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Photodissociation of *p*-Xylene in Polar and Nonpolar Solutions

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The photodissociation of *p*-xylene at 266 nm in *n*-heptane and acetonitrile has been studied with use of nanosecond fluorescence and absorption spectroscopy. The *p*-methylbenzyl radical was identified in *n*-heptane and acetonitrile by its fluorescence, which was induced by excitation at 308 nm. The *p*-xylene radical cation was observed in acetonitrile by its absorption. In *n*-heptane, the decay rate of the S_1 state of *p*-xylene ($(3.2 \pm 0.2) \times 10^7$ s^{-1}) is equal to the growth rate of the *p*-methylbenzyl radical ($(2.7 \pm 0.4) \times 10^7$ s^{-1}), showing that the molecule dissociates via the S_1 state into the radical by C−H bond homolysis (quantum efficiency $\sim 5.0 \times 10^{-3}$). In acetonitrile, the formation of the *p*-xylene radical cation requires two 266 nm photons, and the decay rate of the radical cation ($(1.6 \pm 0.2) \times 10^6$ s^{-1}) equals the growth rate of the *p*-methylbenzyl radical ($(2.0 \pm 0.2) \times 10^6$ s^{-1}). This shows that the radical cation dissociates into the radical by deprotonation (quantum efficiency $\sim 8.9 \times 10^{-2}$).

1. Introduction

On the photochemistry of benzyl C−H bond dissociation of aromatics in solutions, two distinct pathways have been proposed. In nonpolar solution, *o*-xylene was reported to dissociate into the *o*-methylbenzyl radical via one-photon absorption; the dissociation was considered to take place by homolysis of the C−H bond.[1] In polar solution, diphenylmethane was found to produce the diphenylmethyl radical via two-photon absorption; the dissociation was suggested to occur by ionization of the molecule and subsequent deprotonation of the radical cation.[2]

It is not clear whether the different mechanisms arise from the different molecules or different solutions. To understand this problem, we have studied photodissociation of *p*-xylene in nonpolar (*n*-heptane) and polar (acetonitrile) solutions. The different mechanisms have been clarified to occur between the nonpolar and polar solutions. The results are described in this paper.

2. Experimental Section

For the 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 the photolysis light. The fluorescence was induced by a second pulse (308 nm, 8−12 ns) from a XeCl excimer laser (Lumonics 500). The laser power was attenuated with ND filters (Sigma FNDU-50C02-10, -20, -50) and was measured with a thermopile monitor (Ophir 03A-P, DGX). The delay time was adjusted with a digital delay generator (EG&G PAR 9650). The laser beams were focused on a 10 × 10 mm quartz cell coaxially. The fluorescence was collected at right angles with the laser beams into a monochromator (Ritsu MC-10N) and was detected with a photomultiplier (Hamamatsu R636). The output signal from the photomultiplier was fed to a digital oscilloscope (Tektronix 2440, 500 MHz sampling), which was interfaced to a personal computer (NEC PC-9801UV) for data storage.

For the absorption measurement, the photolysis light was the 266 nm laser pulse. The white light was provided with a Xe arc lamp (Ushio UXL-500D-O). The laser and lamp beams were focused on the cell at right angles with each other. The detection apparatus for the white light was the same as that for the fluorescence.

p-Xylene (Kanto Chemical, >98%) was distilled. Naphthalene (Nacalai Tesque, >99%) was recrystallized from ethanol (Kanto Chemical, >99.5%). Methanol (Kanto Chemical, >99.8%), *n*-heptane (Dojindo Spectrosol, >99.0%), and acetonitrile (Dojindo Spectrosol, >99.0%) were used as received. The sample solutions, containing *p*-xylene (4.7×10^{-3} mol dm^{-3}) in *n*-heptane and acetonitrile, were degassed by freeze−pump−thaw cycles. In the quenching experiment, methanol (0.12 mol dm^{-3}) and O_2 (1.9×10^{-3} mol dm^{-3}) were added to the sample solutions. All of the experiments were performed at room temperature (295 K).

3. Results and Discussion

3.1. Reaction Intermediates. The transient species involved in the photodissociation of *p*-xylene were identified by the fluorescence and absorption spectra with nanosecond time resolution.

