

Mechanistic studies on the photogeneration of *o*- and *p*-xylylenes from α,α' -dichloroxylenes

Miguel A. Miranda,^{*a†} Julia Pérez-Prieto,^{*b} Enrique Font-Sanchis,^a and J. C. Scaiano^{*c}

^a Instituto de Tecnología Química/Departamento de Química, Universidad Politécnica de Valencia, Camino de Vera s/n, 46071 Valencia, Spain

^b Departamento de Química Orgánica, Facultad de Farmacia, Universidad de Valencia, Vicent Andrés Estellés s/n, Burjasot, 46100 Valencia, Spain

^c Department of Chemistry, University of Ottawa, Ottawa, Canada K1N 6N5

Two-colour two-laser techniques have unambiguously proved that photolysis of the *o*-*p*-(chloromethyl)benzyl radical leads to the sequential two-photon generation of *o*-*p*-xylylene from α,α' -dichloro-*o*-*p*-xylylene.

Xylylenes are molecules of considerable theoretical and synthetic interest, which have been detected and characterized by different spectroscopic methods.¹ Although benzylic dichlorides have been used as very simple and readily accessible precursors, the involved mechanisms are not completely understood.² It has been recently reported³ that 266 nm laser irradiation of α,α' -dichloro-*o*-xylene (**1a**) produces the dissociation of both C–X bonds *via* a two-photon process; however, the nature of the intermediate species which absorbs the second photon is uncertain. Three possibilities have been considered: the S₁ and T₁ states of **1a** and the *o*-(chloromethyl)benzyl radical (**2a**). Based on the short lifetime of the singlet state of the dichloride and the apparent relative yields of the observed transients, the undetected T₁ state of the dichloride has been suggested as the photochemical precursor of *o*-xylylene.

Our aim was to explore the photochemistry of the benzyl radical **2a** produced after dissociation of one C–X bond of α,α' -dichloro-*o*-xylene, using two-laser two-colour techniques, in order to obtain new data to support or reject the intermediacy of **2a** in the formation of *o*-xylylene. We report here our findings and compare them with those obtained in the photolysis of α,α' -dichloro-*p*-xylene. Based on the obtained results, a mechanism for the formation of *o*- and *p*-xylylenes from their corresponding dichloro precursors is presented.

Laser flash photolysis of deaerated 1.5 mM solutions of **1a** in cyclohexane at 266 nm (Nd: YAG laser, fourth harmonic, < 10 ns, ≤ 20 mJ pulse⁻¹) yielded the transient absorption spectra shown in Fig. 1. Two transients with different lifetimes were

obtained. According to the literature,³ they were assigned to **2a** (with a maximum at 330 nm) and *o*-xylylene (**3a**) (maximum at 360 nm, $\epsilon_{\text{max}} = 3 \times 10^3$ dm³ mol⁻¹ cm⁻¹),⁴ generated through one- and two-photon processes, respectively.

When irradiating with a 266 nm laser it is useful to place a beam diffuser (which eliminates 'hot' spots in the laser beam) close to the sample in order to get a better observation of monophotonic transients.⁵ Actually, a new spectrum obtained under these conditions showed a higher ratio of radical **2a** to the two photon intermediate, **3a** (Fig. 1).

To confirm the radical nature of the transient at 330 nm, oxygenated samples were examined, showing that, while the band at 330 nm was quenched at close to the diffusion controlled limit (see insert Fig. 1), the lifetime of the transient at 360 nm appeared insensitive to the presence or absence of oxygen (data not shown).

Furthermore, to study the photobehaviour of **2a**, two-colour two-laser photolysis experiments⁶ were carried out using 266 nm laser pulses (20 mJ pulse⁻¹) to photolyze **1a** and a 308 nm excimer laser (90 mJ pulse⁻¹) to irradiate **2a**. The two pulses were typically separated by *ca.* 2.5 μ s, a time sufficiently long that the irradiation of excited states of **1a** by the 308 nm laser is impossible. We note that **1a** is transparent at 308 nm. That the benzyl radical **2a** can be the precursor of *o*-xylylene is clearly demonstrated by comparing the spectra obtained upon irradiation with the first and the second laser (Fig. 2). The permanent and irreversible bleaching of the transient with a maximum at 330 nm was concurrent with the jump of the band with a maximum at 360 nm.

Thus, it seems clear that **2a** photolyzes to *o*-xylylene, and a mechanism for the photogeneration of *o*-xylylene from α,α' -dichloro-*o*-xylene is shown in Scheme 1; while triplet **1a** may or may not produce *o*-xylylene, it is clear that there is no need to invoke this undetected process.

