

One- and Two-Photon-Induced Ring-Cleavage Reactions of Strained Benzocycloalkenes via Hot Molecules

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The ring-cleavage reactions of a series of benzocycloalkenes were studied using an ArF excimer laser. Product formation was significantly suppressed in the presence of nitrogen; therefore, the presence of vibrationally excited states (hot molecules), as intermediates, was indicated. The product of highly strained benzocyclobutene was linearly proportional to the laser fluence, whereas those of benzocyclopentene and benzocyclohexene were proportional to the square of the laser fluence in the presence of nitrogen. These phenomena cannot be understood as photochemical bond cleavage in the electronic excited state, but instead appear to be the result of single- and two-photon reactions of hot molecules. The dissociation rate constants were evaluated by a statistical rate theory under the assumption that the reaction occurred from the hot molecule. The reaction rate of highly strained benzocyclobutene was predicted to be faster than the collisional rate with foreign gas, even if it had vibrational energy equivalent to one photon; however, the reaction rates of less strained benzocyclohexene were expected to compete with the collisional rate when the vibrational energy was equivalent to two photons. Benzocyclopentene was an intermediate case and showed both single- and two-photon reactions. The dissociation rate constant of $1.4 \times 10^6 \text{ s}^{-1}$ was successfully obtained from benzocyclopentene under collision-free conditions. This value was in fair agreement with the calculated value. The different dissociation rate constants of the molecules were well-explained in terms of the strain energy. Although the strain energy varies in a wide range (10–130 kJ mol⁻¹), the simple model of the calculations reproduced the observed values of the CH₂–CH₂ bond dissociation in strained benzocycloalkenes.

Introduction

Cleavage of the carbon–carbon and/or carbon–hydrogen bond of the alkyl chain is the primary thermal reaction of alkyl group-substituted aromatic hydrocarbons such as toluene (C–H) and ethylbenzene (C–C).¹ However, ordinal thermal reactions proceed successively under static conditions, and it is difficult to solely study the primary reaction. In addition, the wide distribution of internal energy makes it nearly impossible to obtain a specific reaction rate constant. On the other hand, hot molecules, which are in a highly vibrationally excited state with the equivalent vibrational temperature of a few thousand Kelvins, can be created by VUV light irradiation in the gas phase.² The reactions of hot molecules are ideal for determining the specific rate constants for the following reasons: (1) hot molecules can be produced instantaneously with laser pulses due to an ultrafast internal conversion from an initially prepared electronic excited state, with intramolecular vibrational redistribution in polyatomic molecules being complete within a period much shorter than 1 ns; (2) hot molecules are in a microcanonical state with a small width of energy distribution; (3) the internal energy can be varied because it corresponds to the incidental photon energy plus the energy associated with the experimental temperature; and (4) if the initially prepared hot molecule is still active within the pulse width, it has a chance to absorb another photon; therefore, the photoabsorption-internal conversion sequences can accumulate the energy of several photons as vibrational energy. The reaction of hot molecules can give a specific rate constant that can be compared with the

constant obtained by a statistical reaction theory. The comparison reveals what factors affect the reaction rate constant. The dissociation rate constants of alkylbenzene via hot molecules have already been examined with regard to molecular size, especially in relation to the length of the alkyl chain, deuterium substitution, as well as the differences among structural isomers.³ Although the contribution of these factors has been understood, there is another important factor that determines the rate constants. This critical factor is the molecular strain, which should be compared with calculated figures to achieve further understanding of the reactions. The effects of molecular strain on the reaction rate constants have been well-discussed qualitatively; however, there has been no thorough quantitative treatment of strain energy.⁴

We have investigated the effects of strain energy on the dissociation rate constants of paracyclophanes (PCP).⁵ Our results have indicated that the decomposition reactions are well-explained in terms of a vibrationally excited (hot molecule) mechanism. In previous studies, we have succeeded in adjusting the reaction rate constants to the experimentally observable time window (10^6 – 10^8 s^{-1}) by methyl group substitution on the benzene ring, which increases the degrees of freedom and decreases the reaction rate constant. In the cases of paracyclophanes, it was reasonable to assume the same strain energy for all of the paracyclophane derivatives examined.

