Spectroscopic Studies on Photochemical Formation of *o*-Xylylene in Solution

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The photochemical formation of *o*-xylylene is studied by two-pulse fluorescence and transient absorption spectroscopy. *o*-Xylylene is produced by photolysis of α,α′-dichloro-*o*-xylene, α,α′-dibromo-*o*-xylene, α,α′-bis(trimethylstannyl)-*o*-xylene, and 2-indanone at 266 nm in room-temperature cyclohexane solution. On excitation at 308 nm, the fluorescence of *o*-xylylene is observed with a maximum at 460 nm and a lifetime of 9.3 ± 0.5 ns. The absorption of *o*-xylylene is obtained with a maximum at 370 nm. The formation of *o*-xylylene from α,α′-dichloro-*o*-xylene occurs, by 266-nm two-photon excitation, with an apparent yield of 0.30 ± 0.08 at a fluence of 40 mJ cm^{-2}. Its formation from 2-indanone proceeds, by 266-nm one-photon excitation, with a rate of (1.4 ± 0.1) × 10^7 s^{-1} and a yield of 0.90 ± 0.08.

1. Introduction

o-Xylylene is a reactive molecule that has been studied over the past 30 years. Spectroscopic investigation on *o*-xylylene has given direct evidence for its existence. The absorption,[1−5] fluorescence,[1−4,6] IR,[4,5] and Raman[4] spectra of *o*-xylylene have been observed in low-temperature matrices. The absorption spectrum of *o*-xylylene has been obtained in solution by flash photolysis[7,8] and stopped flow[9] techniques. A rate constant for *o*-xylylene bimolecular decay, where [4+2] and [4+4] dimers are produced, has been measured to be 9.9 × 10^3 dm^3 mol^{-1} s^{-1}.[7,9] However, the fluorescence spectrum of *o*-xylylene in solution has not been reported yet. The mechanisms of the formation of *o*-xylylene are not well understood.

The present paper deals with the formation of *o*-xylylene by photolysis of several precursors at 266 nm in cyclohexane solution at room temperature. The fluorescence, which is induced by excitation at 308 nm, and the absorption are recorded for *o*-xylylene. The number of photons necessary for its formation is determined. A quantum yield and kinetics for its formation are measured. The mechanisms of the photochemical formation of *o*-xylylene are discussed.

2. Experimental Details

α,α′-Dichloro-*o*-xylene (CX, Tokyo Chemical, >95%) and α,α′-dibromo-*o*-xylene (BX, Kanto Chemical, >97%) were recrystallized from *n*-hexane. α,α′-Bis(trimethylstannyl)-*o*-xylene (MSX) was synthesized by the method described elsewhere.[10] 2-Indanone (IN, Aldrich, >98%) was sublimed under vacuum. Naphthalene (Nacalai Tesque) was recrystallized from ethanol. Cyclohexane (Dojindo, spectrosol) was used as received. The sample solutions, which contained CX (6.2 × 10^{-3} mol dm^{-3}), BX (1.1 × 10^{-3} mol dm^{-3}), MSX (∼10^{-3} mol dm^{-3}), and IN (2.8 × 10^{-3} mol dm^{-3}) with cyclohexane, were degassed by freeze−pump−thaw cycles and sealed in a 10 × 10-mm quartz cell under vacuum. The molar extinction coefficient was measured with an absorption spectrophotometer (Hitachi U-3210).

For the two-pulse 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 delay time was adjusted with a digital delay generator (EG&G PAR 9650). The laser beams were focused on the cell coaxially. The fluorescence was detected with a monochromator (Ritsu MC-10N), a photomultiplier (Hamamatsu R636), and a digital oscilloscope (Tektronix 2440). Signals were accumulated with a personal computer (NEC PC-9801UV) to improve an S/N ratio.

