Xylylene Formation from Vibrationally Hot Cyclophanes: Specific Dissociation Rate Constants of Strained Molecules[†]

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Cyclophane derivatives were irradiated with an ArF excimer laser in the gas phase. No triplet states, fluorescence, or cation radicals were observed in the transient spectra. The CH_2-CH_2 bonds dissociated, forming corresponding xylylenes by a two-photon process. The bond dissociations were explained in terms of a multiphoton reaction of hot molecules formed by an internal conversion. In addition, a slow rise of xylylene that originated in the single photon dissociation process of hot cyclophane was observed in the case of methyl-substituted paracyclophanes under low pressure conditions. The specific reaction rates of the dissociations of highly strained paracyclophanes were well explained by a statistical reaction theory, if a simple consideration of strain energy was made in the calculations.

Introduction

Determining specific reaction rate constants is one of the most important topics of research in physical chemistry.[1] The reactions of hot molecules, which are in a highly vibrationally excited state, are ideal for determining of 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; (2) hot molecules are in a microcanonical state with a small width of energy distribution; and (3) the internal energy can be varied because it corresponds to the incidental photon energy plus the energy associated with the experimental temperature. Therefore, the reaction of hot molecules will give a specific rate constant that can be compared with the constant obtained by a statistical reaction theory. The reaction of hot molecules was first proposed in 1962.[2] The dominance of hot molecule formation on irradiation with ultraviolet light was clearly investigated in the 1980s, and excellent agreement has been reported between the rate constants derived by observation and those derived theoretically.[3] Recently, hot molecule formation was reinvestigated with the help of a newly developed forms of spectroscopy. Vacuum-UV ultrafast spectroscopy showed clear evidence of the ultrafast internal conversion.[4] Photofragment translational spectroscopy is effective for discerning the contribution of a hot molecule.[5] Another recent important feature of hot molecule chemistry is a multiphoton process that occurs via hot molecules.[6] An examination of a variety of molecules strongly indicated that the dominant production of hot molecules in the gas phase can be expected in the case of aromatic hydrocarbons.[7] These molecules are suitable candidates for the determination of the specific reaction rate constants.

The issue of strained molecules is one of the most interesting dimensions of specific rate constant determination. The contribution of molecular strain to the dissociation energy is not very clear. Therefore, we addressed the question of how we can consider the strain energy in the dissociation reaction. We examined [2.2]paracyclophane (2PCP) derivatives. Highly strained 2PCP and its derivatives have attracted interests in the over 50 years since their first synthesis. The strained structure affects molecular properties, and has been investigated by spectroscopic, theoretical and crystallographic means.[8] We have examined vacuum-UV photolysis of gaseous 2PCP and methyl-substituted derivatives.[9] Fast production of *p*-xylylene (*p*-quinodimethane) as a result of the two-photonic process via hot 2PCP was found. Unfortunately, the reaction rate of 2PCP is too fast to be determined by a nanosecond laser flash photolysis system.

In this study, we examined the dissociation rate constants of highly strained cyclophanes by an ArF excimer laser in the gas phase. The dissociation rate constants were well explained by the statistical reaction theory if a simple consideration of strain energy was made in the calculations.

Experimental Section

[2.2]Paracyclophane (2PCP, Aldrich) was purified by sublimation under vacuum. 4,7-Dimethyl[2.2]paracyclophane (M2-PCP), 4,7,12,15-tetramethyl[2.2]paracyclophane (M4-PCP), [2.2]-metacyclophane (2MCP), [2.2]metaparacyclophane (2MPCP), and [2.2.2]paracyclophane (3PCP) were synthesized previously by one of the present authors (Y.S.).[10] Nitrogen gas was purchased from Osaka Sanso, and the stated purity was 99.999%. Nitrogen monoxide was obtained from Takachiho Sangyo, and the stated purity was 99.9%.