In the present study, we examined a series of benzocycloalkenes. Cycloalkanes fused with a benzene ring are useful molecules for investigating the effects of molecular strain, as the degree of molecular strain is dependent on the size of the

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ring and different from that observed in the cases of PCP.⁵ In a next step toward understanding the contribution of molecular strain on the reaction rate constants, the photochemistry of benzocycloalkenes such as benzocyclobutene (n4), benzocyclopentene (n5, indan), and benzocyclohexene (n6, tetralin) was studied with an ArF laser in the gas phase. Single- (n4, n5) and two-photon (n5, n6) reactions were observed. As for the single-photon reaction, the decomposition rate constant of n5 was successfully measured. The effect of strain energy on the decomposition rate constant was explained with statistical reaction theory in the case of n5. Unfortunately, the single-photon reaction rate of n4 was too fast, while that of n6 was too slow to be measured; the reaction rates in these cases, however, were evaluated by reaction rate theory and were found to qualitatively match the experimental observations.

Experimental Section

Benzocyclobutene (n4, Aldrich, 99%), benzocyclopentene (n5, Nacalai, 96%), and benzocyclohexene (n6, Nacalai, spectral grade) were purified by trap-to-trap distillation. Nitrogen gas with a stated purity of 99.9999% was purchased from Osaka Sanso. The sample gas pressure was adjusted with a 10-Torr capacitance manometer (MKS Baratron). Additional gas pressure was adjusted with a 1000-Torr capacitance manometer (MKS Baratron). The reaction cell was kept for over 30 min at the experimental temperature (296 K) to achieve equilibrium with the additional gas.

Absorption spectra were measured using a spectrophotometer (Shimadzu UV-2400). Gaseous benzocycloalkenes were irradiated with an ArF excimer laser (Lambda Physik Compex 102, 193.3 nm, fwhm 14 ns, 200 mJ/pulse). Laser fluence was controlled with a NaCl aqueous solution filter, and by adjusting the applied voltage of the laser. Laser fluence was measured using a pyroelectric joule meter (Genetec ED 200 and ED500). Transient species were monitored using a pulsed Xe flash lamp (EG&G FX 425) and a monochromator connected to a photomultiplier tube (Hamamatsu Photonics R758). Two different optical arrangements were constructed for obtaining time-resolved absorption spectra and rise curves under collision-free conditions. For the transient absorption spectra measurements, a perpendicular arrangement between monitor beam and the laser beam was used.⁶ The optical path length was 3 cm, and the laser beam was irradiated in an area of 0.5 cm × 3.0 cm. The transmitted monitor light was divided with a thin beam splitter into two beams after passing through a sample cell. The transmitted beam was focused into a monochromator (Jovin-Yvon HR320, $\Delta\lambda = 1.3$ nm). The reflected beam was also focused into a different monochromator (Jovin-Yvon UV10) and used to normalize the transient absorption spectra. For the dissociation rate constants measurements under a collision-free condition, a coaxial configuration between the monitor beam and the laser beam was used.⁷ The optical path length was 60 cm. A monitor light was focused into a monochromator (Acton Research SpectraPro 150) connected to a photomultiplier tube (Hamamatsu Photonics R758).

Data were collected by using a digital oscilloscope (Sony Tektronix TDS 620B) and analyzed on a Power Macintosh. The samples and cells were renewed at every laser shot to avoid effects due to the accumulation of photoproducts. Data obtained from each single-shot measurement were averaged to obtain better signal-to-noise ratios. Rise profiles were deconvoluted by an instrumental response to obtain kinetic results.

GC-MS (SATURN4D, Varian, SPB-5, 30 m) was used to identify the photoproducts.

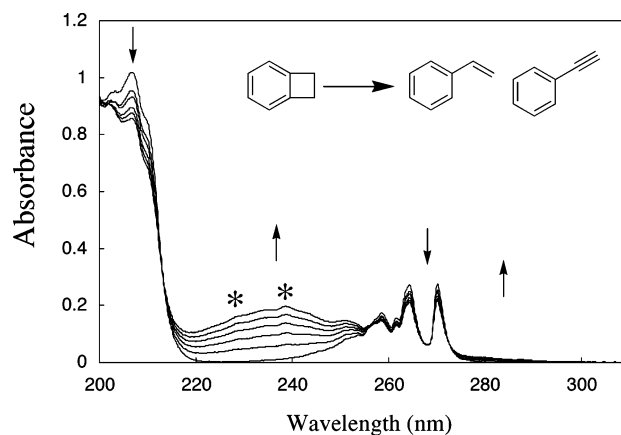


Figure 1. Absorption spectral changes of n4 on laser irradiation (0–5 laser shots). Asterisks indicate the characteristic absorption peaks of phenylacetylene.

