

Laser-flash photolysis of α -brominated *o*-xylenes

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Abstract

The flash photolysis ($\lambda = 266$ nm) of four α -brominated *o*-xylenes in apolar solvents gives two transients characterized, depending on parent compound substitution, as either monoradicals or carbenes, and quinodimethanes. α -Bromomethylbenzyl radical is characterized and the novel species α,α' -dibromo-*o*-xylylene and *o*-(α,α' -dibromomethyl)benzyl carbene are described for the first time. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Our interest in the photochemical generation of radicals and biradicals in liquid phase [1] led us to select a series of α -brominated *o*-xylenes (**1**) to be studied by laser flash-photolysis. Compounds **1**, exposed to UV irradiation (266 nm), might: (i) yield a benzyl radical (and Br^\bullet), through cleavage of just one of the carbon–halogen bonds; (ii) form an *o*-quinodimethane/ Br_2 pair via the cleavage of two carbon–bromine bonds, possibly through a monophotonic process: $D(o\text{-MeC}_6\text{H}_4\text{CH}_2\text{-Br}) = 48.5 \text{ kcal mol}^{-1}$ [2], which may, afterwards, collapse to the same pair of radicals as in (i) above; (iii) eliminate H–Br, forming an *o*-xylylene; or (iv) eliminate Br_2 , leading to a fleeting carbene [3–5], which ought to transform into an *o*-xylylene by means of a [1,4] hydrogen (or bromine) shift. Of course, not all the paths outlined above are open for every member of the series **1a–d** (Scheme 1).

Thus, even if the proposal (ii) is the one that outlines the preferential route to radical formation, the *o*-quinodimethanes formed ought to be observable in a flash photolysis experiment, although a dienophile might be unable [6–8] to trap them, as we have observed [1] on steady-state irradiation of benzenic solutions of **1** ($\lambda_{\text{irr}} = 254$ nm).

2. Experimental

The substituted xylenes **1a** [10], **1b** [11], **1c** [1] and **1d** [12] were prepared according to literature procedures and recrystallized (at low temperature, when necessary) or distilled until a 99.5% purity (by ^1H NMR and by GLC) was attained.

The flash-photolysis experiments were performed (on ca. $10^{-4} \text{ mol l}^{-1}$ isooctane solutions of the xylenes having absorbances of 0.6–0.8, degassed to 5×10^{-5} Torr through five freeze, pump and thaw cycles) with an Applied Photophysics kinetic spectrometer having a quadrupled Nd-YAG laser (266 nm) for excitation, a pulsed xenon short-arc lamp for monitoring the transients and a photomultiplier connected to a Techtronics 2230 oscilloscope for detection. Each decay corresponds to the average of 3–5 laser shots. The comparison of absorption spectra obtained before and after the flash determinations show that absorbing photo-products are not measurably formed in our experimental conditions.

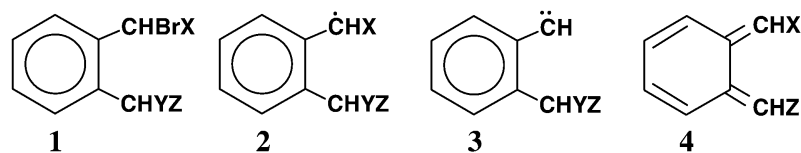
Raw datasets were acquired with a 20.5 point/ μs digital resolution in the time domain. Noise was reduced by applying a 4 MHz FFT filter to the raw datasets. Intensity data were obtained from the kinetic decays by taking 5 point averages bracketing the points corresponding to either 0.5 or 10.0 μs . From the points thus obtained (shown in Figs. 1–3), best-fit spectral curves were generated by using cubic splines as described by Gans and Gill [13].

The measurements in benzene solutions were performed using a XeCl excimer laser (308 nm), as described elsewhere [14], in Victoria University.

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Where: (a) X=Y=Z=H ;
 (b) X=Y=H and Z=Br ;
 (c) X=Br and Y=Z=H ;
 (d) X=Y=Z=Br .

Scheme 1.

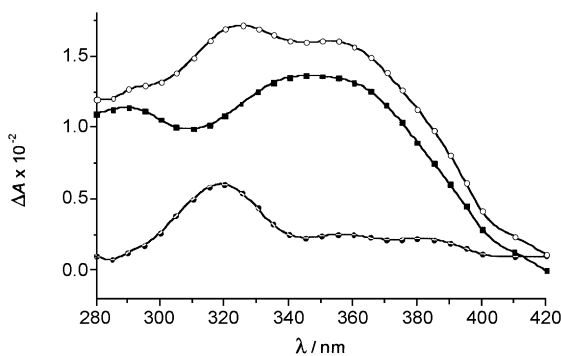


Fig. 1. Transient absorption spectra from **1a** in degassed isooctane solution at 0.5 μs (—○—) and 10.0 μs (—■—); trace (—●—) was obtained by subtracting the latter from the former.

