Mechanism of Formation of o-Methylbenzyl Radical by Photodissociation of o-Xylene in Solution

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Photodissociation of o-xylene in room temperature n-heptane solution has been studied by means of two-pulse laser-induced fluorescence and transient absorption spectroscopy. Excitation of o-xylene at 266 nm into the S_1 state causes the molecule to undergo carbon-hydrogen bond homolysis in its methyl group, resulting in formation of the o-methylbenzyl radical. The fluorescence of the o-methylbenzyl radical has been observed around 500 nm with a lifetime of 4.1 ± 1.0 ns, when it has been excited with a 308-nm pulse after the photolysis pulse. The absorption of the o-methylbenzyl radical has been obtained with maxima at 309 and 320 nm. The formation rate constant of the o-methylbenzyl radical, $(3.1 \pm 0.4) \times 10^7$ s⁻¹, agrees with the decay rate constant of the fluorescence of o-xylene, $(2.7 \pm 0.3) \times 10^7$ s⁻¹. It is concluded that excitation with one photon at 266 nm followed by vibrational relaxation populates the thermal equilibrium S₁ state of o-xylene, from which predissociation occurs.

Introduction

Photodissociation of methyl-substituted benzene molecules has been known to induce carbon-hydrogen bond homolysis in their methyl group and to generate a (methyl-substituted) benzyl radical and a hydrogen atom. The photochemistry of methyl-substituted benzenes has been studied in an effort to elucidate the photodissociation mechanism of these compounds. Various experimental techniques have been employed.

Schwartz and Albrecht¹ have studied the photochemistry of rigid solution of durene at 77 K. It has been shown that carbonhydrogen bond fission producing the 2,4,5-trimethylbenzyl (duryl) radical suffers an abrupt change from a two-photon to a onephoton process upon raising the photolysis light energy from 436 kJ mol⁻¹ (275 nm) to 451 or 476 kJ mol⁻¹ (266 or 252 nm). Haider *et al.*² have investigated the mechanism of formation of the 3,5-dimethylbenzyl radical generated by UV photolysis of matrix-isolated mesitylene. They have reported that the 3,5-dimethylbenzyl radical is produced by photolysis of the triplet state of mesitylene with 249-, 337-, or 405-nm excitation.

Hippler et $al.^3$ have studied the formation mechanism of the benzyl radical from cycloheptatriene in the gas phase after laser excitation. Highly vibrationally excited toluene in the electronic ground state has been found to be produced by electronic excitation of cycloheptatriene at 248 nm followed by internal conversion and unimolecular isomerization. A carbon-hydrogen bond cleavage reaction has been proposed to occur via this hot toluene. Ikeda et al.4-6 have investigated photodissociation of alkylsubstituted benzenes by 193-nm photolysis under a collision free condition. They have discussed that hot alkylbenzene is formed by internal conversion from a photoexcited state and that decomposition of hot alkylbenzene yields the benzyl radical. It has also been reported that hot alkylbenzene absorbs a second photon which causes dissociation into the benzyl radical. Troe's group⁷⁻⁹ has studied formation of the benzyl radical from alkylbenzenes by excitation at 193 nm in the gas phase. Specific and thermally averaged rate constants as well as a quantum yield for dissociation of hot alkylbenzene have been determined. A yield for benzyl formation by two-photon absorption has as well been analyzed.

There have been few reports concerning a photodissociation mechanism of a carbon-hydrogen bond in room temperature solution. Kelley *et al.*^{10,11} have examined the formation kinetics

of the 1- and 2-naphthylmethyl radicals from 1- and 2-(halomethyl)naphthalenes, respectively, in solution by means of a twocolor laser-induced fluorescence experiment. It has been proposed that the $S_2(\pi,\pi^*)$ state energy dissipation process of the parent species involves a channel of intersystem crossing to an upper triplet state which is itself or crosses to a dissociative $T_n(\sigma,\sigma^*)$ state that leads to homolysis of the carbon-halogen bond.

The above studies of photolysis of aromatic molecules present problems which need an empirical investigation on photodissociation of methyl-substituted benzene in solution at room temperature: (1) identification of the excited state from which dissociation occurs; (2) estimation of the number of photons which are required to promote the molecule to its dissociative state. In the present study, two-pulse laser-induced fluorescence and transient absorption experiments have been employed to seek answers for these problems. A formation rate of the omethylbenzyl (o-xylyl) radical has been measured, and dependence of a fluorescence intensity of the o-methylbenzyl radical on incident pulse intensities has been investigated. The photodissociation mechanism of o-xylene in room temperature solution is discussed with these findings.