For the transient absorption measurement, the photolysis light was the 266-nm laser pulse. The laser power was attenuated with neutral density filters (Sigma FNDU-50C02-10, -20, -50, -70, -80) and monitored with a thermopile detector (Ophir 03A-P, DGX). The white light was provided by a Xe flash lamp (Ushio UXL-500D-O). The Xe lamp beam was collimated on the cell at a right angle with the laser beam. The Xe lamp beam passed the region close (0.0−1.6 mm) to the laser irradiation inner surface in the cell to minimize decrease of the laser power by sample absorption. The detection apparatus for the white light was the same as for the fluorescence. The UV filter (Toshiba UV-D33S, 240−400 nm) was inserted in front of the monochromator to reject visible light for the measurement in the short wavelength region (<400 nm). All experiments were performed at room temperature (293 K).

3. Results and Discussion

3.1. Two-Pulse Fluorescence and Transient Absorption Spectra. The two-pulse fluorescence spectra, observed by excitation with the second pulse at 308 nm after photolysis of CX, BX, MSX, and IN with the first pulse at 266 nm, are given in Figure 1. Without the 266-nm pulse, the 308-nm pulse does not induce the fluorescence. The four spectra are identical within an experimental error and exhibit a band at 460 nm. The fluorescence lifetimes, obtained from photolysis of CX, BX, MSX, and IN, agree well and are of a value of 9.3 ± 0.5 ns. The fluorescence is assigned to *o*-xylylene, since it is a common intermediate species that is produced from photolysis of CX,

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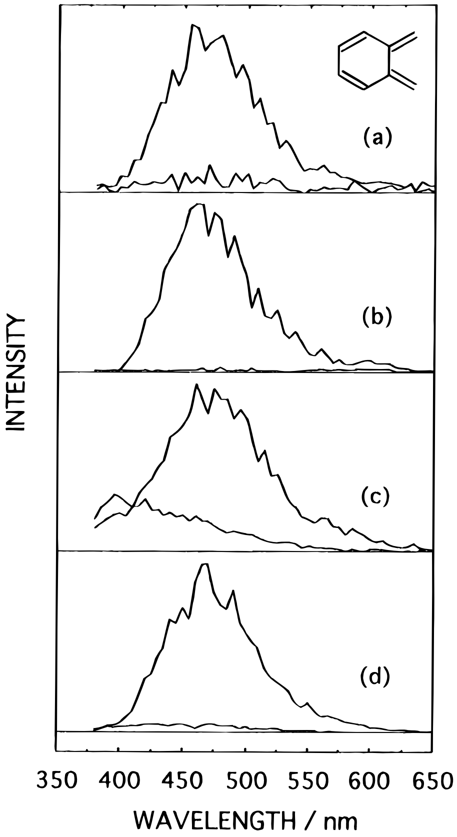
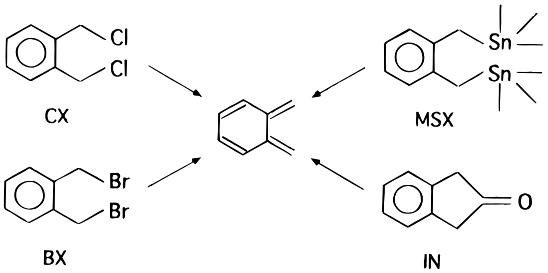


Figure 1. Two-pulse fluorescence spectra of *o*-xylylene observed by excitation with a 308-nm pulse at 1 μs after photolysis of (a) CX, (b) BX, (c) MSX, and (d) IN with a 266-nm pulse. Upper curves in (a–d) are generated with both 266- and 308-nm pulses, whereas lower curves with only a 308-nm pulse. Fluences of 266- and 308-nm pulses: (a) 5.2 and 88; (b) 5.2 and 76; (c) 96 and 110; (d) 6.4 and 7.6 mJ cm^{-2}.

SCHEME 1



BX, MSX, and IN (see Scheme 1). The spectra in Figure 1 are similar to those observed in low-temperature matrices.[2–4,6] The fluorescence intensities do not decrease in 0.2–20-μs delays from the 266- to the 308-nm pulse.