Cyclophanes (CPs) to be photolyzed were dissolved in cyclohexane which could be easily removed. About 100 μL of CP solution was deposited onto the bottom of the sample tube. The solvent was then pumped carefully away until the background pressure was less than 10^{-3} Torr, and the tube was sealed. No residue of solvent was detected. Due to the volatility

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of CPs, concentration was controlled by adjusting the experimental temperature. The temperature was controlled by a chromel−alumel thermocouple and a heater combination. The reaction cell was kept for over 30 min at the experimental temperature to achieve equilibrium with the additional gas. The decomposition of CPs was not observed at the experimental temperature.

Absorption spectra were measured by a spectrophotometer (Shimadzu UV-2400). Gaseous CPs were irradiated by an ArF excimer laser (Lambda Physik Compex 102, 193.3 nm, fwhm 14 ns, 200 mJ/pulse). Laser fluence was controlled by a NaCl aqueous solution filter, and by adjusting the applied voltage of the laser. Laser fluence was monitored by a pyroelectric joule meter (Genetec ED 200 and ED500). Transient species were monitored by a pulsed Xe flash lamp (EG&G FX 425) and a monochromator connected to a photomultiplier tube (Hamamatsu Photonics R758) combination. 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. An 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 path through a sample cell. A transmittance light was focused into a monochromator (Jovin-Yvon HR320, $\Delta\lambda = 1.3$ nm). Reflected light was focused into a 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.[11] An optical path length was 40 cm. A monitor light was focused into a monochromator (Acton Research SpectraPro 150). Additional gas pressure was adjusted with a 1000 Torr capacitance manometer (MKS Baratron).

Data were collected by a digital oscilloscope (Sony Tektronix TDS 620B), and analyzed on a Power Macintosh. The sample and cell was renewed at every laser shot in order to avoid effects due to the accumulation of photoproducts. Data obtained by each single shot measurements were averaged to obtain better signal-to-noise values. Rise profiles were deconvoluted by an instrumental response to obtain kinetic results.

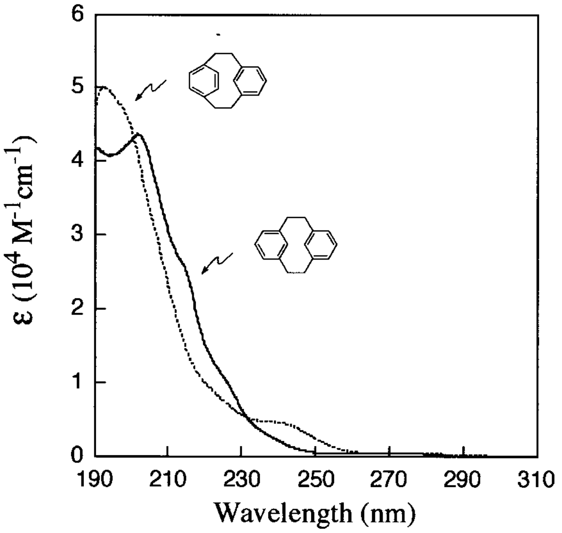

Figure 1. Absorption spectra of 2MCP (solid line, 403 K) and 2MPCP (dotted line, 413 K) in the gas phase.