Experimental Technique

Chemicals. Guaranteed reagent grade o-xylene (Kanto Chemical) and α -chloro-o-xylene (Tokyo Chemical Industry) were purified by distillation. Spectroscopic grade *n*-heptane (Dojindo) was used without further purification. Sample solution of o-xylene or α -chloro-o-xylene in *n*-heptane was degassed by multiple freeze-pump-thaw cycles, and sealed in a 1×1 cm quartz cell. The sample concentrations were ca. 6.8×10^{-3} mol dm⁻³ for o-xylene and ca. 1.0×10^{-2} mol dm⁻³ for α -chloro-o-xylene. The molar extinction coefficient was measured with an absorption spectro-photometer (Hitachi U-2000).

Laser-Induced Fluorescence Measurement. A pulse of the fourth harmonic (266 nm, 4–5 ns) of a Nd:YAG laser (Quanta-Ray GCR-11) was used as phototolysis light. In a one-pulse laser-induced fluorescence experiment the fluorescence generated by only the 266-nm pulse was recorded. A two-pulse laser-induced fluorescence experiment was performed by utilizing a second pulse (308 nm, 8-12 ns) from a XeCl excimer laser (Lumonics 500) to excite the radical. The delay time between the 266- and 308nm pulses was adjusted by a digital delay generator (EG&G Princeton Applied Research 9650). Laser pulse intensities were attenuated by neutral density filters (Sigma Koki) and measured

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by a thermopile detector (Ophir 03A-P, DGX). The 266- and 308-nm laser beams were focused coaxially on the cell to 1.2×12 - and 1.6×4.0 -mm rectangular profiles, respectively. The fluorescence was collected at a right angle to the excitation beams into a 10-cm monochromator (Ritsu MC-10N) and recorded with a photomultiplier (Hamamatsu R666) and a storage oscilloscope (Iwatsu TS-8123, V810, H830). Signals were accumulated with a personal computer (Fujitsu FM-16 β) in order to improve a signal-to-noise ratio.

Transient Absorption Measurement. A pulse of the fourth harmonic (266 nm, 4-5 ns) of a Nd:YAG laser (Quanta-Ray GCR-11) was used for photolysis. Analysis light was provided by a Xe arc lamp (Ushio UXL-500D-O) whose intensity was increased for a period of 4 ms by a lamp pulser. The analysis light was blocked from the cell by an electrical shutter. The shutter was opened before the lamp pulser was triggered; after the intensity of the analysis light reached its plateau and decreased to its usual level, the shutter was closed again. The lamp beam which was collimated to a 0.8-mm diameter fell on the cell at a right angle with the laser beam that was of a 1.2×12 -mm size. The distance from the laser irradiation inner surface of the cell to the lamp beam center path in the cell was 1.9 mm. For measurement in the spectral region of 250-400 nm, a color glass filter (Toshiba UV-D33S) was placed in front of the monochromator. The detection system for the analysis light was the same with the fluorescence measurement.

Results

Laser-Induced Fluorescence Spectra. In the two-pulse fluorescence experiment sample solution containing o-xylene has been excited first at 266 nm and subsequently at 308 nm. The fluorescence induced by the latter pulse has been collected. The fluorescence spectrum depicted by the upper curve in Figure 1a has been observed with the pulse intensities of 10 and 80 mJ $\rm cm^{-2}$ for the 266- and 308-nm pulses, respectively. The delay time between the two pulses has been set at 1 μ s. The spectrum exhibits a broad band located near 500 nm. The fluorescence lifetime is determined to be 4.1 ± 1.0 ns by a convolution method with the 308-nm pulse profile of a 10-ns width in the two-pulse fluorescence experiment. The fluorescence spectrum depicted by the lower curve in Figure 1a has resulted from excitation with only the 308-nm pulse of the intensity of 80 mJ cm⁻². The 308-nm excitation alone fails to induce the 500-nm fluorescence. Examination of Figure 1a establishes that excitation of o-xylene at 266 nm forms a transient species, from which the 500-nm fluorescence is induced by subsequent excitation at 308 nm.

