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Photo-induced dehalogenation of α-bromoacetylarenes

M. Hall [1], L. Chen, C.R. Pandit, W.G. McGimpsey *

Department of Chemistry and Biochemistry, Worcester Polytechnic Institute, Worcester, MA 01609, USA

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Abstract

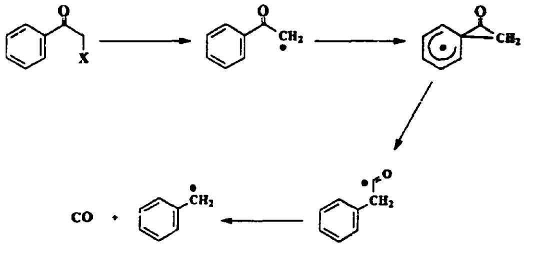
2-Bromo-2'-acetylnaphthalene (**1**), 2-bromo-2'-acetylphenanthrene (**2**) and 2-bromo-9'-acetylanthracene (**3**) undergo photo-debromination following excitation to the singlet S_1 state with quantum yields of 0.34, 0.27 and 0.06, respectively. The initially formed aroylmethyl radicals undergo a 'neophyl-like' rearrangement to an arylacetyl radical that subsequently undergoes decarbonylation to the corresponding arylmethyl radical. The latter are observed spectroscopically. While the lowest excited triplet states are inert towards cleavage, excitation to an upper triplet state in a two-color experiment causes debromination.

Keywords: Acetylarenes; Photochemistry; Debromination; Upper triplet states

1. Introduction

Halogen atom–benzene π-complexes are formed following the photochemical production of halogen atoms in benzene solvent. The π-complexes are transient species with relatively short lifetimes at room temperature (typically ca. 1 μs) and absorption bands in the visible region of the spectrum [1–7]. Some time ago, it was recognized that if reliable extinction coefficients could be established for these species, they would be useful as quantitative, transient dehalogenation probes. A study was undertaken to determine extinction coefficients using α-haloacetophenones as photochemical halogen atom generators (specifically, chlorine and bromine atoms) and valerophenone as an actinometer [6]. (Irradiation of α-haloacetophenones and valerophenone leads, in both cases, to the production of acetophenone.)

Several aspects of this study prompted us to extend our investigations to include other α-haloacetyl aromatic compounds. First, the product investigations carried out in the original study suggested that following dehalogenation, a 'neophyl-like' rearrangement occurs [6,8,9], followed by decarbonylation to form the benzyl radical which, in turn, can react in the presence of a hydrogen atom donor to produce toluene (see Scheme 1). However, it was not possible to directly observe the formation of benzyl radical due to other interfering absorptions in the same spectral region, and therefore no transient evidence could be obtained for this suggestion.



Scheme 1.

Second, there was some question as to the identity of the excited state responsible for dehalogenation, with both the singlet and triplet states being possible precursors. In both α-chloroacetophenone (ClACP) and α-bromoacetophenone (BrACP), the excited singlet state energies are sufficient to prompt carbon–halogen (C–X) bond cleavage. However, it is unclear whether the low fluorescence intensities of these compounds were due to cleavage or ketone-enhanced ISC.

The triplet state energies (69.8 kcal mol^{-1} and 68 kcal mol^{-1} for ClACP and BrACP, respectively) are much closer to the commonly accepted values of the C–X bond energies in these systems (71.2 kcal mol^{-1} for C–Cl and 63.9 kcal mol^{-1} for C–Br) [10–12] bringing into question the role of the triplet states in cleavage. In fact, the triplet lifetime for ClACP is quite short relative to that of acetophenone (155 ns versus several μs) suggesting that the triplet state could be a cleavage precursor. For BrACP the triplet was not observed at all, suggesting either an extremely short triplet

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* Corresponding author.

[1] Undergraduate author.

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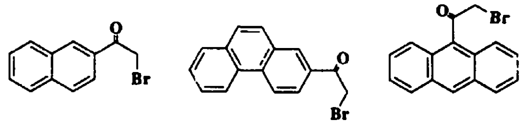
lifetime (beyond the time resolution of the instrumentation) or a failure of the singlet state to undergo ISC.

