Infrared Multiple-Photon Decomposition of β-Propiolactone

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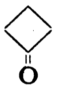
The infrared multiple-photon decomposition of β-propiolactone was found to give only ethylene and carbon dioxide with the same yield as the products, where the material balance was above 90%. This result suggests that the unimolecular decomposition into ethylene and carbon dioxide is a unique reaction channel of the compound at highly vibrationally excited states. It was shown that the decomposition probability was strongly dependent on the fluence but slightly dependent on the pressure.

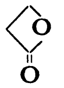
It has been well-established in several studies that there are two nonradical unimolecular reaction modes in the thermal decomposition of cyclobutanone:



$\longrightarrow C_2H_4 + CH_2CO,$ (1)
$\longrightarrow$ △ $+ CO.$ (2)

The decomposition of this compound, induced by the intense infrared radiation from a CO_2 laser, has been widely investigated to obtain information on the energy distribution of highly vibrationally excited molecules, particularly, molecules whose energies are larger than either or both of the dissociation limits.[1–4)]

It is possible for β-propiolactone to undergo three different ring cleavages, where each gives two stable molecules:



$\longrightarrow C_2H_4 + CO_2,$ (3)
$\longrightarrow CH_3CHO + CO,$ (4)
$\longrightarrow CH_2CO + H_2CO.$ (5)

The thermal decomposition of β-propiolactone in the temperature range of 205—255 °C has been found to be a first-order reaction and to yield only ethylene and carbon dioxide in equal amounts.[5)] In the present study we have carried out the infrared multiple-photon decomposition of this compound in order to examine the possible contribution of Reaction (4) or (5) under the excitation conditions at high laser fluences.

Experimental

All the samples were irradiated with the R(20) line (1078.59 cm^{-1}) of the 9.6-μm CO_2 band from a Lumonics 103 TEA laser using and N_2-free lasing medium. The pulse profile showed a fwhm of about 80 ns without tailing. The laser-beam divergence was 2 mrad. The laser was operated in a multiple transverse mode; the intensity distribution across the beam was almost flat within a deviation of 10%.

The laser irradiation was performed in two beam geometries, i.e., mildly-focused and tightly-focused (Fig. 1). A cylindrical cell (2.5 cm diameter and 5 cm long) equipped with KBr windows at both ends was used in the former geometry. The laser beam was mildly focused by a BaF_2 lens with a focal length of 100 cm after passing through a Teflon iris with a 10-mm diameter. The irradiation fluence was controlled by setting the cell at a certain distance from the lens along the beam. The fluence inside the cell could be regarded as being nearly homogeneous along the beam. A cylindrical cell (2.5 cm diameter and 10 cm long) was used with the latter geometry, where the beam was tightly focused at the center of the cell by a BaF_2 lens with a focal length of 7.5 cm. The fluence was extremely inhomogeneous along the beam within the cell; the maximum fluence ϕ_f achieved at the focal point was three orders of magnitude greater than the fluences at both ends of the cell.

β-Propiolactone was purchased from Sigma Chemical Co. and purified by vacuum distillation at −98.5 °C. The sample pressure was controlled by changing the temperature of the sample reservoir connected directly to the cell, for example, 2.5 Torr (1 Torr=133.322 Pa) at the room temperature, 0.43 Torr at 0 °C, and 0.087 Torr at −22 °C.

After connecting the cell to a vacuum line, all samples were

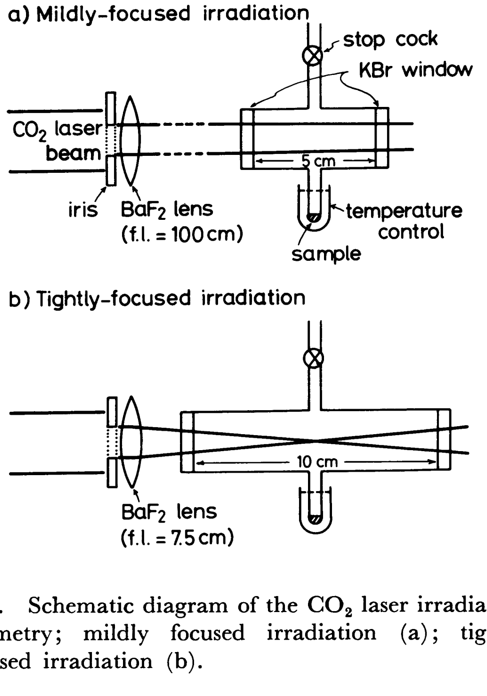


Fig. 1. Schematic diagram of the CO_2 laser irradiation geometry; mildly focused irradiation (a); tightly focused irradiation (b).