The one-pulse fluorescence experiment has been carried out by excitation of the sample solution of o-xylene with only the 266-nm pulse. The fluorescence spectrum generated with the pulse intensity of 8.3 mJ cm⁻² is shown by the upper curve in Figure 1b. Although the spectrum contains a contribution from the fluorescence of o-xylene which has a peak near 285 nm, it exhibits the essentially identical shape with the one shown by the upper curve in Figure 1a. The fluorescence lifetime determined by a convolution method with the 266-nm pulse profile of a 5-ns width in the one-pulse fluorescence experiment agrees with that obtained in the two-pulse fluorescence experiment. The fluorescence spectrum observed with the pulse intensity of 0.90 mJ cm⁻² is shown by the lower curve in Figure 1b. The fluorescence near 500 nm is not seen in the spectrum. Inspection of Figure 1b ensures that the 500-nm fluorescence is induced when the 266-nm pulse intensity is so high that the second photon within the same pulse is absorbed by the transient species.

The spectra in Figure 1a,b resemble well those of the o-methylbenzyl radical observed in rigid glass at 77 K^{12,13} and are similar to those of the benzyl and p-methylbenzyl radicals obtained in solution.¹⁴ This leads to the spectral assignment of the 500-nm fluorescence to the o-methylbenzyl radical. The



Figure 1. Laser-induced fluorescence spectra of the o-methylbenzyl radical. (a) Fluorescence of the o-methylbenzyl radical produced by excitation with a 308-nm pulse at a 1- μ s delay after excitation of o-xylene with a 266-nm pulse (upper curve) and a background produced with only a 308-nm pulse (lower curve). Intensities of 266- and 308-nm pulses are 10 and 80 mJ cm⁻², respectively. (b) Fluorescence of the o-methylbenzyl radical produced by excitation of o-xylene with a 266-nm pulse of an intensity of 8.3 mJ cm⁻² (upper curve), and a wing of fluorescence of o-xylene produced by excitation with a 266-nm pulse of an intensity of 0.90 mJ cm⁻² (lower curve). Asterisks indicate a contribution of stray light from the second harmonic (532 nm) of a Nd:YAG laser. (c) Fluorescence of the o-methylbenzyl radical produced by excitation of α -chloro-o-xylene with a 266-nm pulse of an intensity of 4.5 mJ cm⁻².

fluorescence lifetime of the *o*-methylbenzyl radical determined in the two-pulse fluorescence experiment is much shorter than the lifetimes measured for the *o*-methylbenzyl radical of 870 ns^{15} and 790 ns^{16} in matrices at 77 K and of 810 ns^{17} in the gas phase. Existence of a rapid decay channel may account for the short lifetime in solution. The present lifetime is compared with the reported lifetimes of less than 1 ns¹⁴ for the benzyl radical and of 14 ns¹⁴ for the *p*-methylbenzyl radical in hexane solution.

In order to confirm the assignment of the fluorescence near 500 nm, photodissociation of α -chloro-o-xylene has been studied by using only the 266-nm pulse. The fluorescence spectrum attributable to the o-methylbenzyl radical has been observed, which is depicted in Figure 1c. The fluorescence lifetime determined in the one-pulse fluorescence experiment on α -chloro-o-xylene is in agreement with the lifetimes obtained in the two-and one-pulse experiments on o-xylene. The excitation process responsible for observation of the spectrum involves two distinct parts: the first one that the o-methylbenzyl radical is formed by excitation of α -chloro-o-xylene with the former portion of the 266-nm pulse, and the second that the ground-state radical is subsequently excited with the latter portion of the same pulse.

Transient Absorption Spectra. Transient absorption spectra resulting from excitation of o-xylene with the 266-nm pulse have been recorded and are depicted in Figure 2a. The spectra have contributions from two transient species. The species giving rise to a broad absorption band in the region of 350-500 nm decays with the lifetime of $3.2 \pm 0.2 \ \mu s$. This species is assigned to T_1 o-xylene in agreement with the earlier observation.¹⁸ The species giving absorption bands with maxima at 309 and 320 nm decays more slowly than T_1 o-xylene and disappears at 90 μs . The longer-lived species is assigned to the o-methylbenzyl radical in comparison with the reports on fluorescence excitation spectra of the o-methylbenzyl radical in rigid glass at 77 K^{12,13} and on