On the other hand, laser flash photolysis of deaerated 1.5 mM solutions of α,α' -dichloro-*p*-xylene (**1b**) in cyclohexane at 266 nm (with a beam diffuser) yielded the transient absorption spectrum shown in Fig. 3. Irradiation of oxygenated samples showed that the band at 320 nm was quenched at close to the diffusion controlled limit, but the lifetime of the transient at 290 nm appeared to be insensitive to the presence of oxygen. Thus, the band at 320 nm can be assigned to the *p*-(chloromethyl)benzyl radical (**2b**) by comparison with the band of the *p*-methylbenzyl radical in solution.⁷ On the other hand, the band at 290 nm is assigned to *p*-xylylene in accordance with literature data.⁸ At first glimpse, the formation of *p*-xylylene from **1b** appeared to be more efficient than the generation of *o*-xylylene from **1a**, even if both dihalides were photolyzed under the same conditions [compare curve (b) in Fig. 1 and the transient in Fig. 3]. However, this could also reflect a different molar extinction coefficient of both xylylenes. Although ϵ_{max} of **3b** has not been reported, electronic spectra calculated for xylylenes⁹ indicate that a much higher intensity should be expected for the absorption of the *para* than for the *ortho* derivative.

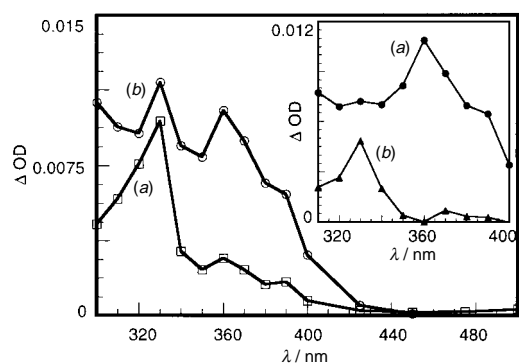


Fig. 1 Transient absorption spectra recorded following laser excitation (266 nm) of **1a** under nitrogen 2 μ s after laser pulse (a) with diffuser and (b) without diffuser. Insert: (a) spectrum of *o*-xylylene obtained 2.32 μ s after irradiation in the presence of oxygen without diffuser; (b) spectrum of **2a** obtained by normalizing and subtracting the spectrum of *o*-xylylene from the spectrum obtained in the absence of oxygen.

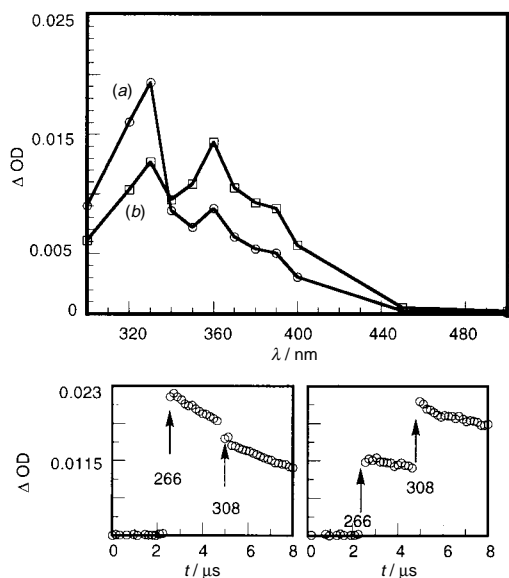


Fig. 2 Top: (a) Transient absorption spectrum recorded following laser excitation (266 nm) of **1a** under nitrogen 1.12 μ s after laser pulse. (b) Transient absorption spectrum obtained upon two laser-two colour excitation of **1a**. The intermediate generated by means of a 266 nm laser pulse is photolyzed after 2 μ s by a second laser at 308 nm. Bottom: Kinetic trace at 330 nm (left) and 360 nm (right); the bleaching at 330 nm corresponds to the disappearance of **2a** and the jump at 360 nm corresponds to the formation of **3b**.

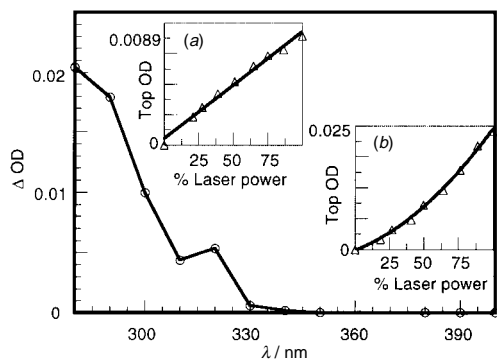
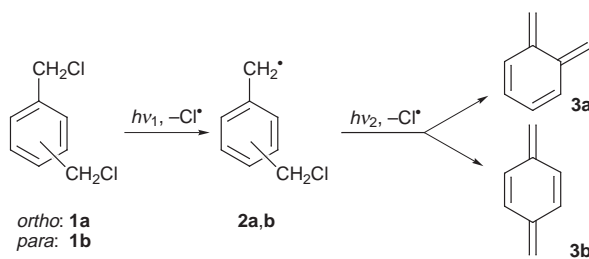


Fig. 3 Transient absorption spectrum recorded following laser excitation (266 nm) of **1b** under nitrogen 0.8 μ s after laser pulse. Inserts (a) and (b) show the effect of the laser power on signal intensities monitored at 320 and 290 nm, respectively.