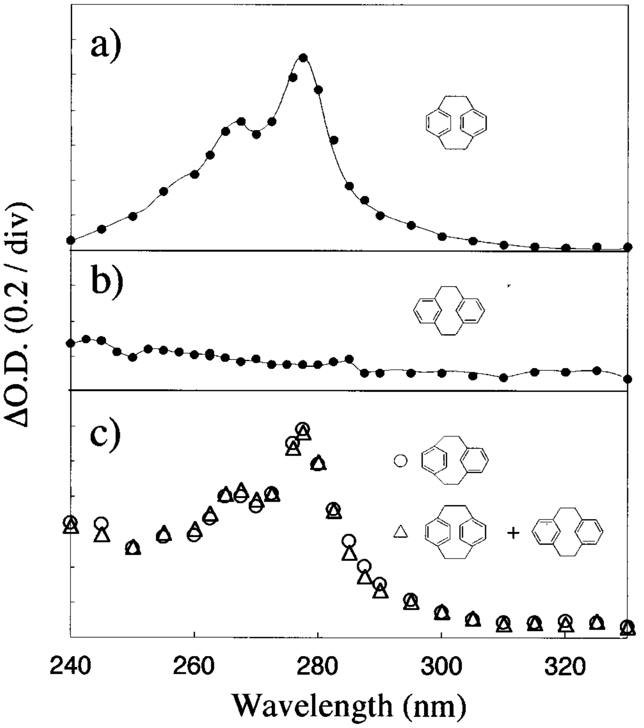

Figure 2. (a) Transient absorption spectra of 2PCP (0.23 Torr, 458 K, 10.4 ± 0.8 mJcm^{-2}, 615 Torr of nitrogen). (b) Transient absorption spectra of 2MCP (1.84 Torr, 453 K, 8.5 ± 0.6 mJ cm^{-2}, 610 Torr of nitrogen). (c) The comparison of transient absorption of 2MPCP (open circle, 1.3 Torr, 423 K, 11.0 ± 1.0 mJ cm^{-2}, 570 Torr nitrogen), and reproduced spectrum with that of 2MCP and 2PCP (open triangle). The ground-state absorption was corrected. Data were taken at 100 ns after the laser pulse.

Results

Xylylenes Formed by a Multiphoton Process under High-Pressure Conditions. Figure 1 shows the gaseous absorption spectra of 2MCP and 2MPCP. Absorption spectra taken in the gas phase are consistent with those reported in the condensed phase[12] with a small spectral shift toward the short wavelength side. As was reported in our earlier paper, 2PCP derivatives decomposed to the corresponding *p*-xylylenes (*p*-quinodimethane) as a result of ArF laser irradiation.[9] In the present study we photolyzed other cyclophanes (CPs) such as 2MCP and 2MPCP. To observe vibrationally relaxed products, the transient absorption spectra were measured in the presence of several hundred Torr of nitrogen. Figure 2 compares the transient absorption spectra of 2PCP, 2MCP, and 2MPCP. The transient spectrum of 2PCP (Figure 2a) clearly shows *p*-xylylene formation as was reported previously.[9] 2MCP (Figure 2b) shows a structureless and broad spectrum over the entire wavelength region. Analogy with 2PCP photolysis suggests that *m*-xylylene would be formed from 2MCP by CH_2-CH_2 bond cleavage. The absorption spectrum of *m*-xylylene was measured in a low-temperature rigid matrix; however, the spectrum features are not clear.[13] 2MPCP (Figure 2c, open circle) has a transient spectrum similar to that of 2PCP, although a broad peak was observed around 320 nm. We then tried to reproduce the transient spectrum of 2MPCP with that of 2MCP and 2PCP. Reasonable agreement was observed between the transient spectra of 2MPCP and the sum spectrum of 2MCP and 2PCP, as shown in Figure 2c. From the results described above, we concluded that a CH_2-CH_2 bond dissociation occurred in the case of 2MPCP. Similarly, a bond cleavage should occur in the case of 2MCP. 2MCP forms two *m*-xylylenes, and 2MPCP forms *m*- and *p*-xylylene.

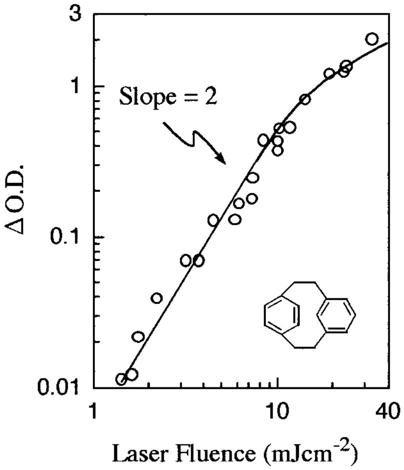

Figure 3. Correlation between xylylenes produced from 2MPCP and laser fluence in the presence of 570 Torr of nitrogen (1.3 Torr, 423 K, 277 nm).