Results and Discussion

Photoproducts Formed by Single-Laser Shots and Prolonged Laser Irradiation. All of the benzocycloalkenes photolyzed with an ArF laser were analyzed by GC-MS and UV absorption spectroscopy. Photodecomposition of the benzocycloalkenes was easily observed on the basis of their absorption spectral changes. For example, the absorption spectral changes of n4 are shown in Figure 1. New absorption at around 240 nm appeared with some isobestic points as original absorption decreased. After a single laser shot irradiation, photoproducts were collected and analyzed with a GC-MS. It should first be noted that the overall products were significantly suppressed in the presence of nitrogen gas. Photolysis of n4 gave structural isomer styrene and 2H loss product phenylacetylene. Styrene has a broad absorption between 220 and 260 nm that corresponds to the product absorption, as seen in Figure 1. Appearance of phenylacetylene was confirmed by its characteristic absorption peaks, as indicated by two asterisks in Figure 1. The major products of n5 were 1-methylstyrene and indene. Laser irradiation of n6 gave *o*-allyltoluene, 1,2-dihydronaphthalene, naphthalene, and indene. From the product analysis, the major products were found to be an allylic isomer of reactant (n4, styrene; n5, 1-methylstyrene; n6, *o*-allyltoluene) and dehydrogenated product (n4, phenylacetylene; n5, indene; n6, 1,2-dihydronaphthalene). Chapman et al.⁸ claimed that 75% of the thermolysis goes by distal bond (β -position) cleavage (a carbene intermediate formation) and 25% via proximal bond (α -position) cleavage forming styrene. It is unable to determine which mechanism is dominant in VUV photolysis by steady-state absorption spectra and products analysis. The formation of 1-methylstyrene indicating the bond cleavage occurred at the distal bond (β -position) in the case of n5. There are three possible bonds (α , β , γ) to be cleaved in the case of n6. The formation of *o*-allyltoluene as a major product indicated that β -position was dissociated. After a prolonged irradiation, some secondary products were formed such as ethylbenzene, phenylacetylene, *o*-methylphenylacetylene, and styrene from n5 and n6.

The chemical reactions of n4 have attracted much attention,⁹ and thermal decomposition of n4 has been well-studied.⁸ Flash thermolysis of n4 gave styrene as a major product. Irradiation of n4 with 254 nm light gave dihydropentalenes instead of styrene in pentane solution.¹⁰ Benzocyclobutene (n4) having bulky substituents on the cyclobutene ring showed bond cleavage of the cyclobutene ring in solution photolysis.¹¹ Photolysis of n4 in this study gave styrene as a major product,

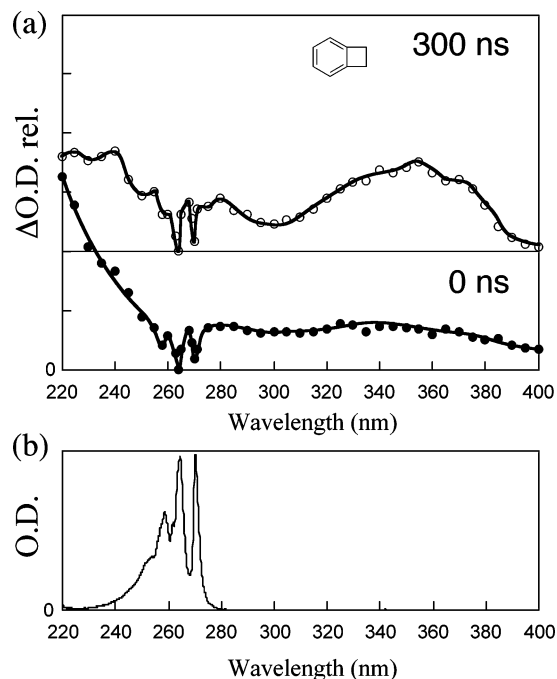


Figure 2. (a) Transient absorption spectra of benzocyclobutene (n4, 296 K, 1.5 Torr) in the presence of 380 Torr nitrogen. Data were taken 300 ns (○) and 0 ns (●) after the laser pulse. Data taken at 300 ns are shifted upward for clearer presentation. (b) Absorption spectrum of benzocyclobutene.

