4	
313.0 nm	0.4	43
253.7 nm	0.8	

The Branching Ratio under a Variety of Excitation Procedures. The ratio of Ch 2/Ch 1 under various excitation methods are summarized in Table 1. In the photochemistry of cyclobutanone, it was established[10,42] that the triplet state (T_1, about 80 kcal mol^{-1} above S_0) of cyclobutanone decomposes exclusively to cyclopropane and CO. It was also established[10,43] that the singlet excited state (S_1, about 87 kcal mol^{-1} above S_0) undergoes $S_1 \rightarrow T_1$ intersystem crossing at a low photoexcitation energy and $S_1 \rightarrow S_0$ internal conversion at a high photoexcitation energy. The resulting hot ground state decomposes unimolecularly along the thermal dissociation channels. A molecular predissociation is also supposed to set on below 313 nm. The observed branching ratios in the photochemistry of cyclobutanone are understood according to the above scheme.

If a certain inverse intersystem crossing (or internal conversion) proceeds following the multiple photon absorption, a relatively large branching ratio is expected according to the above discussion. The observed small branching ratio in the MPD experiments denies the possibility. The fast intramolecular energy randomization and the very large difference in state densities between the ground and excited electronic states do not allow the excitation of the upper electronic states. Until now, the observation of the inverse intersystem crossing seems to be limited to the relatively simple molecule, F_2CO.[44]

Conclusion

(1) Multiple photon dissociation of cyclobutanone with 9.6 μm R(14) TEA CO_2 laser line proceeds along the same two channels as those observed in the thermal decomposition; the major one yields ethylene and ketene, and the minor one, cyclopropane and CO. Under stronger irradiations, the primary produced cyclopropane partly isomerizes to propylene, and some subsequent multiple photon absorptions of the primary products result in the formation of secondary products, particularly acetylene.

(2) From the comparison between the experimental results and a statistical model calculation concerning the laser energy effect on the product yields, the branching ratio, and the degrees of the subsequent isomerization from the primary produced cyclopropane, no sound evidence is found to reject the hypothesis that, during the laser pulse, the cyclobutanone molecules remain in external and also internal equilibria and dissociates at rates which are predicted from the unimolecular rates observed in conventional thermal experiments.

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