The most significant difference between *m*-xylylene and *p*-xylylene is in a subsequent reaction. The spectral change in *p*-xylylene was not observed for a few microseconds after the laser pulse. On the contrary, *m*-xylylene showed a slow spectral change even in the presence of 610 Torr of nitrogen. No appreciable pressure dependence of 2MCP was observed in the rise curves (typically at 255 nm). The unimolecular reaction would then be attributable to the instability of *m*-xylylene. To obtain more information about the transient, the spectra were taken in the presence of nitrogen monoxide. Nitrogen monoxide can trap the carbon-centered radical, as in the case of the phenyl radical.[14] The slow rise observed at 255 nm was diminished in the presence of 8 Torr of NO and 610 Torr of nitrogen, indicating that the reaction between *m*-xylylene and NO obstructed the unimolecular reaction of *m*-xylylene.

Figure 3 shows the correlation between the transient absorption of 2MPCP and laser fluence. The slope of the plot indicated that the formation of *p*-xylylene is a two-photon process. Saturation of the transient absorbance was observed above 10 mJ cm^{-2}. This finding can be explained in terms of the depletion of the ground state of 2MPCP. Two-photonic transient formation was also observed in the cases of 2MCP, 2PCP, M2-PCP, and M4-PCP. The reaction completed within the laser pulse duration indicated a fast reaction rate constant of ($>2 \times 10^8$ s^{-1}).

Slow Rise of Xylylenes from Methyl-Substituted Paracyclophane under Low-Pressure Conditions. A significant difference was found between the time profiles of CPs under low-pressure conditions and those measured in the presence of a foreign gas. The formation of xylylenes was completed within the laser pulse in the presence of foreign gas. Figure 4a shows the transient profiles of M4-PCP under low pressure conditions. Laser flash photolysis of M4-PCP as well as M2-PCP produced both instantaneously formed and gradually formed species. The absorption of the former built up within the duration of the laser pulse. The absorption of the latter, which was diminished in the presence of foreign gas, built up over a submicrosecond time scale. On the contrary, the slow rise of *p*-xylylene from 2PCP was not observed even though the experiments were performed under collision-free conditions. The formation of *p*-xylylene was completed within the laser pulse duration. The fast two-photon reaction is dominant in the case of 2PCP.[9] As judged from the time-resolved spectra, the slow rise observed in the cases of M2-PCP and M4-PCP did not originate in the dissociation of CH_2−H bonds but in the formation of *p*-xylylenes.[9] In addition, the vibrational relaxation of hot molecules does not correspond to the rise profile, because the molecular collision is negligible under low-pressure conditions. These results suggest that multiple instances of the same chemical reaction (CH_2−CH_2 bond cleavage) occurred concurrently, but with different rate constants, in the cases of methyl-substituted 2PCPs. Observation of the slow dissociation process strongly supports the hot molecule mechanism.

We then assumed a time-dependent function of the concentration of photoproducts at the observed wavelength ($F(t)$) to determine the rate constants of the rise profiles. The function has a single time constant (k_{obs}) and two parameters, C_1 and C_2:

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

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

where $C_1 = A - S$ and $C_2 = P + S$. P, S, and A represent the absorption of xylylene formed by a multiphoton process, the precursor hot CP, and xylylene formed by a single-photon process, respectively. The observed rise profiles were deconvoluted with an instrumental response function. We evaluated k_{obs} and the ratio C_2/C_1 on the basis of the averaged rise profiles.

As is clearly seen in Figure 4a, the amounts of the fast-rise and slow-rise components depend on the laser fluence. As the laser fluence increases, the contribution of fast rise components increases dramatically. Figure 4b shows the correlation between the transient absorption of M2-PCP and laser fluence. The open and full circles represent the amount of fast- and slow-rise components, respectively. This figure shows that the fast-rise component is proportional to the square of the laser fluence, while the slow-rise component is linearly proportional to the laser fluence. The fast rise is attributed to the two-photon process being completed within the laser pulse duration, as in the case of 2PCP. The slow-rise component was diminished in the presence of foreign gas. Therefore, we concluded that the slow-rise component originates in the reaction of the hot molecules.