Table 1. Product Analysis of the CO_2 Lasers Irradiation of β-Propiolactone at Various Laser Fluences

Irradiation geometry	Reactant pressure / Torr	Fluence / J cm^{-2}	Product	C_2H_4/CO_2	Decomposition probability, (P_d)
MF[a]	0.43	0.34	none	—	0
TF[b]	0.43	<780	C_2H_4, CO_2	0.97	1.1×10^{-1}
MF	2.5	0.34	C_2H_4, CO_2	0.73	8.0×10^{-4}
MF	2.5	0.52	C_2H_4, CO_2	0.97	5.1×10^{-3}
MF	2.5	0.60	C_2H_4, CO_2	0.93	1.1×10^{-2}
MF	2.5	0.66	C_2H_4, CO_2	0.96	1.9×10^{-2}
MF	2.5	0.69	C_2H_4, CO_2	0.97	2.9×10^{-2}
MF	2.5	0.93	C_2H_4, CO_2	0.98	7.8×10^{-2}
MF	2.5	1.04	C_2H_4, CO_2	1.01	1.1×10^{-1}
MF	2.5	1.32	C_2H_4, CO_2	1.00	1.6×10^{-1}
MF	2.5	1.90	C_2H_4, CO_2	0.70	2.6×10^{-1}
TF	2.5	<350	C_2H_4, CO_2	0.98	1.6×10^{-1}
TF	2.5	<530	C_2H_4, CO_2	0.98	1.3×10^{-1}
TF	2.5	<640	C_2H_4, CO_2	0.99	0.9×10^{-1}
TF	2.5	<760	C_2H_4, CO_2	0.99	0.9×10^{-1}
Break down	2.5	<780	C_2H_4, CO_2	0.96	1.4×10^{-1}
			CH_3CHO, CO	—	1.6×10^{-2}

a) Mildly focused. b) Tightly focused.

passed through the two traps and cooled to −196 and −98.5 °C. Noncondensable gases such as H_2, CO, and CH_4 at −196 °C were not detected as products of the photolysis. A large fraction of unreacted β-propiolactone was captured by the trap at −98.5 °C. The condensable gases at −196 °C were analyzed by gas chromatography using a 3-m column of Porapak-Q at 50 °C.

Results and Discussion

The enthalpy changes of Reactions (3), (4), and (5) are −2.55, 12.95, and 36.7 kcal mol^{-1} (1 kcal=4.184 kJ), respectively.[5,6] Therefore, the activation energies of Reactions (4) and (5) are expected to be considerably larger than that of Reaction (3), i.e., 45.81 kcal mol^{-1}.[5] We checked the possible occurrence of Reaction (4) or (5) in the tightly-focused irradiation of β-propiolactone, although fluence homogeneity was sacrificed. At very high fluences a certain fraction of the molecules could be excited to much higher levels than the reaction thresholds. The experimental results are summarized in Table 1 for reactant pressure of 2.5 Torr. The decomposition probability P_d used in the table is meaningful only for irradiation with a homogeneous fluence, since it depends strongly on the fluence in IRMPD.[6]

$$P_d = (N_p/N_i) \times (1/t) \qquad \text{(I)}$$

where N_p represents the number of product molecules, N_i the number of reactant molecules in the irradiation volume, and t the number of laser pulses. For tightly-focused irradiation, P_d is considered to be merely the average value over the decomposition in the inhomogeneous fluence region. The laser imput energy for the tightly-focused irradiation was controlled by changing the diameter of the iris during the experiment. Table 1 tabulates the results obtained through product analyses. The IRMPD of β-propiolactone gave only ethylene and carbon dioxide as products, being similar to the pyrolysis at 205—255 °C. There was no other product, even for photolysis at a high fluence of 760 J cm^{-2}. In general, an increase in the fluence causes shifts in the vibrational energy distribution of excited molecules to the higher-energy side.[7] However, the reaction channel of β-propiolactone involves only a decomposition into ethylene and carbon dioxide, even at fairly

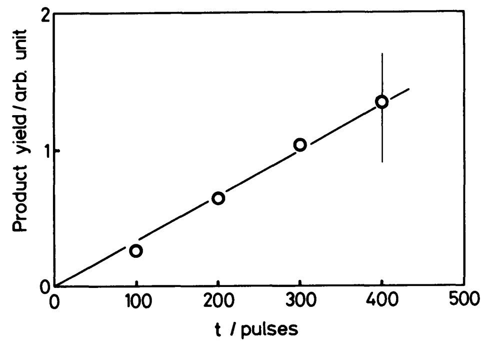


Fig. 2. Relation between product yield and laser pulse number t for multiple-photon decomposition of β-propiolactone. β-propiolactone, 2.5 Torr; fluence, 0.66 J cm^{-2}; irradiation laser wavenumber, R(20) (1078.59 cm^{-1}). The bar at 400 pulses indicates the experimental scatter.