The fluorescence spectra, shown in Figure 1, were observed by excitation with the 308 nm pulse after photolysis of *p*-xylene with the 266 nm pulse. Excitation with only the 308 nm pulse did not induce the fluorescence. The fluorescence band appears at 490 nm in *n*-heptane and at 500 nm in acetonitrile; it is assigned to the *p*-methylbenzyl radical.[3] The lifetime of the

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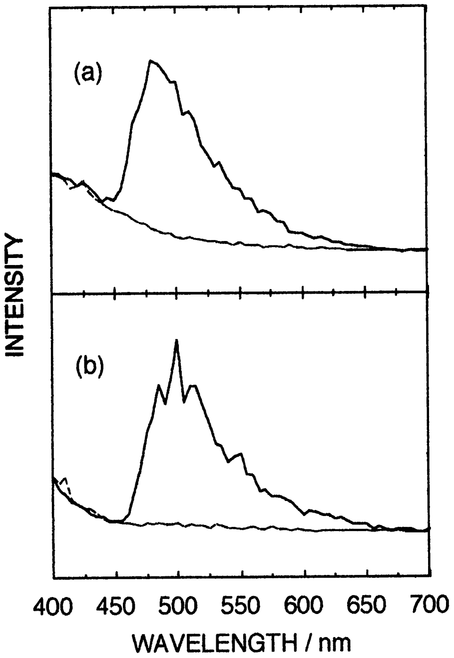

Figure 1. Fluorescence spectra of the *p*-methylbenzyl radical observed in (a) *n*-heptane and (b) acetonitrile by excitation with the 308 nm pulse at 1 μs after excitation of *p*-xylene with the 266 nm pulse. The upper curves were generated with both the 266 and the 308 nm pulses, while the lower ones were generated with only the 308 nm pulse.

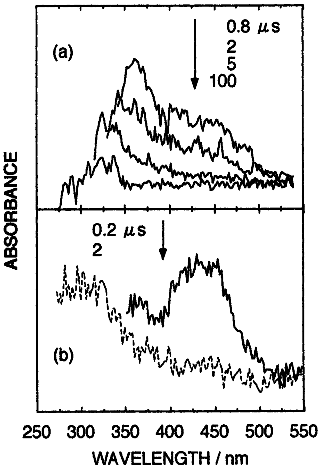

Figure 2. Absorption spectra of the *p*-xylene triplet and *p*-xylene radical cation observed in (a) *n*-heptane and (b) acetonitrile after excitation of *p*-xylene with the 266 nm pulse. The spectra were generated at (a) 0.8, 2, 5, 100, and (b) 0.2, 2 μs after the 266 nm pulse.

excited (D_1) state of the *p*-methylbenzyl radical is 14 ± 2 ns in *n*-heptane and 6.2 ± 0.1 ns in acetonitrile; the former is in agreement with the reported lifetime of 14 ns in hexane.[3] The *p*-methylbenzyl radical decays at a 100 μs delay from the 266 to the 308 nm pulse.

The absorption spectra, shown in Figure 2, were recorded by excitation of *p*-xylene with the 266 nm pulse. The spectra in the shorter wavelength region were not obtained within a shorter delay, because of an interruption from the fluorescence of *p*-xylene. The absorption band at 435 nm in acetonitrile is assigned to the *p*-xylene radical cation.[4] This absorption was quenched by methanol (nucleophile), but not affected by O_2 (triplet scavenger). The *p*-xylene radical cation decays at a 2 μs delay. The broad absorption band at 340−500 nm in *n*-heptane is attributed to the T_1 state of *p*-xylene by comparison to that of the T_1 state of benzene[5] and *o*-xylene.[1,6] It is also seen at 280−500 nm in acetonitrile, overlapping with the band of the *p*-xylene radical cation. The lifetime of the T_1 state of *p*-xylene is 3.4 ± 0.3 μs in *n*-heptane. A weak absorption band at 320 nm is overlapped by the band of the T_1 state of *p*-xylene in *n*-heptane and acetonitrile; it is assignable to the *p*-methylbenzyl radical.[3,7,8] (The quantum yield is estimated at $\sim$5.0 × 10^{-3} for the formation of the *p*-methylbenzyl radical from *p*-xylene in *n*-heptane (see section 3.4).)