Figure 5 shows the typical rise profiles of M2-PCP and M4-PCP. The formation of *p*-xylylene from M2-PCP is faster than from M4-PCP. The rate constants were almost identical in the pressure ranges of 0.05−0.30 Torr (M2-PCP) and 0.06−0.17 Torr (M4-PCP), being regarded as ones under collision-free conditions. The data were then averaged. The obtained rate constants are listed in Table 1.

Discussion

The Hot Molecule Mechanism is Operative in the Photochemistry of Cyclophanes in the VUV Region. As we have reported in an earlier paper, 2PCP decomposed to the corresponding *p*-xylylenes as a result of ArF laser irradiation.[9] The decomposition mechanism was well explained in terms of the multiphoton hot molecule mechanism. If a molar extinction coefficient of a hot molecule is larger than that of the ground-state molecule, the multiphoton reaction would take place efficiently. For example, the molar extinction coefficient (193.3 nm) of benzene in the ground state is ca. 4650 M^{-1} cm^{-1} at room temperature, while it is ca. 9000 M^{-1} cm^{-1} at 3389 K for hot benzene. The second photon was absorbed by the hot benzene and decomposed.[15] Similarly, second-photon absorption expected to occur in hot CPs. A strong absorption band originated in the allowed transition of the benzene moiety presumably exists in the region where wavelengths are shorter than 190 nm. It is expected that this band will be broadened and have a high molar extinction coefficient at the laser

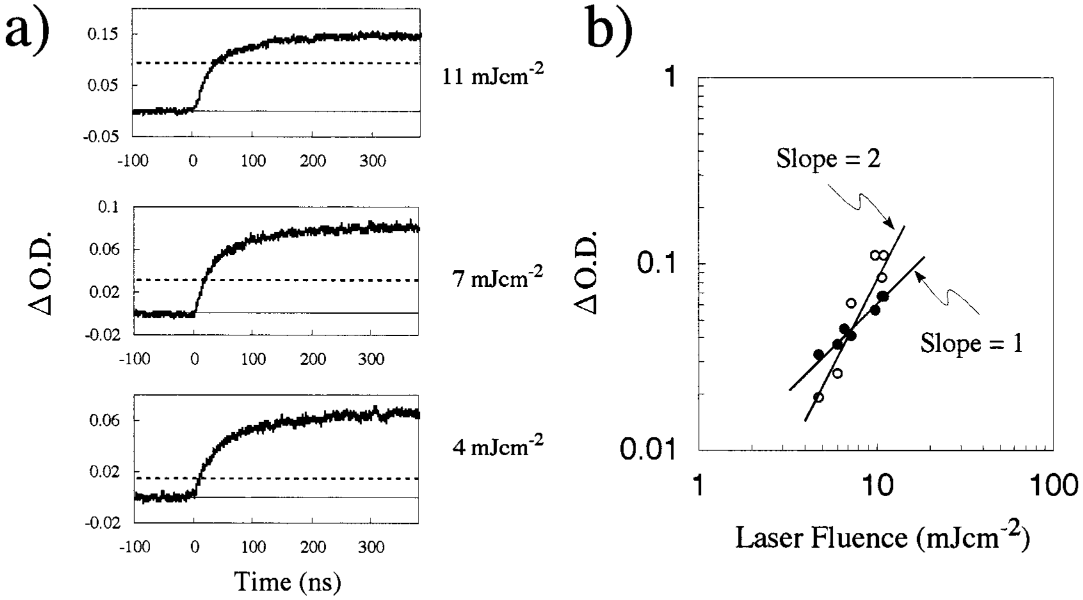

Figure 4. (a) Rise profiles of dimethylparaxylylene formation form M4-PCP (0.17 Torr, 413 K, 275 nm) at different laser fluence. Dashed line is the boundary line between fast- and slow-rise components. (See text.) (b) Correlation between the absorbance of methylparaxylylene and laser fluence. Methylparaxylylene formed by slow process (full circle) and by fast process (open circle) from M2-PCP (0.30 Torr, 423 K, 280 nm) were plotted against the laser fluence.