which indicates the presence of a similar primary reaction in both VUV photolysis in the gas phase and thermolysis: cleavage of the CH₂–CH₂ bond of the cyclobutene ring. The only difference is the formation of phenylacetylene in the photolysis. Even single-shot irradiation of n4 gave both styrene and phenylacetylene. However, it should be noted that the VUV photolysis of gaseous styrene under the same conditions also gave phenylacetylene. It is not clear whether the formation of phenylacetylene is a secondary photoreaction of styrene within the laser pulses or the subsequent reaction of hot (vibrationally excited) styrene having sufficient excess internal energy. Decomposition of n6 by focused CO₂ laser irradiation (10.6 μm)¹² was studied in relation to the thermolysis of n6.¹³ The products from n6 were n4, styrene, *o*-allyltoluene, indene, 1,2-dihydronaphthalene, naphthalene, and phenylacetylene by CO₂ laser irradiation. Contrary to the results of the VUV laser irradiation, n4 and styrene were the major products of n6. If a biradical intermediate was formed via C–C bond cleavage, there were three possible primary processes: n4 (*o*-xylylene) formation by ethylene loss, *o*-allyltoluene formation by radical rearrangement, or 1,2-dihydronaphthalene formation by the loss of two hydrogen radicals. Because the carbon-loss products were not observed as major products of the single-laser shot in the cases of benzocycloalkenes, the stepwise cleavage of two C–C bonds of n6 forming n4 would not be an energetically favored process in the case of VUV photolysis. Irradiation of a focused CO₂ laser onto n4 gave only styrene,¹² indicating that the formation of phenylacetylene by VUV laser irradiation in this study may not have originated from hot styrene (*o*-xylylene) but instead a secondary photoreaction of styrene (*o*-xylylene), which was formed instantaneously with a laser pulse.

Xylylene and Biradicals in the Transient Absorption Spectra. Figure 2 shows the transient absorption spectra of n4 in the presence of 380 Torr of nitrogen. The spectrum of the vibrationally cooled product appearing at around 350 nm (300 ns, ○ in Figure 2a) can be assigned to *o*-xylylene, which was

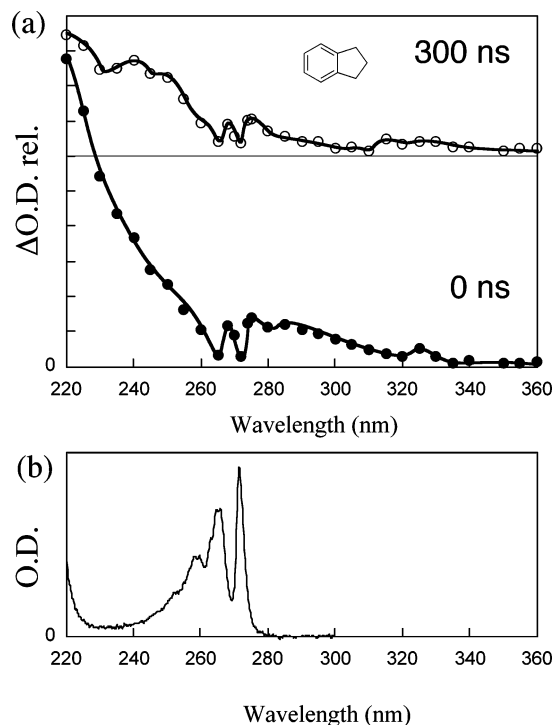


Figure 3. (a) Transient absorption spectra of benzocyclopentene (n5, 296 K, 0.9 Torr) in the presence of 280 Torr nitrogen. Data were taken 300 ns (○) and 0 ns (●) after the laser pulse. Data taken at 300 ns are shifted upward for clearer presentation. (b) Absorption spectrum of benzocyclopentene.