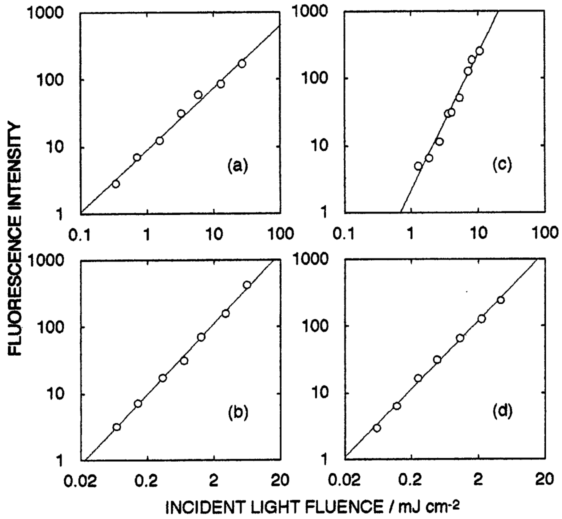

Figure 3. Logarithmic plots of the fluorescence intensity of the *p*-methylbenzyl radical versus the (a), (c) 266 and (b), (d) 308 nm pulse fluences. The fluorescence was induced in (a), (b) *n*-heptane and (c), (d) acetonitrile by excitation with the 308 nm pulse at (a), (b) 1 and (c), (d) 2 μs after excitation of *p*-xylene with the 266 nm pulse. Monitoring wavelength: 500 nm.

The spectral observation of the radical cations has not been reported for the photodissociation of phenylmethane, diphenylmethane, triphenylmethane, or their analogues into the benzyl-type radicals. The present results show that the *p*-methylbenzyl radical is formed in *n*-heptane and that the *p*-xylene radical cation and *p*-methylbenzyl radical are formed in acetonitrile from the photolysis of *p*-xylene.

3.2. One- or Two-Photon Photochemistry. The number of photons required for the formation of the *p*-methylbenzyl radical from *p*-xylene was determined by the dependence of the radical fluorescence intensity on the 266 (photolysis) and 308 (probe) nm pulse fluences. The saturation behavior arising from depletion of the S_1 state of the molecule ($\epsilon = 4.2 \times 10^3$ dm^3 mol^{-1} cm^{-1} (270 nm))[5] and the ground (D_0) state of the radical ($\epsilon = 7.4 \times 10^3$ dm^3 mol^{-1} cm^{-1} (320 nm))[7] was avoided by reduction of the pulse fluences. The complication in the nonlinear region of the Beer's law was removed at the dilute radical concentration ($\epsilon c < 10^{-2}$ cm^{-1} (308 nm)).

The fluorescence intensity of the *p*-methylbenzyl radical is plotted logarithmically as a function of the 266 nm pulse fluence in Figure 3a (*n*-heptane) and c (acetonitrile). The observed points are fitted linearly with slopes of 0.93 ± 0.13 for *n*-heptane and of 2.02 ± 0.34 for acetonitrile. It is clear that the radical formation requires one 266 nm photon in *n*-heptane but two 266 nm photons in acetonitrile. (No linear laser-power dependence is observed for the radical fluorescence intensity in acetonitrile; that is, no one-photon formation is detected for the radical in acetonitrile.)

The observation of the one-photon dissociation in nonpolar solution is in agreement with the earlier finding of the *o*-methylbenzyl radical formation[1] from *o*-xylene in nonpolar solution. The result of the two-photon dissociation in polar

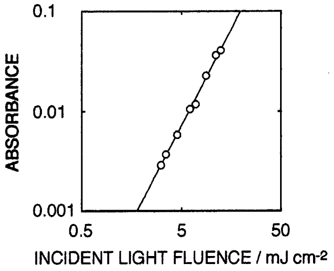

Figure 4. Logarithmic plot of the absorption intensity of the *p*-xylene radical cation versus the 266 nm pulse fluence. The absorption was produced in acetonitrile by excitation of *p*-xylene with the 266 nm pulse. The absorption intensity was calculated by subtraction of the background: $A_{RC} = A_{435} - (A_{390} + A_{480})/2$.

solution agrees with the reports of the diphenylmethyl[2] and triphenylmethyl[9] radical formation, respectively, from diphenylmethane and triphenylmethane in polar solutions.

The logarithmic plots of the fluorescence intensity of the *p*-methylbenzyl radical versus the 308 nm pulse fluence are shown in Figure 3b (*n*-heptane) and d (acetonitrile). Linear fitting results in slopes of 1.06 ± 0.08 for *n*-heptane and of 1.02 ± 0.09 for acetonitrile. Clearly, one 308 nm photon populates the fluorescent (D_1) state of the radical in *n*-heptane and acetonitrile.

For the formation of the *p*-xylene radical cation from *p*-xylene in acetonitrile, the number of required photons was determined by the dependence of the radical cation absorption intensity on the 266 nm (photolysis) pulse fluence. Because the radical cation absorption band lies on the background in the absorption spectra (Figure 2b), the absorption intensity was calculated by subtraction of the background, that is, by $A_{RC} = A_{435} - (A_{390} + A_{480})/2$.