Figure 2. Transient absorption spectra of the o-methylbenzyl radical and triplet o-xylene. (a) Absorption of the o-methylbenzyl radical and triplet o-xylene recorded at 1-, 2-, 10-, 25-, and 90- μ s delays after excitation of o-xylene with a 266-nm pulse of an intensity of 140 mJ cm⁻² (from top to bottom curve). (b) Absorption of the o-methylbenzyl radical recorded at 0.1-, 1.5-, and 20- μ s delays after excitation of α -chloro-oxylene with a 266-nm pulse of an intensity of 120 mJ cm⁻² (from top to bottom curve).

absorption spectra of the benzyl and *p*-methylbenzyl radicals in solution.¹⁴ The band position of 320 nm also agrees with the one measured for the *o*-methylbenzyl radical in solution.¹⁹

To confirm the spectral assignment of the absorption bands at 309 and 320 nm, photolysis of α -chloro-o-xylene with the 266nm pulse has been examined. The absorption spectra of the o-methylbenzyl radical have been clearly observed, which exhibit prominent bands located at 309 and 320 nm, as shown in Figure 2b. No absorption attributable to T₁ α -chloro-o-xylene has been observed in contrast with the case of o-xylene. The decay rate of the o-methylbenzyl absorption is dependent on the intensity of the 266-nm pulse, indicating a second-order decay process of the radical.

The quantum yield of formation of the o-methylbenzyl radical by photodissociation of o-xylene is estimated quantitatively on the basis of the extinction coefficient of 2.4×10^2 dm³ mol⁻¹ cm⁻¹ measured for o-xylene at the excitation wavelength of 266 nm and of the extinction coefficient of 1.0×10^4 dm³ mol⁻¹ cm⁻¹ reported for the o-methylbenzyl radical at the absorption maximum of 321.5 nm in cyclohexane.¹⁹ The geometries of the excitation and analysis beams (the small dimensions of which may lead to a large error) give a primary o-methylbenzyl formation yield by o-xylene dissociation of ca. 1.8×10^{-2} . It is shown that the carbon-hydrogen bond homolysis is a minor path. High efficiency of other paths, including radiative decay to the S₀ state and nonradiative decay by intersystem crossing to the T₁ state, will be responsible for the low yield of o-methylbenzyl formation.

Formation and Decay Rates. To examine an energy dissipation process in the S₁ state of o-xylene, the decay rate of the o-xylene fluorescence and the formation rate of the o-methylbenzyl radical have been studied. The fluorescence time profile of o-xylene has been observed at 300 nm after excitation at 266 nm. The o-xylene fluorescence decays with the decay rate constant of (2.7 ± 0.3) $\times 10^7$ s⁻¹, as shown in Figure 3a. The dependence of the fluorescence intensity of the o-methylbenzyl radical at 500 nm on the delay time between the 266- and 308-nm pulses has been investigated using o-xylene as the precursor. The o-methylbenzyl fluorescence intensity, which reflects the ground-state o-methylbenzyl concentration, increases after 266-nm excitation with the formation rate constant of $(3.1 \pm 0.4) \times 10^7$ s,⁻¹ as shown in Figure 3b. The absorption time profiles of the o-methylbenzyl radical have been tested at 310 and 325 nm after excitation of



Figure 3. Fluorescence time profile of o-xylene and dependence of a fluorescence intensity of the o-methylbenzyl radical on a delay time between exciting pulses. (a) Decay of o-xylene fluorescence, which is induced by excitation at 266 nm and monitored at 300 nm. (b) Increase of an intensity of o-methylbenzyl fluorescence, which is induced by excitation at 308 nm after excitation of o-xylene at 266 nm and monitored at 500 nm. (c) Time profile of a 266-nm pulse.

o-xylene at 266 nm. However the strong fluorescence of o-xylene has interfered with observation of the radical absorbances in the time range of Figure 3, and the formation rate of the omethylbenzyl radical is not able to be determined from the absorption time profiles. Examination of Figure 3a,b makes it evident that the decay rate constant of the o-xylene fluorescence is equal to the formation rate constant of the o-methylbenzyl radical within an experimental error. The finding gives an explanation of a predissociation mechanism of the methyl carbonhydrogen bond from the thermal equilibrium S₁ state and not from the Franck-Condon state of o-xylene. It is also shown, by inspecting Figure 3b,c, that no rapid formation process exists which occurs within the duration of the 266-nm pulse. From this fact a possibility of formation of the o-methylbenzyl radical by absorption of two photons at 266 nm is denied.