The shape of the fluorescence spectra does not change with variation of the 266-nm pulse fluence (5–100 mJ cm^{-2}) or the delay (0.2–100 μs) between the 266- and 308-nm pulses. The fluorescence decay can be fitted by a single-exponential function (9.3 ± 0.5-ns lifetime) in the 420–520-nm region. These observations deny any contribution from the fluorescence of the *o*-(Z-methyl)benzyl radicals (Z = Cl, Br, $Sn(CH_3)_3$, C=O), which are generated from the precursors by cleavage of one C–Z bond with the 266-nm pulse, though the fluorescence of the *o*-methylbenzyl radical has been reported to appear at 500 nm with a lifetime of 4.1 ± 1.0 ns in solution.[11] The fluorescence intensity of the *o*-(Z-methyl)benzyl radicals may be much weaker than that of *o*-xylylene.

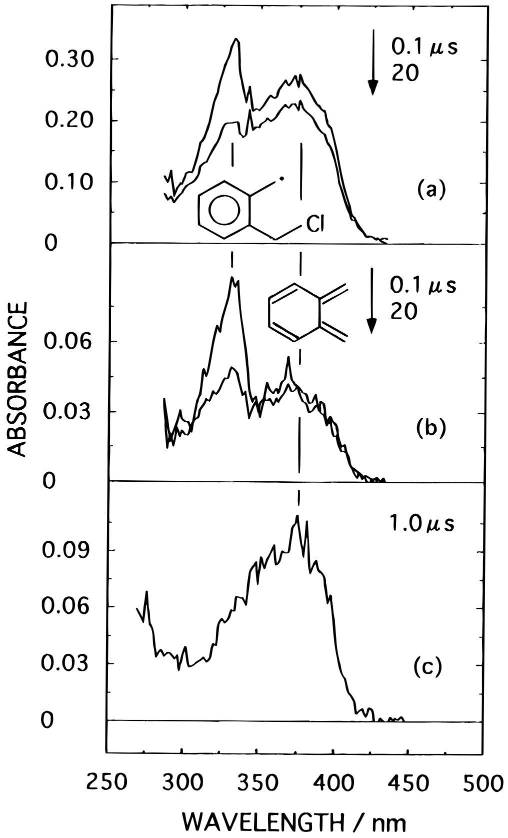


Figure 2. Transient absorption spectra of *o*-xylylene and an *o*-(chloromethyl)benzyl radical recorded after photolysis of (a, b) CX and (c) IN with a 266-nm pulse. Fluences of a 266-nm pulse: (a) 94; (b) 32; (c) 32 mJ cm^{-2}.

The transient absorption spectra, observed by photolysis of CX with the 266-nm pulse, are given in Figure 2a,b. A band at 330 nm is assigned to the *o*-(chloromethyl)benzyl radical, in comparison with the band of the *o*-methylbenzyl radical in solution.[11] The *o*-(chloromethyl)benzyl band disappears at a 100-μs delay. A band at 370 nm is assigned to *o*-xylylene, since it is similar to the bands observed in low-temperature matrices.[2–5] The band position is in accordance with the ones obtained in solution.[7,9] The band shape, however, differs from the one reported by Scaiano *et al*;[8] the long wavelength tail ends at 410 nm in the present spectra, whereas it extends to 500 nm in their spectrum. The *o*-xylylene band decays a little at a 20-μs delay. The intensity ratio of the *o*-xylylene to the *o*-(chloromethyl)benzyl band increases when the 266-nm pulse fluence increases.

The transient absorption spectrum, recorded by photolysis of IN with the 266-nm pulse, is given in Figure 2c. A band at 370 nm is assigned to *o*-xylylene, since it is identical with that in Figure 2a,b. The *o*-xylylene band does not decay at a 20-μs delay. Observation of the absorption in the 280–340-nm region is interrupted by the fluorescence of an impurity within a 0.2-μs delay. No absorption assignable to the benzyl radical is obtained in longer delays (<20 μs).

A broad absorption band at 340 nm is observed by photolysis of BX. It is assigned to the *o*-(bromomethyl)benzyl radical, compared with the band of the *o*-methylbenzyl radical in solution.[11] A broad band at 380 nm is obtained by photolysis of MSX. It is assignable to the trimethylstannyl radical, in comparison with the band of the tri-*n*-butylstannyl radical in solution.[12] The absorption due to *o*-xylylene is obscured by that of the *o*-(bromomethyl)benzyl and trimethylstannyl radicals for photolysis of BX and MSX, respectively.