obtained in the flash thermolysis.¹⁴ The initial intermediate (0 ns, ● in Figure 2a), which has a broad shape as compared with that of the cooled product, can be assigned to hot (vibrationally excited) *o*-xylylene. The presence of this peak indicates that there was fast bond-breaking of n4 and that the formation of *o*-xylylene occurred within our instrumental response even in the presence of 380 Torr of nitrogen gas. Figure 3 shows the transient absorption spectra of n5 in the presence of 280 Torr of nitrogen. The depletion of the ground state can be clearly observed; however, the spectra have a broad and structureless feature in contrast to that of n4. The transient absorption of n6 also has no characteristic spectrum. The transient absorption spectrum at 0 ns, in which the absorbance increased monotonically as the wavelength decreased, can be attributed to the hot n5. This feature is common in the absorption spectra of hot molecules.¹⁵ If the transient species is a benzyl-type radical formed by a C–C bond cleavage, sharp peaks will appear in the UV region, as observed in the case of toluene photolysis (the benzyl radical has a maximum absorption at 253.5 nm).¹⁶ UV photolysis of n6 in a 3-methylpentane rigid matrix gives sharp peaks originating from a 2,3,4-trihydronaphthyl radical, a hydrogen deficient radical of n6 at 272 and 333 nm.¹⁷ However, such characteristic absorption peaks do not appear in the transient absorption spectra of n5 and n6. The results of the product analysis indicate that the C–C bond should be cleaved in all of the benzocycloalkenes examined. As clearly shown in the transient absorption spectra, the observation of *o*-xylylene indicated that C–C bond cleavage occurred at the distal bond (β -position) in the case of n4. On the contrary, the cleavage position is unable to be confirmed by the transient absorption spectra in the cases of n5 and n6. The most possible intermediates observed in the transient spectra of n5 and n6 are corresponding biradicals. The triplet state of benzocycloalkenes was not considered to be an intermediate state due to the lack

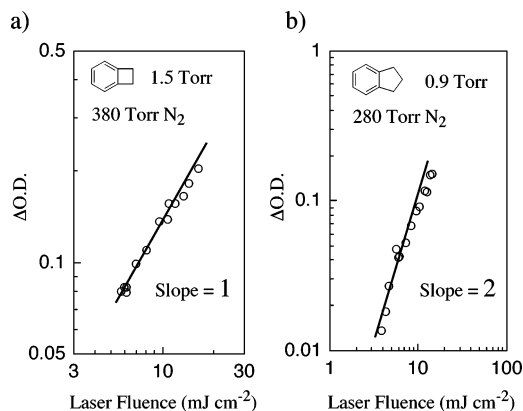


Figure 4. Correlation between transient absorbance at 300 ns and laser fluence. (a) Benzocyclobutene (n4, 296 K, 1.5 Torr, 380 Torr N₂), (b) indan (n5, 296 K, 0.9 Torr, 280 Torr N₂).

of triplet absorption. It is expected to appear in the visible region by an analogy of benzene.¹⁸

A Different Number of Photons Is Required for the Decomposition of Benzocycloalkenes. Figure 4 shows the correlation between the transient absorption of n4 and n5 at 300 ns after the laser pulse and laser fluence. The products from n4 were linearly proportional to the laser fluence, while those of n6 and n5 (not shown) were proportional to the square of the laser fluence. The initial intermediates at 0 ns, which appear to be hot molecules, were linearly proportional to the laser fluence for all benzocycloalkenes. The formation of products with two photons occurred nearly instantaneously; however, the molar absorption coefficient of products is smaller than the hot molecule of reactant, and the formation efficiency is not so large. As a result, the contributions of hot molecule on the absorbance at 0 s dominate over the products, contributing to the linear laser fluence dependence. This feature is obvious in the absence of foreign gas because the hot molecule survives for a long time. Taking into account the ionization potentials¹⁹ of benzocycloalkenes, ionization could take place with two photons if the electronic excited states act as intermediate states. However, the transient spectra showed no absorption in the visible region where the absorption of radical cations is expected to appear.²⁰ The contribution of cation radicals was negligible. Therefore, the electronic excited state is not a candidate for the intermediate state of the two-photon reaction. This striking difference in the laser fluence dependencies in benzocycloalkenes is a very characteristic feature of benzocycloalkene reactions found in this study. It is difficult to attribute the observed results to an ordinary photochemical reaction. These phenomena cannot be understood as a photochemical bond cleavage in the electronically excited state.