In order to investigate the formation process of the omethylbenzyl radical via the T_1 state of o-xylene, the absorption time profiles of T_1 o-xylene and the o-methylbenzyl radical, as well as the dependence of the fluorescence intensity of the o-methylbenzyl radical on the delay time between the exciting pulses, have been examined. The absorption time profiles of the o-methylbenzyl radical observed at 310 and 325 nm after excitation of o-xylene at 266 nm are depicted in Figure 4a.b. There is a contribution from the strong fluorescence of o-xylene that interferes with observation of the absorption signal at 310 nm during the time interval of $0-5 \ \mu s$. The o-methylbenzyl absorbances at 310 and 325 nm decrease slowly and identically with each other, leaving absorbances due to a stable product of which an absorption continuum arises in the range of 300-350 nm. The absorption time profile of $T_1 o$ -xylene monitored at 350 nm after excitation at 266 nm is depicted in Figure 4c. The T_1 o-xylene absorbance decays faster than that of the radical. The decay rate constant of the T_1 state is determined to be (3.1 ± 0.2) \times 10⁵ s⁻¹. The dependence of the fluorescence intensity of the o-methylbenzyl radical at 500 nm on the delay time between the 266- and 308-nm pulses, which has been observed using o-xylene as the precursor, is shown in Figure 4d. The shape of the fluorescence spectrum of the o-methylbenzyl radical is not affected within the time range of Figure 4. The fluorescence intensity decreases slowly. A plot of the reciprocal value of the fluorescence intensity versus the delay time yields a straight line, indicating a second-order decay process of the radical. The decay rate of the o-methylbenzyl radical oberved from the dependence of the



Figure 4. Absorption time profiles of the o-methylbenzyl radical and triplet o-xylene and dependence of a fluorescence intensity of the o-methylbenzyl radical on a delay time between exciting pulses. (a) Decay of o-methylbenzyl absorption, which is produced by excitation of o-xylene at 266 nm and monitored at 310 nm. (b) Same decay as in part a monitored at 325 nm. (c) Decay of triplet o-xylene absorption, which is produced by excitation at 266 nm and monitored at 350 nm. (d) Decrease of an intensity of o-methylbenzyl fluorescence, which is produced by excitation at 308 nm after excitation of o-xylene at 266 nm and monitored at 300 nm.

fluorescence intensity on the delay time in Figure 4d is identical with the ones obtained from the absorption time profiles in Figure 4a,b. It is concluded, after examining Figure 4a–d, that there are no relations between the triplet decay and the radical formation and between the triplet decay and the radical decay.

Photodissociation of o-xylene yields a hydrogen atom as well as the o-methylbenzyl radical. Addition of a hydrogen atom to o-xylene may produce the dimethylcyclohexadienyl radical. The cyclophexadienyl radical is known to exhibit absorption bands at 317 and 410-560 nm in solution at 77 K.²⁰ Formation of the dimethylcyclohexadienyl radical is considered not to affect observation of the fluorescence intensity of the o-methylbenzyl radical on the following grounds: (1) The concentration of the dimethylcyclohexadienyl radical is less than that of the omethylbenzyl radical, and the absorbance of the dimethylcyclohexadienyl radical at 308 nm will be too low to reduce the probability of the o-methylbenzyl radical absorbing a photon in the 308-nm pulse. (2) Even if the dimethylcyclohexadienyl radical fluoresces, there will be no contribution from the fluorescence of the dimethylcyclohexandienyl radical at the wavelength of 500 nm, where the fluorescence intensity of the o-methylbenzyl radical is determined.