The $S_2 \leftarrow S_0$ and $S_1 \leftarrow S_0$ absorption bands of IN appear in the 240–280-nm (~10^2 dm^3 mol^{-1} cm^{-1}) and 290–330-nm

(~10^0 dm^3 mol^{-1} cm^{-1}) ranges, respectively. Excitation with the 308-nm pulse at 1 μs after excitation of IN to the $S_2(\pi,\pi^*)$ state with the 266-nm pulse produces the *o*-xylylene fluorescence. Excitation of IN to the $S_1(n,\pi^*)$ state with the 308-nm pulse alone does not induce the *o*-xylylene fluorescence, since *o*-xylylene is formed from IN so slowly ((1.4 ± 0.1) × 10^7 s^{-1}, see Section 3.3) that it cannot be excited to its fluorescent state by the second photon within the 10-ns duration of the 308-nm pulse. The *o*-xylylene absorption is observed at 1 μs after excitation of IN to the $S_2(\pi,\pi^*)$ state with the 266-nm pulse. The identical absorption is obtained at 1 μs after excitation of IN to the $S_1(n,\pi^*)$ state with the 308-nm pulse.

3.2. Photolysis Pulse Fluence Dependence and Quantum Yields. The number of photons required for the formation of *o*-xylylene and the *o*-(chloromethyl)benzyl radical by dissociation of CX and IN has been determined from the dependence of their absorbances on the photolysis pulse fluence. For dissociation of CX, the observed absorbance must be separated into the *o*-xylylene and *o*-(chloromethyl)benzyl components, because of overlap of the corresponding bands in the 300−400-nm region. *o*-Xylylene does not decay within a 20-μs delay, as shown by the delay dependence of its fluorescence intensity. The *o*-(chloromethyl)benzyl radical decreases by a bimolecular process in the same delay. Thus, the observed absorbance $A(\lambda,t)$ at the wavelength λ and the delay t is represented, using the initial absorbances of *o*-xylylene $A_X(\lambda,0)$ and the *o*-(chloromethyl)benzyl radical $A_B(\lambda,0)$, by the following equation:

$$A(\lambda,t) = A_X(\lambda,0) + 1/(1/A_B(\lambda,0) + K_Bt) \qquad (1)$$

K_B is a parameter defined as $K_B = k_B/\epsilon_B(\lambda)l$, where k_B is the bimolecular decay rate constant of the *o*-(chloromethyl)benzyl radical, ϵ_B is its extinction coefficient, and l is the path length of the white light. For dissociation of CX, the initial absorbances of *o*-xylylene and the *o*-(chloromethyl)benzyl radical are obtained by fitting the absorption time profiles at 370 and 330 nm within a 20-μs delay according to eq 1. For dissociation of IN, only the *o*-xylylene absorption band is observed, and the initial absorbance of *o*-xylylene is read directly from the absorption time profile at 370 nm.

For dissociation of CX, the logarithmic plots of the initial absorbances of the *o*-(chloromethyl)benzyl radical and *o*-xylylene versus the photolysis pulse fluence are given in Figure 3a. The formation process of the *o*-(chloromethyl)benzyl radical is represented by a straight line with a slope of 0.93 ± 0.10. Dissociation of one C−Cl bond in CX is shown to occur by 266-nm one-photon excitation. The formation process of *o*-xylylene is described by linear fitting with a slope of 2.05 ± 0.20. Dissociation of two C−Cl bonds in CX is proved to require 266-nm two-photon excitation.

For dissociation of IN, the plot of the initial absorbance of *o*-xylylene as a function of the photolysis pulse fluence is given in Figure 3b. Linear fitting results in a slope of 1.04 ± 0.06 to represent the formation process of *o*-xylylene. Elimination of a C═O group in IN is found to proceed by 266-nm one-photon excitation.