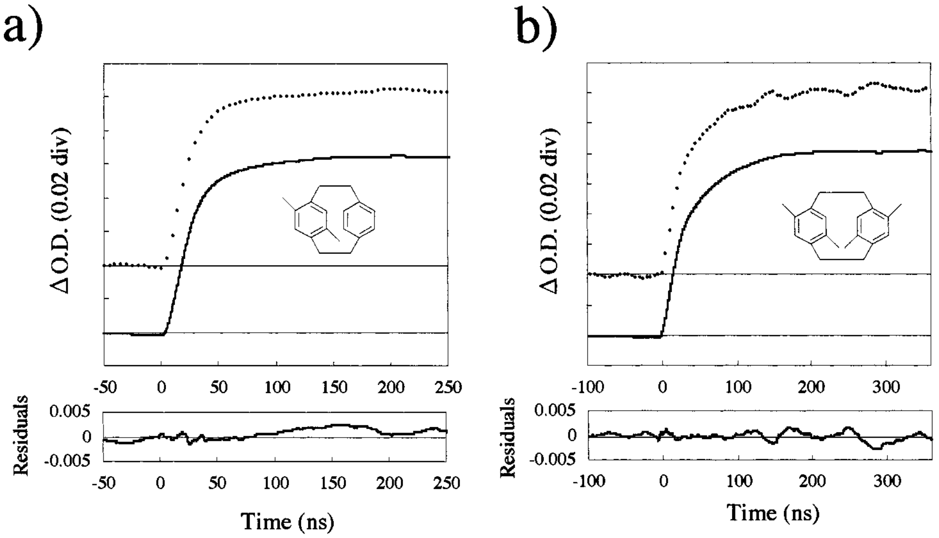

Figure 5. Rise profiles of paraxylylene formed from methyl-substituted paracyclophanes. (a) M2-PCP (0.3 Torr, 423 K, 280 nm, 9.0 mJ cm^{-2}). (b) M4-PCP (0.17 Torr, 413 K, 275 nm, 9.4 mJ cm^{-2}). Dotted lines are observed signals, and solid lines are fitting curves simulated by using eq 1 and profiles of instrumental response.

TABLE 1: Observed (k_d) and Calculated (k_{calcd}) Dissociation Rate Constants of Cyclophane Derivatives

	strain energy (kJ mol^{-1})[a]	k_{obs} (s^{-1})[b]	k_{calcd} (s^{-1})[c] 1 *hν*	2 *hν*
M2-PCP	123	5.1×10^7	6.5×10^7	7.9×10^{11}
M4-PCP	123	2.1×10^7	2.1×10^7	4.8×10^{11}
2PCP	123	$>2 \times 10^8$	2.1×10^8	1.3×10^{12}
2MCP	50	*d*	1.6×10^5	2.3×10^{10}
2MPCP	98	*d*	2.1×10^7	3.6×10^{11}
3PCP[7]	0	1.9×10^7	$<10^3$	5.7×10^7

[a] Data were taken from the literature. See the text for details. [b] Dissociation rate constants measured under collision-free conditions. [c] Specific reaction rate constants calculated on the basis of RRKM theory. See text for details. [d] Not measured because of the existence of the successive reaction of *m*-xylylene.

wavelength at high temperatures. Observationally, we found that efficient two-photon reactions occurred for all of the CPs examined, although the species corresponding to the hot CPs were not observed in the transient absorption spectra. Thus an efficient two-photon absorption by the hot CPs occurred, and xylylene was formed during the laser pulse duration. The hot CPs with single photon energy (193.3 nm) correspond to equivalent vibrational temperatures of 1610 K (2MCP), 1580 K (2MPCP), 1590 K (2PCP), 1440 K (M2-PCP), and 1310 K (M4-PCP), the temperatures being estimated with vibrational energies obtained theoretically.[7] The absorption of the second photon will increase the temperature. At such high temperatures, a chemical reaction is expected to occur.