The absorption intensity of the *p*-xylene radical cation is plotted logarithmically against the 266 nm pulse fluence in Figure 4. The observed points are fitted with a line of slope of 1.94 ± 0.14. It is evident that the ionization proceeds via 266 nm two-photon absorption in acetonitrile.

The quadratic laser-power dependence of the radical cation yield has not been reported for the photodissociation of methyl-substituted aromatics. The present measurement of the *p*-xylene radical cation shows that its formation requires two photons in the photolysis of *p*-xylene.

3.3. Reaction Kinetics. For the transient species leading to dissociation to the *p*-methylbenzyl radical, the decay kinetics was compared to the growth kinetics of the radical. The growth rate of the *p*-methylbenzyl radical was evaluated from the dependence of its fluorescence intensity on the delay of the 308 nm pulse after photolysis of *p*-xylene with the 266 nm pulse. The decay rates of the S_1 state of *p*-xylene and the *p*-xylene radical cation were determined, respectively, from their fluorescence and absorption time profiles after photolysis of *p*-xylene with the 266 nm pulse.

The dependence of the fluorescence intensity of the *p*-methylbenzyl radical in *n*-heptane on the delay from the 266 to the 308 nm pulse is shown in Figure 5a. The growth rate of the ground (D_0) state of the radical is calculated to be $(2.7 \pm 0.4) \times 10^7$ s^{-1}. The fluorescence time profile of *p*-xylene in *n*-heptane is shown in Figure 5b. The decay rate of the S_1 state of the molecule is $(3.2 \pm 0.2) \times 10^7$ s^{-1}. It is clear that the growth rate of the radical is equal to the decay rate of the S_1 state of the molecule. This shows that the C−H bond homolysis takes place via the S_1 state of *p*-xylene in *n*-heptane.

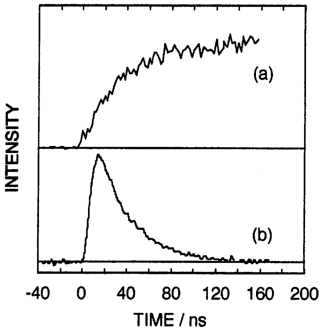

Figure 5. Time evolution of the fluorescence intensities of (a) the *p*-methylbenzyl radical and (b) *p*-xylene recorded in *n*-heptane after excitation of *p*-xylene with the 266 nm pulse. The *p*-methylbenzyl fluorescence was induced by excitation with the 308 nm pulse, of which the delay time is the abscissa for (a). Monitoring wavelengths: (a) 500, (b) 300 nm.

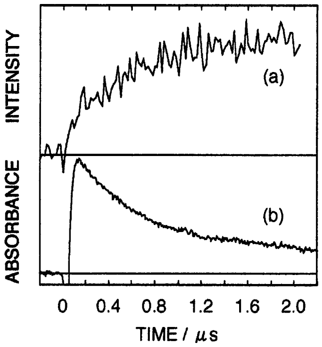

Figure 6. Time evolution of (a) the fluorescence intensity of the *p*-methylbenzyl radical and (b) the absorption intensity of the *p*-xylene radical cation recorded in acetonitrile after excitation of *p*-xylene with the 266 nm pulse. The *p*-methylbenzyl fluorescence was induced by excitation with the 308 nm pulse, of which the delay time is the abscissa for (a). Monitoring wavelengths: (a) 500, (b) 440 nm.

The dependence of the fluorescence intensity of the *p*-methylbenzyl radical in acetonitrile on the delay from the 266 to the 308 nm pulse is shown in Figure 6a. The growth rate of the radical is $(2.0 \pm 0.2) \times 10^6$ s^{-1}. The absorption time profile of the *p*-xylene radical cation in acetonitrile is shown in Figure 6b. The decay rate of the radical cation is $(1.6 \pm 0.2) \times 10^6$ s^{-1}. Clearly, the growth of the radical has a rate equal to the decay of the radical cation, showing that the deprotonation occurs from the *p*-xylene radical cation in acetonitrile.