All of the present results indicate that the hot molecule mechanism is effective. In the case of hydrocarbons, especially benzene derivatives, we observed fast internal conversion in the gas phase when these compounds were excited by VUV light. The real-time investigation of the ultrafast internal conversion process has been well-demonstrated by Radloff et al.²¹ As a result of the fast internal conversion, the highly vibrationally excited state, a so-called hot molecule, was formed. The hot molecules react with a specific rate constant. If the reaction rate is slower than the collisional rate, the reaction is suppressed. However, if the molar absorption coefficient of the hot molecule is large enough, the second photon can be absorbed by the hot molecule and fast internal conversion takes place again. Such absorption-internal conversion sequences result in an accumulation of photon energy as a vibrational energy and

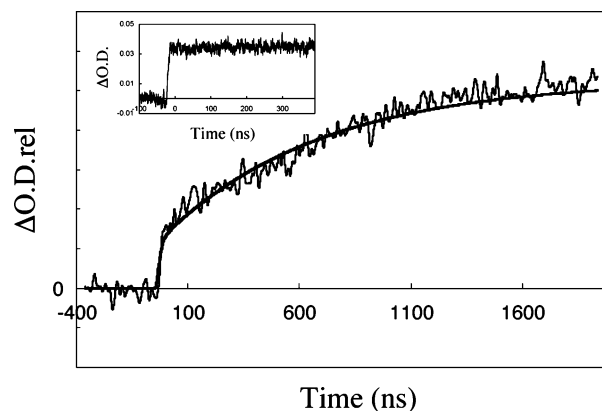


Figure 5. Transient time profile of benzocyclopentene (n5, 0.1 Torr, 296 K, 260 nm, 12 mJ cm⁻²). The solid thick full line is the fitting curve by eq 1. The inset shows the transient time profile of tetralin (n6, 0.09 Torr, 296 K, 230 nm).

cause the molecules to enter an extremely high vibrationally excited state. Even if the dissociation rate is low with single-photon absorption, second photon absorption results in a greatly increased reaction rate.²² We have examined a series of diphenylalkanes and observed up to a three-photon reaction,²³ as well as a two-photon reaction of benzene.²⁴ The two-photon absorption was sufficient to induce fragmentation of diphenylpropane, whereas three-photon absorption was necessary to induce dissociation of triphenylmethane.²⁵ These results indicate that the number of vibrational modes affects the reaction rate of the hot molecule. As the molecular size increases, the reaction rate decreases because the number of vibrational modes increases. The numbers of vibrational modes are 42 (n4), 51 (n5), and 60 (n6), respectively. Supposing that the bond dissociation energy is the same, the observed results (single- and two-photon reactions) cannot be explained by such a small difference in the number of vibrational modes. To elucidate this problem, the absolute reaction rate should be measured.

Decomposition of Hot Benzocycloalkenes under Low-Pressure Conditions. In the presence of a foreign gas, a slow hot molecule reaction will be suppressed because the collisions remove the internal energy; therefore, the transient time-profiles were measured under low-pressure conditions to obtain the reaction rate constants. The time profiles of the transients n4 and n6 did not show any increase or decrease for over 1 μ s after the instantaneous rise with a laser pulse (n6, inset of Figure 5). The results indicate that the reaction rate was too fast (we observed instantaneously formed products) or too slow (we observed a hot reactant that reacted too slowly) in the observed time-scale. On the other hand, the transient time evolution of n5 consisted of fast and slow rise components under low-pressure conditions, as shown in Figure 5. The slow rise component of n5 was diminished in the presence of a foreign gas, indicating that this slow rise is not assigned to the relaxation of a hot molecule. In addition, this observation indicated the negligible contribution of bimolecular collision because bimolecular collision should not be suppressed with foreign gas. We then assumed a time-dependent function of the concentration of the n5 photoproduct at the observed wavelength ($F(t)$) to determine the rate constant of the rise profile. The function has a single time constant (k_{obs}) and two parameters, C_1 and C_2 :

$$F(t) = P + S \exp(-k_{\text{obs}}t) + A(1 - \exp(-k_{\text{obs}}t)) \quad (1)$$