The photochemistry of CPs in the condensed phase can be described as follows. Photodissociation of 2PCP[16] and photocyclization of 2MCP[17] have been reported. Photoirradiation of 2PCP in a low-temperature rigid matrix produced intermediate species such as *p*-xylylene and biradical species in which two benzyl radicals are linked together by an ethylene bridge in the *p*-position.[18] These two species can be distinguished by their absorption spectra. Biradical abstracts hydrogen from the parent CPs finally formed stilbene derivatives and alkylated phenanthrene.[19] In contrast, the final products after the thermolysis of CPs are styrene, xylenes, benzene, toluene, and benzocyclobutene. Successive thermal rearrangement and interconversion of xylylene isomers occurred during the pyrolysis process (930 °C, 0.1 Torr).[20] Only *p*-xylylene was successfully trapped on a cold surface after the flash vacuum thermolysis (2PCP, 655 °C).[21] *p*-Xylylene further polimerizes to form polyparaxylylenes.[22] Through the examination of transient absorption spectra, no absorption corresponding to the biradical species was found. The enthalpy difference between biradical and *p*-xylylene is only 20 kJ mol^{-1}.[9] It is reasonable to assume that the subsequent dissociation reaction of biradical to *p*-xylylene occurs in a short time. The rate determining step is the first bond dissociation process. The spontaneous dissociation of the two CH_2-CH_2 bonds does not occur because the internal vibrational energy is insufficient to break the two bonds simultaneously if the hot molecule mechanism is operating.

The subsequent reaction of *m*-xylylene may be originated in the isomerization to more stable one. Both *p*- and *o*- xylylene, which have less biradicaloid character than *m*-xylylene,[23] were successfully characterized by absorption spectroscopy. Thermolysis of 2MCP formed *p*-xylene (35%) rather than *m*-xylene (3%).[24] This fact suggested that *m*-xylylene would not be stable compared with *o*- and *p*-xylylene. The similar interconversion of *m*-xylylene, observed in the thermolysis, was also occurred in the case of laser flash photolysis experiment.

As was clearly shown in the preceding section, reactions proceed with two photons. The ionization potentials of the CPs are 8.1 eV (2PCP),[25] 8.24 (2MCP),[26] and 7.75 eV (M2-PCP, M4-PCP).[25] Therefore, the energy corresponding to two photons (12.8 eV) is enough to ionize any of the CPs. However, no transient absorption appeared in the visible region, where absorption of the cation radical and $T_n \leftarrow T_1$[27] should occur. In the case of 2MCP, the internal conversion yield is estimated to be almost unity even in the condensed phase.[17] The two-photon process via a triplet state occurs in a low-temperature matrix;[18c] however, all of the results indicate that the intermediates in the two-photon process is not in an electronic excited state but in an electronic ground state. It should be noted that it was not a radical cation but radical-like products that were formed, even though a multiphoton reaction took place. These observations are the characteristic features of a multiphoton reaction that occurs via a hot molecule.[7] A simple summation of the photon energy exceeds the ionization potential; however, the photon energy is distributed over the whole vibrational mode in a very short time after an ultrafast internal conversion. If the photon energy is distributed equally to each vibrational mode, the energy is only a few kJ mol^{-1} per vibrational mode. Therefore, the absorption of the second photon does not provide enough energy to ionize the molecule. Ionization does not occur, but the reaction rate of the hot molecule increases due to the accumulation of vibrational energy as a result of photoexcitation/internal conversion sequences. All of the results indicate that the VUV photochemistry of CPs can be explained in terms of a hot molecule mechanism.