Dependence of Fluorescence Intensity on Incident Pulse Intensities. To determine whether the carbon-hydrogen bond cleavage proceeds by a route that involves a one-photon or a two-photon process, the dependence of the fluorescence intensity of the o-methylbenzyl radical on the intensities of the 266- and 308-nm pulses has been studied by using o-xylene as the precursor. The delay time between the two pulses has been fixed at 1 μ s, and the fluorescence intensity has been monitored at 500 nm. The radical fluorescence spectrum maintains its shape within the intensity range examined, although fluorescence from impurities in the shorter wavelength region (below 450 nm) becomes dominant in a spectrum obtained with a weak intensity of the 266-nm pulse. A rough estimation of pumping efficiency for the states involved in excitation is made by using the following extinction coefficients: 2.4×10^2 dm³ mol⁻¹ cm⁻¹ measured for S_0 o-xylene at the excitation wavelength of 266 nm; 4.2×10^3 $dm^3 mol^{-1} cm^{-1}$ taken for S₁ o-xylene from the value reported for S_1 benzene at the absorption maximum of 270 nm in cyclohexane;²¹



Figure 5. Logarithmic plots of a fluorescence intensity of the omethylbenzyl radical as a function of 266- and 308-nm pulse intensities. The fluorescence is induced by excitation with a 308-nm pulse at a 1- μ s delay after excitation of o-xylene with a 266-nm pulse and monitored at 500 nm. (a) The intensity of a 266-nm pulse is varied in a range of 0.35-28 mJ cm⁻², and the intensity of a 308-nm pulse is fixed to 30 mJ cm⁻². (b) The intensity of a 266-nm pulse is fixed to 28 mJ cm⁻², and the intensity of a 308-nm pulse is of 0.34-30 mJ cm⁻².

 $1.0 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ reported for the ground-state o-methylbenzyl radical at the absorption maximum of 321.5 nm in cyclohexane.19 The decrease of the concentration of the groundstate radical by absorption of a photon during the 266-nm pulse is ignored in the two-pulse fluorescence experiment, since the major portion (ca. 82%) of the radical is formed after the 266-nm pulse. The radical disappearance during the time interval of 1 us does not affect determination of the fluorescence intensity. Beer's law complication is removed at the dilute level of the radical concentrations. A logarithmic plot of the radical fluorescence intensity versus the 266-nm pulse intensity of the range of 0.35-28 mJ cm⁻² is depicted in Figure 5a. The concentration of the S_0 state is little diminished by excitation with the 266-nm pulse. The probability of excitation of the S_1 state to the S_n state with the 266-nm pulse increases from 0.0038 to 0.27 upon increasing the 266-nm pulse intensity from 0.35 to 28 mJ cm⁻². This is due to the pumping rate constant of the S_1 state to the S_n state reaching 5.4×10^7 s⁻¹ at the 266-nm pulse intensity of 28 mJ cm⁻². The pumping rate of the S1 state is able to compete at the higher pulse intensities (in the range of 6.1-28 mJ cm⁻² corresponding to the three right-hand points in Figure 5a) with the decay rate of the S_1 state for which the decay rate constant is measured to be (2.7 \pm 0.3) \times 10⁷ s⁻¹. A straight line is drawn to fit the observed points in Figure 5a, giving a slope of 1.11 ± 0.12 . It turns out that the carbon-hydrogen bond fission occurs via a one-photon route. A possibility of a radical formation process by two-photon absorption is excluded. The saturation behavior observed at a higher intensity of the 266-nm pulse (above 28 mJ cm⁻²) is understood to arise from depletion of the S_1 state which reduces the radical formation efficiency. The radical fluorescence intensity is plotted as a function of the 308-nm pulse intensity of the range of 0.34-30 mJ cm⁻² in Figure 5b. The probability of excitation of the ground-state radical with the 308-nm pulse increases from 0.0092 to 0.81 on increasing the 308-nm pulse intensity from 0.34 to 30 mJ cm⁻². The probability of pumping



Figure 6. Logarithmic plot of a fluorescence intensity of the *o*-methylbenzyl radical as a function of a 266-nm pulse intensity. The fluorescence is induced by excitation of *o*-xylene at 266 nm and monitored at 500 nm. The intensity of a 266-nm pulse is varied in a range of 1.8-15 mJ cm⁻².

of the excited-state radical to a higher state is not estimated for lack of its extinction coefficient. The observed points are fitted in Figure 5b with a straight line, of which a slope is determined to be 0.95 ± 0.15 . It is clear that the radical absorbs one photon before it fluoresces. The saturation effect appearing at a higher 308-nm pulse intensity (above 30 mJ cm⁻²) is interpreted in terms of depletion of the ground-state radical. The results presented by the two-pulse experiment lead to a conclusion that one photon at 266 nm is used for formation of the *o*-methylbenzyl radical. It is also concluded that a second photon at 308 nm brings about population of the fluorescent state of the radical.