To establish the nature of the process leading to radical **2b** and *p*-xylylene, an investigation of the effects of light intensity on the relative intensity of their signals was carried out by attenuating the laser beam with a set of calibrated neutral density filters. Inserts (a) and (b) in Fig. 3 show that there is a linear relationship between the formation of **2b** and the laser power, while a parabola is obtained in the case of **3b**; thus, the evidence supports a one-photon process for the benzylic radical and a two-photon process for *p*-xylylene.

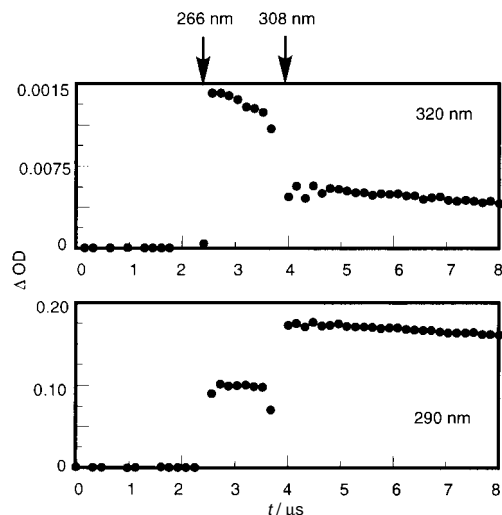


Fig. 4 Two laser-two colour photolysis of **1b**. Top: kinetic trace at 320 nm; the bleaching corresponds to the disappearance of **2b**. Bottom: kinetic trace at 290 nm; the jump corresponds to the formation of **3b**.

The photobehaviour of radical **2b** was studied by using two-colour two-laser experiments; the 266 nm laser was used to generate this radical, which was further irradiated with pulses from the 308 nm laser. That **2b** can be the precursor of **3b** is clearly demonstrated by comparing traces obtained for both transients (Fig. 4). Thus, the bleaching at 320 nm was coincident with the jump at 290 nm. Based on this evidence the mechanism for the photogeneration of *p*-xylylene from α,α' -dichloro-*p*-xylene is also that of Scheme 1.

In summary, this work has demonstrated that benzyl radicals are the key light absorbing transients in the two-photon generation of *o*- and *p*-xylylenes from the corresponding dichloroxylenes.

J. C. S. thanks the National Sciences and Engineering Research Council of Canada for support. Spanish DGICYT (MAM, Project no. PB94-0539) and Spanish Ministry of Education (EFS, Grant) are gratefully acknowledged.

Notes and References

† E-mail: mmiranda@qim.upv.es

- L. A. Errede, *J. Am. Chem. Soc.*, 1961, **83**, 949; E. Migirdicyan and J. Baudet, *J. Am. Chem. Soc.*, 1975, **97**, 7400; J. J. McCullough, *Acc. Chem. Res.*, 1980, **13**, 270; Y. Ito, M. Nakatsuka and T. Saegusa, *J. Am. Chem. Soc.*, 1982, **104**, 7609; V. Wintgens, J. C. Netto-Ferreira, H. L. Casal and J. C. Scaiano, *J. Am. Chem. Soc.*, 1990, **112**, 2363.
- K. L. Tseng and J. Michl, *J. Am. Chem. Soc.*, 1977, **99**, 4840; K. Haider, M. S. Platz, A. Despres, V. Lejeune, E. Migirdicyan, T. Bally and E. Haselbach, *J. Am. Chem. Soc.*, 1988, **110**, 2318.
- M. Fujiwara, K. Mishima, K. Tamai, Y. Tanimoto, K. Mizuno and Y. Ishii, *J. Phys. Chem.*, 1997, **101**, 4912.
- W. S. Trahanovsky and J. R. Macias, *J. Am. Chem. Soc.*, 1986, **108**, 6820.
- M. A. Miranda, J. Pérez-Prieto, E. Font-Sanchis, K. Kónya and J. C. Scaiano, *J. Org. Chem.*, 1997, **62**, 5713.
- J. C. Scaiano, L. J. Johnston, W. G. McGimpsey and D. Weir, *Acc. Chem. Res.*, 1988, **21**, 22.
- R. F. C. Claridge and H. Fisher, *J. Phys. Chem.*, 1983, **87**, 1960.
- G. Kaupp, *Angew. Chem., Int. Ed. Engl.*, 1976, **15**, 442; J. M. Pearson, M. A. Six, D. J. Williams and M. Levy, *J. Am. Chem. Soc.*, 1971, **93**, 5034; R. Marquardt, W. Sander, T. Laue and H. Hopf, *Leibigs Ann.*, 1995, 1643.
- C. R. Flynn and J. Michl, *J. Am. Chem. Soc.*, 1974, **96**, 3280.

Received in Liverpool, UK, 12th March 1998; 8/02016G