$$= C_1(1 - \exp(-k_{\text{obs}}t)) + C_2$$

where $C_1 = A - S$ and $C_2 = P + S$. P , S , and A represent the

TABLE 1: Reaction Rate Constants of Benzocycloalkenes and Paracyclophanes

	strain energy (kJ mol ⁻¹)	<i>k</i> (s ⁻¹)			
		single-photon reaction		two-photon reaction	
		experiment	calculated	experiment	calculated
n4	128	>10 ⁸	1.0 × 10 ¹⁰	b	2.3 × 10 ¹²
n5	28.5	1.4 × 10 ⁶	3.5 × 10 ⁶	>10 ⁸	7.2 × 10 ¹⁰
n6	10.5	<10 ⁶	1.1 × 10 ⁵	>10 ⁸	1.4 × 10 ¹⁰
PCP ^c	123	>10 ⁸	2.1 × 10 ⁸	>10 ⁸	1.3 × 10 ¹²
M2-PCP ^d	123	5.1 × 10 ⁷	6.5 × 10 ⁷	>10 ⁸	7.9 × 10 ¹¹
M4-PCP ^e	123	2.1 × 10 ⁷	2.3 × 10 ⁷	>10 ⁸	4.8 × 10 ¹¹

^a Dissociation energy is assumed to be 329 kJ mol⁻¹. Strain energy was assumed to be the same as that of the corresponding cycloalkene taken from ref 28. ^b Not observed. ^c [2.2]Paracyclophane. Data were taken from ref 5. ^d 4,7-Dimethyl[2.2]paracyclophane. Data were taken from ref 5. ^e 4,7,12,15-Tetramethyl[2.2]paracyclophane. Data were taken from ref 5.

absorption of product formed by a multiphoton process, the precursor hot n5, and product formed by a single-photon process, respectively. The observed rise profiles were deconvoluted with an instrumental response function. We evaluated *k*_{obs} on the basis of the averaged rise profile of n5 as 1.4 × 10⁶ s⁻¹.

To further our understanding of the effects of molecular strain (structure) on the reaction rate constants, the specific reaction rate constants were estimated by statistical reaction theory. The vibrational energies for the ground and activated complexes were evaluated in the following manner. The vibrational energies required for the RRKM calculation were obtained by Gaussian 94 (RHF, 6-31G(d,p)).²⁶ A scaling factor of 0.91 was used to adjust the calculated data to the experimental data. The vibrational frequencies of the activated complex were tentatively assumed to be 90% of those in the ground state. The calculated rate constants can be compared with the values under collision-free conditions. The CH₂–CH₂ bond dissociation was assumed to occur from the product analysis. Therefore, the dissociation energy of the CH₂–CH₃ bond in ethylbenzene (328.8 kJ mol⁻¹)²⁷ was used. The position where the bond cleaved occurred was judged from both products analysis and transient absorption spectra. The C–C bond cleavage occurred at the β-position in three benzocycloalkene examined. Therefore, the numbers of possible dissociative bonds are one (n4) and two (n5, n6), respectively. We made the simplest assumption that the strain energy for benzocycloalkenes is the same as that of related cycloalkenes. The strain energy (kJ mol⁻¹) was taken from the literature: 128 (cyclobutene), 28.5 (cyclopentene), 10.5 (cyclohexene).²⁸ For the threshold energy, we used the difference between the dissociation energy and the strain energy. The internal energy consisted of the photon energy of 619 kJ mol⁻¹ and the vibrational energy at the experimental temperature. The calculated specific reaction rate constants are compared with the observed rate constants in Table 1. The results of paracyclophanes, which were obtained by the same method and the same parameters for RRKM calculations, are also listed for comparison.⁵ Although n4 has only one dissociative bond, the reaction rate is the fastest of the molecules studied. The observed rate constant of n5 was in fair agreement with the calculated figure. The calculated values of n4 and n6 supported the experimental observation qualitatively: The single-photon reaction of n4 was too fast and that of n6 was too slow to observe by our instrumental setup. Reactions that were faster than our instrumental response were two-photon hot molecule reactions. The agreement of the results strongly supports the view that

the precursor of the reaction is a hot molecule and that the reaction takes place with a specific reaction rate constant. In the cases of PCP, we have succeeded in comparing the specific reaction rate constants and calculated figures with fixed strain energy.⁵ Although the strain energy varies in a wide range (10–130 kJ mol⁻¹), the simple model of the calculations reproduced again the observed values of the CH₂–CH₂ bond dissociation in strained benzocycloalkenes. It is concluded that the quantitative consideration of strain energy in the hot molecule reactions used in our calculation is convenient and also generally applicable.

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