The dependence of the fluorescence intensity of the omethylbenzyl radical on the intensity of the exciting pulse has been investigated by excitation of sample solution of o-xylene with the 266-nm pulse alone. A convolution method with the 266-nm pulse profile of a 5-ns width and with the o-methylbenzyl formation rate constant of $(3.1 \pm 0.4) \times 10^7$ s⁻¹ reveals that a portion (ca. 18%) of the radical is formed within the duration of the 266-nm pulse. It is thus possible for the portion of the radical to absorb a photon during the same pulse. A logarithmic plot of the fluorescence intensity at 500 nm as a function of the 266-nm pulse intensity of the range of 1.8-15 mJ cm⁻² is presented in Figure 6. The probability of the S_1 state excited to the S_n state with the 266-nm pulse increases from 0.019 to 0.15, and the probability of the ground-state radical excited to the upper state with this pulse increases from 0.047 to 0.39, when the pulse intensity increases from 1.8 to 15 mJ cm⁻². A straight line gives a slope of 1.78 ± 0.27 to fit the observed points, showing a twophoton process for excitation. One photon is used to break the carbon-hydrogen bond, and a second photon is absorbed by the fragment radical, populating its fluorescent state. At a lower intensity of the 266-nm pulse (below 1.8 mJ cm⁻²), the radical fluorescence is hidden by the fluorescence from the precursor, and the fluorescence intensity of the radical is not able to be determined. At a higher 266-nm pulse intensity (above 15 mJ cm⁻²), observed points deviate downward from the straight line, showing saturation. The saturation process is explained to be caused by depletion of the S_1 state and/or by depletion of the ground-state radical. The result obtained by the one-pulse experiment establishes a conclusion that two photons at 266 nm are required to form the o-methylbenzyl radical and to populate its fluorescence state. This is consistent with the results obtained in the two-pulse experiment, where two photons of different energies at 266 and 308 nm are used for excitation.

Discussion

Energy Dissipation Mechanism. Excitation of *o*-xylene at 266 nm (451 kJ mol⁻¹) populates the $S_1(\pi,\pi^*)$ state (the vibrational ground level of 435 kJ mol⁻¹) with an excess vibrational energy. Several channels of energy dissipation are available from this

SCHEME 1



Franck-Condon state (see Scheme 1). One channel is vibrational relaxation in the S_1 state followed by radiative decay from the vibrational ground level of the S_1 state to the S_0 state. This process is manifested to be very effective for o-xylene by its fluorescence (Figure 3a). A second process is intersystem crossing. Intersystem crossing occurs after vibrational relaxation to populate the T_1 state (Figure 4c). It is also feasible directly from the Franck-Condon state to some higher T_m state or to the T_1 state. Finally dissociation is available, which proceeds from an excited state within the singlet or triplet manifold excluding such associative states as the $S_1(\pi,\pi^*)$ and $T_1(\pi,\pi^*)$ states. Vibrational relaxation to the thermal equilibrium $S_1(\pi,\pi^*)$ state, whose population is governed by the Boltzmann distribution law, leads to intersystem crossing directly or indirectly to a dissociative $T_n(\sigma,\sigma^*)$ state, followed by the carbon-hydrogen bond fission. The bond cleavage is shown to occur by predissociation not from the Franck-Condon state but from the thermal equilibrium S_1 state, since the decay rate constant of the o-xylene fluorescence, $(2.7 \pm 0.3) \times 10^7$ s⁻¹, agrees with the formation rate constant of the o-methylbenzyl radical, $(3.1 \pm 0.4) \times 10^7 \text{ s}^{-1}$ (Figure 3a,b). The energy dissipation mechanism from the thermal equilibrium S_1 state of *o*-xylene is therefore characterized by two channels: one that populates an upper triplet state, which either is dissociative itself or crosses to a dissociative level resulting in fragmentation, and a second that involves radiative decay to the S₀ state and nonradiative decay by intesystem crossing to the T_1 state. The low quantum yield of formation of the o-methylbenzyl radical, ca. 1.8×10^{-2} , identifies the former channel as a minor one.

The T_1 state of *o*-xylene is populated by intersystem crossing from the S_1 state. The energy dissipation process from the T_1 state is concluded not to contain a channel of internal conversion to a dissociative state, because the formation rate constant of the *o*-methylbenzyl radical, $(3.1 \pm 0.4) \times 10^7$ s⁻¹, is 2 orders of magnitude larger than the decay rate constant of T_1 *o*-xylene, $(3.1 \pm 0.2) \times 10^5$ s⁻¹ (Figures 3b and 4c).