3. Results and discussion

Time resolved UV absorption spectra of dry degassed isooctane solutions of compounds **1a–d**, obtained by flash-photolysis with the fourth harmonic (266 nm) of a Nd³⁺-YAG laser, gave rise to time-dependent spectra (Figs. 1–3) having at least one absorption maximum disappearing at shorter times (hereby labeled **I**), and a persistent absorption (hereby labeled **II**), whose decay to zero is too slow (of the order of hundreds of milliseconds) to be fully observed in our apparatus (absorption maxima presented in

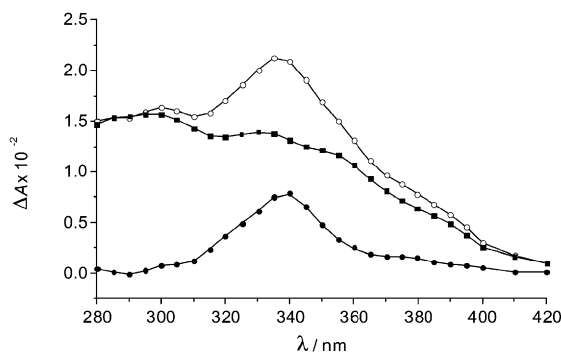


Fig. 2. Transient absorption spectra from **1b** in degassed isooctane solution at 0.5 μs (—○—) and 10.0 μs (—■—); trace (—●—) was obtained by subtracting the latter from the former.

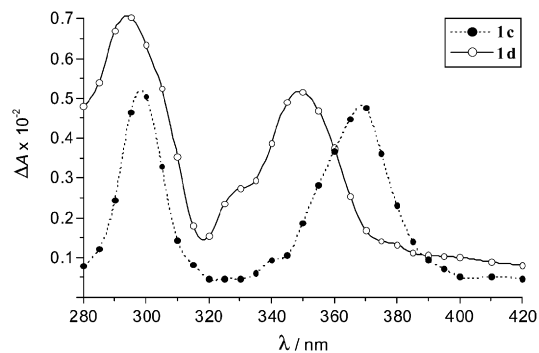


Fig. 3. Transient absorption spectra from **1c** or **1d** in degassed isooctane solution at 0.5 μs .

Table 1). However, it was possible to estimate the apparent lifetime of transient **II** (335 ms for **1b**) by turning off the pulsing unit of the analysis lamp during signal monitoring. The fact that this persistent absorption was not due to stable photoproducts was verified, in all cases, by comparing the steady-state UV absorption spectra obtained from the test solutions before and after the experiments.

3.1. Transients I

The transients **I** here investigated can be divided into two groups (see discussion below): those arising from precursors possessing only bromomethyl substituents (**1a** and **b**) are radicals, while those formed from molecules bearing gem-dibromomethyl groups (**1c** and **d**) are carbenes.

Table 1
UV absorption maxima for transients observed

Compound	Solvent	Transient I λ (nm)	Transient II λ (nm)
1a	LFP; isooctane ^a	2a 320	4a ca. 355
1b	LFP; isooctane ^a	2b 338	4a ca. 355
1b	LFP; benzene ^b	2b 333	
1c	LFP; isooctane ^a	3c 298	4a 368
1d	LFP; isooctane ^a	3d 295	4d 350
1d	LFP; benzene ^b		4d 361

^a Nd-YAG laser ($\lambda = 266$ nm).

^b Eximer laser ($\lambda = 308$ nm) [14].

Various authors [15–19] reported values for the absorption maxima assigned as $D_3 \leftarrow D_0$ electronic transition for substituted benzyl radicals (all of them around 320 nm), permitting to conclude that neither the presence of different substituents nor significant changes in the polarity of the solvent do cause major shifts in the absorption maxima of these species [15–19].

In the case of compounds **1a** and **1b** (i.e., those bearing bromomethyl moieties), the maxima (Table 1) of the transient absorption spectra (Figs. 1 and 2) obtained from the decay curves are consistent with literature $D_3 \leftarrow D_0$ data [15–19], permitting to ascribe the transient of faster decay (**I**) to monoradicals formed after the light-promoted homolytic cleavage of one C–Br bond.