The earlier studies suggested that the diphenylmethane[2] and triphenylmethane[9] radical cations dissociated, respectively, into the diphenylmethyl and triphenylmethyl radicals, although they did not observe the radical cations. (The reason they could not detect the diphenylmethane radical cation was explained by the interpretation that the radical cation decomposed with a rate of $>5 \times 10^7$ s^{-1}, i.e., with a rate by which the radical cation disappeared within the photolysis pulse width of 20 ns.[2]) The studies on the pulse radiolysis of *p*-xylene (as the acid-catalyzed water-elimination reaction of the OH adduct of *p*-xylene)[4] and on the laser flash photolysis of peroxydisulfate and *p*-xylene (as the reaction of the photochemically produced SO_4^- radical anion with *p*-xylene)[10] observed the absorption of the *p*-xylene radical cation and the deprotonation of the radical cation to the *p*-methylbenzyl radical. The present measurement of the *p*-xylene radical cation in the photodissociation of *p*-xylene also shows that the radical cation decomposes into the *p*-methylbenzyl radical.

3.4. Quantum Efficiencies. The quantum efficiencies were estimated for the formation of the *p*-methylbenzyl radical from dissociation of the S_1 state of *p*-xylene and the *p*-xylene radical cation.

The quantum efficiency of the radical formation from the C−H bond homolysis via the S_1 state was measured by comparison of the radical absorbance ($\epsilon = 7.4 \times 10^3$ dm^3 mol^{-1} cm^{-1} (320 nm))[7] (in the sample solution) with the triplet naphthalene absorbance ($\epsilon = 1.4 \times 10^4$ dm^3 mol^{-1} cm^{-1} (415 nm))[11] (in the reference solution) as the standard after excitation with the 266 nm pulse. By the use of the intersystem crossing yield of 0.68 for naphthalene,[11] the radical formation efficiency is estimated to be $\sim 5.0 \times 10^{-3}$ from the S_1 state in *n*-heptane. The C−H bond homolysis is a minor channel from the S_1 state.

The quantum efficiency of the radical formation from the deprotonation of the radical cation was measured by comparison of the radical absorbance with the radical cation absorbance ($\epsilon = 2.1 \times 10^3$ dm^3 mol^{-1} cm^{-1} (435 nm))[4] after excitation with the 266 nm pulse. The radical formation efficiency is calculated to be $\sim 8.9 \times 10^{-2}$ from the radical cation in acetonitrile. The deprotonation channel of the radical cation is more effective.

There arises a question as to why a one-photon route is not observed for the formation of the *p*-methylbenzyl radical in acetonitrile. A rough estimate of the $S_n \leftarrow S_1$ (or $T_n \leftarrow T_1$) pump rate may provide a clue for seeking an answer.

When the 266 nm (photolysis) pulse has a 2 mJ cm^{-2} fluence in the ~4 ns duration, the average photon irradiance (I_0) amounts to 6.7×10^{23} (photons) cm^{-2} s^{-1}. For the $S_n \leftarrow S_1$ transition ($\epsilon = 4.2 \times 10^3$ dm^3 mol^{-1} cm^{-1} (270 nm))[5] of *p*-xylene, the absorption cross section (σ) is 1.6×10^{-17} cm^2. The $S_n \leftarrow S_1$ pump rate (σI_0) is then estimated as 1.1×10^7 s^{-1}, which is comparable to the $S_1 \rightarrow S_0$ spontaneous decay rate of $(3.2 \pm 0.2) \times 10^7$ s^{-1}. If the $S_n \leftarrow S_1$ transition leads ultimately to the ionization to the radical cation, the deprotonation (from the radical cation) with higher efficiency ($\sim 8.9 \times 10^{-2}$) would be a more effective process for the radical formation than the homolytic C−H bond cleavage (from the S_1 state) with lower efficiency ($\sim 5.0 \times 10^{-3}$). If the $T_n \leftarrow T_1$ transition ($\epsilon = 1.1 \times 10^4$ dm^3 mol^{-1} cm^{-1} (235 nm))[5] of *p*-xylene leads to the ionization, a similar estimate can be made.

These arguments indicate that, for the formation of the *p*-methylbenzyl radical in acetonitrile, the two-photon route is more effective than the one-photon route in the present photolysis pulse fluence range, and that the one-photon route is not detected in the present experimental condition.

4. Conclusion

From the photolysis of *p*-xylene, the *p*-methylbenzyl radical is formed by one-photon absorption in *n*-heptane but by two-photon absorption in acetonitrile. In *n*-heptane, *p*-xylene dissociates via the S_1 state into the *p*-methylbenzyl radical. In acetonitrile, the *p*-xylene radical cation is produced via a two-photon process, and it decomposes into the *p*-methylbenzyl radical. The reason the one-photon formation of the *p*-methylbenzyl radical is not observed in acetonitrile is that the two-photon process has a higher yield than the one-photon process in the experimental condition.

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