The carbon-hydrogen bond fission has been reported to occur from the vibrationally excited levels of the S_0 states of toluene by excitation to the S_3 state at 193 nm in the gas phase.^{4,5,7} This makes a difference from the present observation which shows, after incorporating the experimental data, that the predissociation mechanism from the thermal equilibrium S_1 state is reasonable for photodissociation of *o*-xylene in solution. If internal conversion occurs from the S_1 state to the vibrationally excited levels of the S_0 state of *o*-xylene in solution, it will be followed by rapid vibrational relaxation from the vibrational excited levels to the vibrational ground level in the S_0 state, and the bond fission will not compete with vibrational relaxation.

One-Photon Route for Dissociation. The excitation process involved in the two-pulse fluorescence experiment has been assumed to consist of two parts: (1) excitation of o-xylene at 266 nm forming the o-methylbenzyl radical; (2) subsequent excitation at 308 nm populating the fluorescent state of the radical. Proof of the assumption that the 308-nm pulse excites the ground-state o-methylbenzyl radical is given by the result in Figure 4, where the dependence of the radical fluorescence intensity on the delay

time is coincident with the change of the radical absorbances that reflect the concentration of the ground-state radical. The onephoton mechanism for excitation at 308 nm is shown to be valid by observation of the linear dependence of the radical fluorescence intensity on the 308-nm pulse intensity in Figure 5b. The assumption that the 266-nm pulse causes dissociation of o-xylene into the o-methylbenzyl radical is proved by the time evolutions in Figure 3, where the fluorescence intensity of the radical increases after the 266-nm pulse, establishing the increase of the radical concentration after this pulse. The one-photon route for excitation with the 266-nm pulse is found to be efficient by studying the linear dependence of the radical fluorescence intensity on the 266-nm pulse intensity in Figure 5a. The two-photon dissociation mechanism by 266-nm excitation is shown to be impossible, firstly because a rapid rise component within the 266-nm pulse duration is absent in the radical formation curve in Figure 3b and secondly because the radical fluorescence intensity does not exhibit any quadratic dependence on the 266-nm pulse intensity in Figure 5a.

The vibrational ground level of the S_1 state of o-xylene, which is populated by excitation at 266 nm followed by vibrational relaxation, has an energy of 435 kJ mol⁻¹. The energy is sufficient to fragment the precursor into the o-methylbenzyl radical and a hydrogen atom, because the energy required to cleave a benzylic carbon-hydrogen bond is estimated to be 368 kJ mol⁻¹ for toluene.²² The simple energetic argument does not provide any difficulty for the one-photon dissociation mechanism from the thermal equilibrium S_1 state.

Excitation of mesitylene with 249-nm pulses in matrices at 77 K has been reported to produce the 3,5-dimethylbenzyl radical by a two-photon route.² It has been suggested that a photon at 249 nm brings about population of the T_1 state of the precursor, which is then excited by a second photon at 249 nm into the T_n state where dissociation of a carbon-hydrogen bond occurs. The T₁ state may live at 77 K long enough to be irradiated by the second photon regardless of the magnitude of its absorption cross section. Alternatively the thermal energy provided at 77 K may be too low to cause intersystem crossing from the vibrational ground level of the S_1 state to the upper-lying dissociative state. The two-photon dissociation mechanism discussed for formation of the 3,5-dimethylbenzyl radical in low-temperature matrices is different from the one-photon mechanism proposed by the present work. The latter does not deny a possibility of the two-photon route in matrices at 77 K. It shows that the one-photon dissociation route is consistent with the experimental data on photodecomposition of o-xylene in room temperature solution.

Conclusion

Excitation of o-xylene to the S₁ state produces the omethylbenzyl radical in n-heptane solution. The two-pulse laserinduced fluorescence experiment has shown that the decay rate constant of the fluorescence of o-xylene is equal to the formation rate constant of the o-methylbenzyl radical. It has also been shown that a single photon is required to form the o-methylbenzyl radical from o-xylene. The predissociation mechanism from the thermal equilibrium S_1 state which is populated by one-photon excitation followed by vibrational relaxation is consistent with the observation.

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