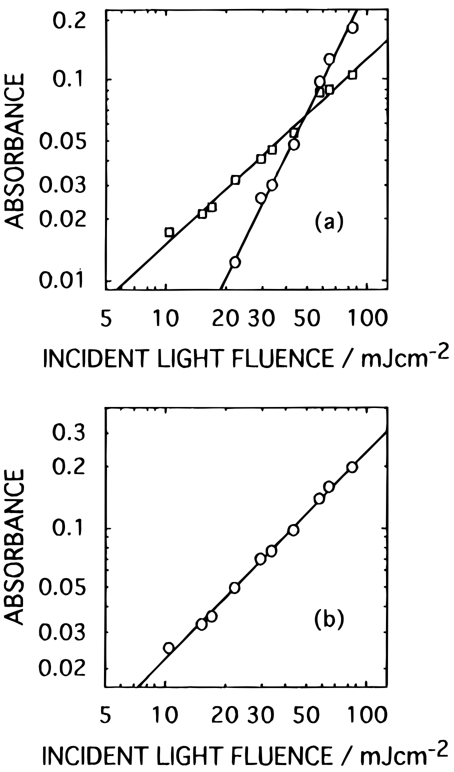


Figure 3. Laser power dependence of absorption intensities of *o*-xylylene (circles) and an *o*-(chloromethyl)benzyl radical (squares) observed by photolysis of (a) CX and (b) IN at 266 nm. Monitoring wavelengths: 370 (circles); 330 (squares) nm.

The quantum yields for the formation of the *o*-(chloromethyl)benzyl radical and *o*-xylylene from dissociation of CX and IN have been measured by comparing their initial absorbances with the triplet naphthalene one. The transient absorption signals (0.02−0.2 absorbance) are obtained by excitation of the sample solutions (2.0 cm^{-1} absorbance (266 nm)) of CX, IN, and naphthalene with the 266-nm pulse (2−40 mJ cm^{-2}). The extinction coefficient for the *o*-(chloromethyl)benzyl radical is assumed to be 1.0 × 10^4 dm^3 mol^{-1} cm^{-1} (330 nm) from the value for the *o*-methylbenzyl radical.[13] The extinction coefficients used for *o*-xylylene and triplet naphthalene are 3.0 × 10^3 dm^3 mol^{-1} cm^{-1} (370 nm)[9] and 1.4 × 10^4 dm^3 mol^{-1} cm^{-1} (415 nm),[14] respectively. The intersystem crossing yield for naphthalene is 0.68.[14] For dissociation of CX, the *o*-(chloromethyl)benzyl yield is determined to be 0.19 ± 0.03. The apparent *o*-xylylene yield, which is directly proportional to the photolysis pulse fluence, is estimated to be 0.30 ± 0.08 at a 40 mJ cm^{-2} fluence. For dissociation of IN, an estimate for the *o*-xylylene yield of 0.90 ± 0.08 is made.

As it is found that the formation of *o*-xylylene from dissociation of CX proceeds via a 266-nm two-photon process, a question arises about an intermediate species that absorbs the second 266-nm photon. For the intermediate species, three possibilities can be considered: (1) the S_1 state of CX, (2) the T_1 state of CX, and (3) the *o*-(chloromethyl)benzyl radical. The fluorescence of CX is not observed, showing that the S_1 state of CX decays rapidly (<1-ns lifetime). If so, the S_1 state of CX does not absorb the second photon within the 5-ns duration of the photolysis pulse. The apparent *o*-xylylene yield becomes higher than the *o*-(chloromethyl)benzyl yield in fluences of >50 mJ cm^{-2}, as seen from Figure 3a with consideration of the extinction coefficients for *o*-xylylene (3.0 × 10^3 dm^3 mol^{-1} cm^{-1})[9] and the *o*-(chloromethyl)benzyl radical (1.0 × 10^4 dm^3 mol^{-1} cm^{-1}).[13] This means that *o*-xylylene is not produced by excitation of the *o*-(chloromethyl)benzyl radical. Therefore, the T_1 state of CX is suggested to be the intermediate species. To check this point, the fraction of the T_1 state absorbing the second photon for CX has been evaluated. The extinction coefficient of 1.1 × 10^4 dm^3 mol^{-1} cm^{-1} (266 nm) for the $T_n \leftarrow T_1$ absorption of benzene[15] is used. An assumption is made that the $S_1 \rightarrow T_1$ intersystem crossing occurs rapidly. The fraction of the T_1 state excited to the T_n state for CX is calculated to be 0.85 at a 40 mJ cm^{-2} fluence. The high photolysis pulse fluence seems to be sufficient to account for the formation of *o*-xylylene