high vibrational temperatures. When the focal fluence exceeded 760 J cm^{-2}, we observed an optical breakdown accompanied by the formation of a small amount of acetaldehyde and carbon monoxide in addition to the formation of ethylene and carbon dioxide. Acetaldehyde and carbon monoxide may be produced from electronically excited species or ionic species, because optical breakdown is essentially an electric discharge.[8]

Figure 2 shows the pulse-number dependence of the ethylene yield, where the laser fluence is 0.66 J cm^{-2}. The ethylene yield was always almost equal to the carbon dioxide yield and both yields increased linearly with the pulse number. Thus, these compounds can be produced directly from β-propiolactone. The decomposition probability was estimated to be 0.019±0.005 pulse^{-1}. Since β-propiolactone tends to be adsorbed on the walls, the adsorbed molecules on the front window might attenuate the laser intensity or decompose more efficiently than those in the gas phase. However, it may be concluded that there was no serious influence of adsorbed molecules in the present experiment. This is because the decomposition probability always remained constant throughout the irradiation period.

The material balance in the IRMPD of β-propiolactone was obtained from a comparison of the reactant consumption with the product yields. The experimental conditions were as follows: β-propiolactone pressure, 2.5 Torr; laser fluence, 0.66 J cm^{-2}; pulse number, 400 pulses. The consumption was measured with infrared absorption spectrophotometry, while the production yields of C_2H_4 and CO_2 were determined through gas chromatography. The consumption of β-propiolactone was 22.23 Torr ml, and the production yields of C_2H_4 and CO_2 were 20.25 and 21.57 Torr ml, respectively. The high material balance of 90% supports that β-propiolactone decomposes into only C_2H_4 and CO_2.

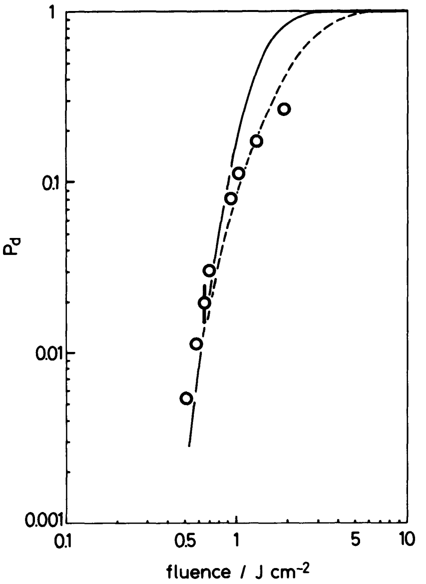


Fig. 3. Decomposition probability P_d(O) versus laser fluence observed for IRMPD of 2.5-Torr β-propiolactone. Solid curve shows the calculated P by assuming $\sigma_n=\sigma_0$. Dashed curve shows the calulated P_d by assuming $\sigma_n=\sigma_0$ $(E_n<E_a)$ and $\sigma_n=\sigma_0\times n^{-0.5}$ $(E_n\geq E_a)$.

The pressure effect on P_d was examined briefly in the irradiation of β-propiolactone at 2.5, 0.43, and 0.087 Torr, where the laser fluences were about 1.8 J cm^{-2}. The observed decomposition probabilities were 0.26 pulse^{-1} for 2.5 Torr, 0.18 pulse^{-1} for 0.43 Torr, and 0.17 pulse^{-1} for 0.087 Torr. Although the pressure variation was almost 30-fold, the probability changed from 0.26 to 0.17 pulse^{-1}. Thus, the pressure did not have a serious effect on the IRMPD of this compound. The slight decrease of P_d with decreasing pressure may be due to the so-called bottle-neck effect in a multiple-photon absorption process.[9]

The decomposition probability is plotted against laser fluence in Fig. 3, for a pressure of 2.5 Torr. P_d strongly depends on the laser fluence ϕ in a low fluence region, where P_d is approximately proportional to 7th power of ϕ. In a higher fluence region, however, the increase of P_d becomes much milder with increasing ϕ. Such a fluence dependence of P_d has been frequently observed for IRMPD.[10,11]