Specific Reaction Rate Constants of Strained Paracyclophane Derivatives: A Comparison between Experiments and Statistical Reaction Theory. In principle, both single and multiphoton hot molecule reactions could be observed concurrently, although their reaction rates are very different. These reactions can be best distinguished when the reaction rates differ by several orders of magnitude. The slow reaction should occur within a measurable time duration, and the fast reaction should be completed within the instrumental response of our nanosecond laser flash photolysis system. Suppression of the slow reaction can be achieved either by adding a foreign gas or by increasing the concentration of the reactant itself, as the hot molecules deactivate by virtue of molecular collisions. We can diminish the one-photon process of a hot molecule by adjusting the pressure. For transient absorption measurements, experiments were carried out in the presence of a large amount of foreign gas to observe vibrationally relaxed products. Under these conditions, the collisional deactivation rate of a hot molecule is much faster than the reaction rate constant of a hot molecule having energy corresponding to a single photon. Assuming that the collisional frequency is 5×10^7 Torr^{-1} s^{-1}, the collisional rate is calculated to be 2.9×10^{10} s^{-1} (570 Torr of nitrogen). Therefore, only the fast hot molecule reaction was observed. For the single-photon hot molecule reaction to be observed, the molecular collision rate must be smaller than the reaction rate constant. In addition, the molar absorption coefficient of the hot molecules increased and/or decreased with time due to the vibrational cooling. The experiments were then carried out under low-pressure conditions. We have measured specific reaction rate constants for the formation of *p*-xylylenes (Table 1).

As was clearly shown in Figure 5, the reaction rate became slower with methyl substitution. As the number of vibrational modes increases, the rate constant would decrease if the hot molecule mechanism is operating. The number of vibrational modes of the various CPs are 90 (2PCP), 108 (M2-PCP), 126 (M4-PCP), and 138 (3PCP). The order of the reaction rate constants would be 2PCP > M2-PCP > M4-PCP > 3PCP, if the reaction threshold energy does not differ among these. To compare the experimental data with that obtained by statistical reaction theory, the same conditions were assumed when the calculations were performed. The vibrational energies required for RRKM calculation were obtained by Gaussian 94 (RHF, 6-31G).[28] A scaling factor of 0.9085 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 are the values under collision-free conditions. The dissociation energy of the CH_2-CH_3 bond cleavage in ethylbenzene (328.8 kJ mol^{-1})[29] was used. The strain energies (kJ mol^{-1}) of the CPs were taken from the literature: 2PCP (122.6),[30] 2MCP (49.8), and 2MPCP (97.9).[31] The strain energy of methyl-substituted 2PCPs was assumed to be the same as that of 2PCP. We hypothesize that 3PCP has no strain energy. 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. Thermal distribution of internal energy is important in rate constant calculations because CPs have rather broad distribution compared with small molecules due to the large number of oscillators. The semiclassical equilibrium distribution of vibrational energy[32] was calculated; for example, the largest molecule (M4-PCP at 413 K) has the average thermal energy of 84.2 kJ mol^{-1} (fwhm 34.4 kJ mol^{-1}).[33] The thermal distribution was taken into account for evaluating the specific reaction rate constants. The calculated specific reaction rate constants of CPs are compared with the observed rate constants in Table 1. The observed rate constants are in fair agreement with the calculated figures. These results strongly support the view that the precursor of the slower reaction is a hot molecule. Reactions that were faster than our instrumental response are expected for two-photon hot molecule reactions. It is surprising that such a simple model of the calculations reproduced the observed values.

The reactions of hot molecules produced by laser irradiation are the most useful for determining of the specific reaction rate constants because of the narrow energy distribution and instantaneous response of the hot molecule formation. For investigating the effect of strain energy on the specific reaction rate constants, CPs provide representative example; however, some difficulties arise in high-temperature experiments. In addition, accurate rate constant measurement is limited by an accessible time-window. In the transient absorption measurements taken in the gas phase, the observable time-scale is limited by the molecular movements, as the target molecules will escape from the observing volume. Under our experimental conditions, reliable data may be obtained until 1 μs after the laser pulse. Using our instruments, the observable time window is 10^6−10^8 s^{-1}, but the lower limit of the reaction rate constant measurement can be extended by other detection techniques. Reaction rates on the order of 10^4−10^5 s^{-1} were measured with the multimass ion imaging technique[34] and the time-of-flight technique.[35] Using substitution to decrease the reaction rate constant by increasing the vibrational modes is valid; however, a molecule becomes nonvolatile as its molecular size increases. Tunable lasers are strong tools which can vary the internal energy of a molecule. For further investigation of faster hot molecule reactions, a VUV short laser pulse is necessary. VUV picosecond or femtosecond lasers will extend the measurable rate range up to 10^{13} s^{-1}.

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