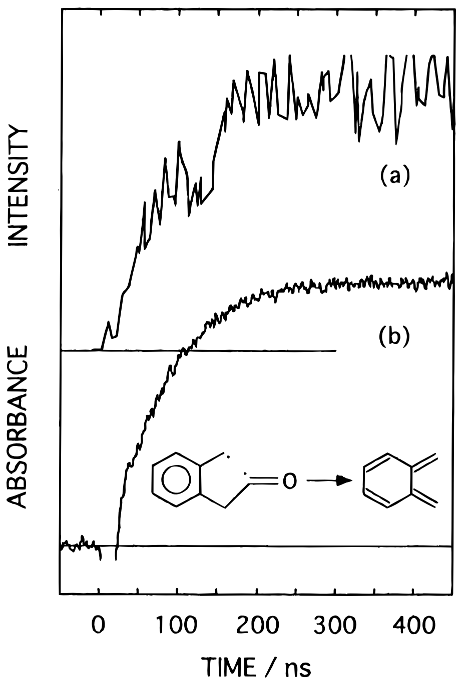


Figure 4. Time evolution of (a) fluorescence and (b) absorption intensities of *o*-xylylene produced by photolysis of IN at 266 nm. Fluorescence is induced by excitation at 308 nm, of which a delay time is an abscissa for (a). Monitoring wavelengths: (a) 470; (b) 370 nm.

by dissociation from the T_n state of CX. The analysis suggests that the second 266-nm photon is absorbed by the T_1 state of CX to dissociate two Cl atoms.

3.3. Formation Kinetics. The fluorescence intensity of *o*-xylylene, from dissociation of CX and BX, is observed to rise within the 5-ns duration of the photolysis pulse. The fluorescence intensity of *o*-xylylene, from dissociation of MSX, is detected to be weak, reflecting a low dissociation yield. Exact kinetics has not been analyzed for dissociation of CX, BX, or MSX.

Although photolysis of IN may produce the acyl benzyl biradical $^{\bullet}(CO)CH_2C_6H_4CH_2^{\bullet}$, the fluorescence and absorption only assignable to *o*-xylylene are observed in 0.02−100-μs delays. No absorption due to the acyl benzyl biradical is obtained, because of interruption of the fluorescence of an impurity in the 280−340-nm region. The rise of the fluorescence and absorption intensities of *o*-xylylene, generated by photolysis of IN with the 266-nm pulse, is given in Figure 4. The fluorescence intensity is monitored by variation of the delay of the 308-nm pulse. Measurement of the absorption intensity within a 0.02-μs delay is interrupted by the fluorescence of an impurity. The rise rates of the fluorescence and absorption intensities agree well and are of a value of $(1.4 \pm 0.1) \times 10^7\ s^{-1}$.

It is known that dibenzyl ketone causes rapid α-cleavage ($>10^{10}\ s^{-1}$) from the $T_1(n,\pi^*)$ state to form the phenylacetyl radical,[16] which subsequently undergoes decarbonylation to the benzyl radical.[17−19] Decarbonylation rates of 10^6−$10^7\ s^{-1}$ have been reported for the phenylacetyl radical.[17−19] From this viewpoint, the present result on the formation of *o*-xylylene with the rate of $(1.4 \pm 0.1) \times 10^7\ s^{-1}$ may be interpreted in terms of decarbonylation of the acyl benzyl biradical to *o*-xylylene.

4. Conclusion

Upon photolysis at 266 nm, CX, BX, MSX, and IN generate *o*-xylylene. CX dissociates two Cl atoms, by two-photon absorption, with an apparent yield of 0.30 ± 0.08 at a fluence of 40 mJ cm^{-2}. Dissociation of a C−Sn bond occurs in MSX. IN eliminates a C=O group, by one-photon absorption, with a rate of $(1.4 \pm 0.1) \times 10^7\ s^{-1}$ and a yield of 0.90 ± 0.08.

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