In order to obtain detailed information on infrared multiple-photon excitation (IRMPE), the absorption cross section σ_n and collisional deactivation rate $k_{d,n}$ were estimated from a simulation of the observed fluence dependence of P_d. Here, $k_{d,n}$ is a rate constant for a following collisional deactivation reaction:

$$A^*(v=n) + M \longrightarrow A^*(v=n-1) + M, \qquad (6)$$

where $A^*(v=n)$ denotes the vibrationally excited molecule at level n. The method has been already reported elsewhere.[11,12] Briefly speaking, the stochastic calculation was carried out for the energy-grained master equations using assumed values of σ_n and $k_{d,n}$. The pulse was assumed to have a rectangular profile with a duration of 80 ns. The specific reaction rates during unimolecular decomposition were calculated using the QRRK theory.[13] Arrhenius parameters $A=1.17\times10^{16}$ s^{-1} and $E_a=45.81$ kcal mol^{-1} have been previously reported regarding a pyrolysis study of this compound.[5] The following vibrational frequencies were used for the activated complex: $(100)^4$ $(300)^1$ $(500)^1$ $(800)^2$ $(1000)^1$ $(1200)^4$ $(1500)^2$ $(1700)^1$ $(3000)^4$.[5] The best-fit simulation in a low fluence region was obtained for the following parameters: $k_{d,n}=3.2\times10^7\times(E_n/E_a)$ s^{-1} and $\sigma_n=\sigma_0=4\times10^{-19}$ cm^{-2}. Rossi and Barker have reported that the average energy transfered per collision depends strongly on vibrational energy for azulene*.[14] This may support the assumption of the energy-dependent $k_{d,n}$ employed here. The calculated fluence depen-

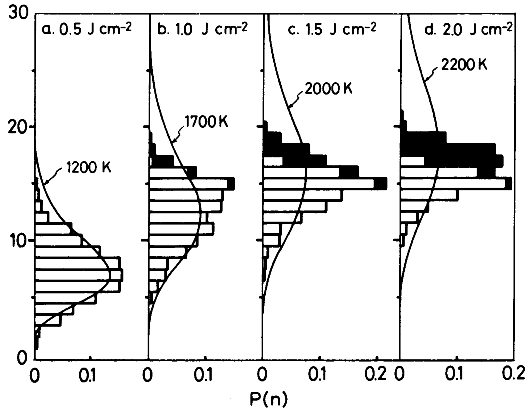


Fig. 4. Typical vibrational population distribution for β-propiolactone irradiated at various fluences. Filled areas indicate the fractions of decomposition. Solid lines show the Boltzmann distributions (Eq. II) by assuming cerain temperatures.

dence of P_d is represented by the solid curve in Fig. 3. Although the curve satisfactorily reproduces the observed dependence in the low-fluence region, there is a large discrepancy in the high-fluence region. The discrepancy may be explained in several different ways. One possible reason is that the volume irradiated in a high-fluence region is so small that the collisional quenching of excited molecules by unexcited molecules on the outer boundary of the reaction volume contributes more effectively to the reduction of P_d as compared with low fluence irradiation. Another possible reason is that a crude estimation of the absorption cross sections causes such a significant discrepancy. The absorption cross section is assumed to decrease with increasing internal energy in most of the IRMPD.[12] For example, we can improve the simulation by employing an energy-dependent absorption cross section, that is, for $E_n<E_a$, $\sigma_n=\sigma_o$; and for $E_n \geqq E_a$, $\sigma_n=\sigma_o \times n^{-0.5}$. The improved result is indicated by the dashed line in Fig. 3. At present, the simulations seem to have somewhat unavoidable uncertainties because of the lack of kinetic parameters for β-propiolactone together with an incomplete understanding of the multiple-photon absorption process. The simulation of the fluence dependence of P_d alone is thought to be insufficient to determine a unique parameter set, σ_n and $k_{n,d}$.[15]

Figure 4 shows the calculated vibrational energy distributions at various fluences, where the above-mentioned improved parameters were used. Filled areas represent the calculated decomposition fractions and solid curves represent the Boltzmann distribution $P(n)$ defined by the following equation:

$$P(n) = \frac{\rho(E_n)\exp(-E_n/\mathrm{kT})}{\sum\rho(E_n)\exp(-E_n/\mathrm{kT})} \qquad \text{(II)}$$

where $\rho(E_n)$ is the density of states at level n. The temperature was tentatively assumed as indicated in each distribution of Fig. 4. These values seem to be almost equal to the vibrational temperatures reported in IRMPD of polyatomic molecules.[16,17] The distribution estimated in the stochastic method agrees fairly well with the Boltzmann distribution in the low fluence region, where the decomposition hardly takes place. However, these two distributions do not agree with each other in the high-fluence region, where the docomposition of the molecules at vibrational levels above E_a ($n=15$) apparently disturbs the Boltzmann distribution. The vibrational temperature can not be defined exactly in the multiple-photon excitation, since the excitation is essentially regarded as a nonequilibrium process.

In conclusion, the reaction channel in the IRMPD of β-propiolactone is entirely a molecular decomposition into ethylene and carbon dioxide. Other decomposition channels with larger activation energies could not be observed at all during the irradiation of the compound at fluences as high as 700 J cm^{-2}. Since the pre-exponential factor A for the lowest channel has a large value of 10^{16} s^{-1}, the molecules excited to the levels above E_a ($n=15$) are thought to decompose rapidly before any further excitation due to light absorption.

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