While the **2a** absorption maximum value ($\lambda = 320$ nm: $2^2A_2 \leftarrow 1^2B_2$) is in accordance with literature data [15–19], the observed value for **2b** ($\lambda_{\max} = 338$ nm, in line with $\lambda_{\max} = 340$ nm, by Fujiwara et al. [9]) shows a shift to a longer wavelength (ca. 20 nm) in relation to those reported for related compounds [15–19]. This unexpected value should be attributed to the effect exerted by the bromomethyl substituent in *ortho* position, more pronounced for **2b** than for radicals in which the halogen is directly linked to the ring [15,16,19–21].

Probably, the enhancement in the substituent effect is caused by the electron-density dispersion induced by the presence of a bromo atom in a position that favours the attainment of a five-membered ring-like intermediate, which is unlike for all previously described benzyl radicals. This interpretation also holds for the *o*-(α -chloromethyl)benzyl radical that presents [9] an absorption maximum at 330 nm, as chlorine should provide the same kind of stabilization to the radical center (to a lesser extent, for it is a harder halogen).

To confirm the assignment of these transients, a qualitative quenching experiment was performed, by the addition of cyclohexene (CHx, a hydrogen donor better than isooctane) to the **1b**/isooctane system: the rate constant related to processes involving H^\bullet abstraction is increased (Fig. 4), the

decay constant becoming short enough to allow the decay to be well described by a mono-exponential, with a lifetime of 2.8 μ s. Piperylene and oxygen are also quenchers for transients **I** (see Fig. 4), reinforcing the radical character of these species, as radicals are known [16,20] to react with oxygen giving peroxy derivatives.

The comparison of the kinetic profiles presented in Fig. 4, in the presence and in the absence of CHx, shows that immediately after the shot the absorbance intensities have essentially equal values at $t = 0$, an indication that the excited state precursor of the radicals is not significantly quenched by CHx. In addition, the quenching efficiency exhibited by piperylene in our system permits to conclude that it is deactivating the precursor of the transients observed, i.e., probably the triplet is the parent state as there is no support for the idea that piperylene could be a much more efficient quencher for radicals than cyclohexene.

For compounds **1c** and **1d** (i.e., those bearing the dibromomethyl moiety) we observed meaningful changes both in the decays (the lifetime of **I** is shorter than those observed for **1a,b**) and in the λ of the maxima (around 300 nm) determined from the absorption spectra (shown in Fig. 3). These data should be explained by the presence of a bromine atom attached to the radical center (i.e., the *ipso*-carbon), which turns α -elimination a possible decay route after light absorption, leading to the formation of carbenes, a path well supported by the extant literature [3–5]. Thus, for **1c,d**, we assign the transient of faster decay (**I**) to carbenes **3c,d**. This interpretation is supported by the maxima determined from the transient absorption spectra (Table 1), in agreement with previously reported data ($\lambda_{\max} = 305$ and 315 nm, for **3c** [3] and mesitylcarbene [4], respectively). Moreover, the transients from **1c,d** are efficiently quenched by oxygen (data not shown), in line with the results of Adamasu et al. [5]. It is worth to point out that the λ_{\max} value for **3d** (295 nm, reported here for the first time) indicates that for carbenes there is no bathochromic shift (akin to that observed for radical **2b**).

3.2. Transients II

The second, long-living, transient observed in the photolyses of all the compounds under investigation is always an *o*-xylylene: **4a** is obtained in the photolyses of **1a–c**, while its dibromo derivative **4d** is formed from **1d**.

The transients **II** are not cations, despite Tokumura's suggestions [16,20,21] in that sense. In fact, Fujisaki et al. [22,23] have shown that benzyl cation absorbs at $\lambda_{\max} = 303$ nm, while McClelland et al. [24] reported $\lambda_{\max} = 310$ nm for the *p*-methylbenzyl cation. The data for a series of related benzyl cations displayed in Table 1 of the paper by McClelland et al. [24] are in this same range.

So, if a benzyl cation were the transient **II** observed in the photolysis of **1a**, it ought to show a maximum at ca. 310 nm, because only *o*-methylbenzyl cation could possibly arise from **1a** and there is no reason to suppose that it should

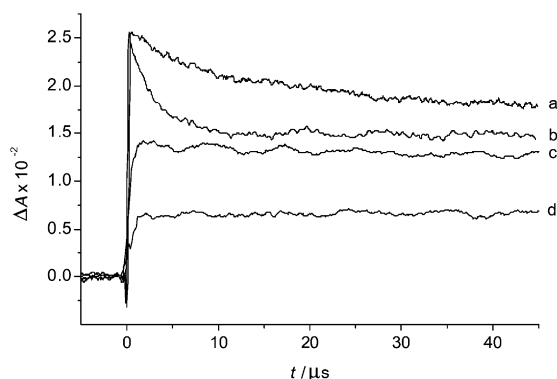


Fig. 4. Absorption decay kinetic profiles from **1b** in degassed isooctane solution at 340 nm: (a) neat and in the presence of (b) $4.0 \times 10^{-2} \text{ mol l}^{-1}$ cyclohexene, (c) $1.5 \times 10^{-2} \text{ mol l}^{-1}$ oxygen gas, (d) $1.0 \times 10^{-3} \text{ mol l}^{-1}$ piperylene.

present spectral features much different from those due to its *para* isomer [24]. In fact, the transient **II** observed in the photolysis of **1a** absorbs at much longer wavelengths (Table 1).

Once cations are excluded, the fact that the transients **II** are not deactivated by oxygen (both a triplet and a radical quencher) indicates the presence of *o*-xylylenes. Comparison of decays **c** and **d** in the experiments for **1b** shown in Fig. 4 support well this attribution because oxygen does not react with quinodimethanes, as does piperylene. In addition, as the baseline is not zero even in decay **d** (Fig. 4), we can conclude that transient **II** arises, at least in part, not from **I** but from the singlet excited state.

Our results in the flash photolysis of **1b** confirm the data reported recently by Fujiwara et al. [9] referring to the formation of *o*-xylylene during the photolysis of the same parent compound. In the present work, we have found that this process is monophotonic as, for dissociation of **1b**, logarithmic plots of the initial absorbances versus photolysis pulse fluences, in the range of 10–100 mJ cm⁻², are represented by straight lines, with slopes 1.05 ± 0.10 for the formation of **2b** and 0.85 ± 0.10 for the formation of **4a**. These data confirm our initial hypothesis that the energy of a single 266 nm photon ($h\nu_{266} = 107.5 \text{ kcal mol}^{-1}$) should suffice to break two C–Br bonds, a result diverse from the biphotonic route operating for α, α' -dichloro-*o*-xylene [9].

The transient spectrum arising from **1a** presents a broad absorption band, its maximum being shifted somewhat to lower wavelengths relative to its expected value due to convolution with residual absorption of the respective transient **I** being still not negligible at 50 μ s. So, by analogy with our other results (and those of Fujiwara et al. [9]) we assign this transient **II** as being the same unsubstituted *o*-quinodimethane (**4a**), although its formation, with overall elimination of HBr, must be a biphotonic process because [25] $D[o\text{-MeC}_6\text{H}_4\text{CH}_2\text{-H}] = 87.2 \text{ kcal mol}^{-1}$.

The *o*-xylylene **4a** (i.e., transient **II**) is also formed upon photolysis of (scrupulously dry, aldehyde free) **1c**. As there is no spectral feature superposition from **3c** (transient **I**), in this case an absorption band showing λ_{max} at 370 nm is observed in its UV spectrum, in good agreement with the published [26] values.

The photolysis of **1d** gives rise to a transient **II**, very similar to **4a**, but displaying a broad absorption band, with $\lambda_{\text{max}} = 350 \text{ nm}$. By analogy with the results obtained from **1a-c** and structural considerations, this species must be the novel α, α' -dibromo-*o*-xylylene **4d**. The λ_{max} at shorter wavelength than that due to **4a** being suggestive that this is the third example of an *o*-xylylene twisted about the “essential” single bonds, akin to the previously reported [27,28] α, α' -dimethyl-*o*-xylylene and $\alpha, \alpha, \alpha', \alpha'$ -tetramethyl-*o*-xylylene.

It is well documented in the literature that *o*-quinodimethanes usually present long apparent lifetimes [26–28]. Also, neither **4a** nor **4d** were suppressed upon addition of CH_x, which might seem surprising in view of the fact that Hornback and Barrows [29] had succeeded in trapping

α, α' -dimethyl-*o*-xylylene (generated by steady-state UV irradiation) with the same dienophile. However, as we have reported before [1], no Diels–Alder adducts of either **4a** or **4d** were obtained on prolonged steady-state UV irradiation of **1a-d**, in the presence of cyclohexene. So, we regard the results of Hornback and Barrows [29] as an exceptional case, the more so as the same authors also failed [6] to obtain adducts from other structurally related *o*-xylylenes with this dienophile.

3.3. Photolyses in benzene

Time resolved UV absorption spectra of dry degassed benzene solutions of compounds **1b** and **1d**, obtained by flash-photolysis with a XeCl excimer (308 nm) laser, were also acquired. Both experiments gave rise to spectra whose appearance was similar to those observed in isooctane, except that, as expected, apparent lifetimes of the observed transients **I** were ca. 10-fold longer in benzene. Besides this, a third transient with $\lambda_{\text{max}} = 550 \text{ nm}$ was observable in both cases, which is attributable to the formation of the known Br•–benzene complex [30], thus confirming the presence of bromo radicals in the system investigated here.

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