In this paper, we report the investigation of the photochemical debromination of 2-bromo-2′-acetylnaphthalene (**1**), 2-bromo-2′-acetylphenanthrene (**2**) and 2-bromo-9′-acetylanthracene (**3**) (see Scheme 2). These systems were chosen because their extended π-systems are known to produce a significant red-shift in the arylmethyl radical absorption maxima [13–15] and therefore are expected to provide transient evidence for the occurrence of the neophyl rearrangement. Also, since the triplet, T_1, states of **1**–**3** have more $\pi\pi^*$ character compared to the $n\pi^*$ triplets of ClACP and BrACP, their T_1 energies were expected to be similar to those of the parent aromatics, i.e. lower than the C–Br bond energy, and therefore they should be inert towards cleavage. We expected this behavior to provide the opportunity to investigate the role of the singlet state in cleavage without interference from T_1 states.



1 2 3

Scheme 2.

However, we did not expect to unambiguously identify the cleavage precursor as the singlet state since a dissociative upper triplet (formed directly by ISC from the singlet manifold) has been suggested as the precursor of dehalogenation in aryl halides and halothiophenes [16,17]. Compounds **1**–**3** should provide, however, the opportunity of probing the reactivity of upper triplet states towards debromination (see Ref. [7]). Since the T–T absorption spectra of **1**–**3** are expected to be similar to those of the parent aromatics [18] and fall within a region of the visible spectrum that is accessible by our pulsed laser sources, it should be possible to investigate the behavior of upper excited triplet states by performing two-color experiments on these compounds.

2. Experimental details

2.1. Materials

2-Bromo-2′acetylnaphthalene (**1**), 2-acetylnaphthalene (**4**), naphthalene (**7**), 2-acetylphenanthrene (**5**), phenanthrene (**8**), 9-acetylanthracene (**6**) and anthracene (**9**) were obtained from Aldrich and were recrystallized twice prior to use. 2-Bromo-2′-acetylphenanthrene (**2**) and 2-bromo-9′-acetylanthracene (**3**) were synthesized as outlined below. All solvents were spectrophotometric grade and were used as received from Aldrich.

2.1.1. Synthesis

Compounds **2** and **3** were prepared from the corresponding parent acetylaromatics by treatment with phenyltrimethylammonium tribromide by a method adapted from the literature [19] and described below.

2.1.1.1. Preparation of phenyltrimethylammonium sulfomethylate

A solution of freshly distilled *N,N*-dimethylaniline (12.4 g, 12.9 ml, 0.10 mol) in toluene (50 ml) was heated to 40°C in a water bath. The solution was removed from the heat and dimethylsulfate (Aldrich, sure seal, 9.5 ml, 0.10 mol) was added dropwise, over 10 min. The reaction mixture turned pale pink within minutes and the sulfomethylate began to crystallize. The reaction was stirred at room temperature for 1 h and the heated on a steam bath for 1 h. After cooling to room temperature, the resulting suspension was collected by filtration, washed with dry toluene (10 ml) and dried under house vacuum. Yield: 22.6 g, 90%.

2.1.1.2. Preparation of phenyltrimethylammonium tribromide

A solution of phenyltrimethylammonium sulfomethylate (10 g, 0.040 mol) in 48% HBr (10 ml) was diluted with water (10 ml). Bromine (7.8 g, 2.5 ml, 0.049 mol) was added to the reaction mixture over 20 min, with stirring. Immediately, an orange–yellow precipitate formed. The suspension was stirred for 5 h at room temperature, collected by filtration, washed with water (10 ml), and dried under house vacuum. Crude phenyltrimethylammonium tribromide (10.3 g) was crystallized from acetic acid (25 ml). The crystallized product was collected by suction filtration, washed with acetic acid (25 ml) and dried under house vacuum for 12 h. Phenyltrimethylammonium tribromide was obtained as orange crystals. Yield: 12.9 g, 86%.

2.1.1.3. Preparation of 2-bromo-2′-acetylphenanthrene (2)

A suspension of 2-acetylphenanthrene (1.10 g, 5.00 mmol) in anhydrous THF (10 ml) was warmed until the solution was clear. After the solution was cooled to room temperature, phenyltrimethylammonium tribromide (1.88 g, 5.00 mmol) was added in small portions over 10 min. A white precipitate formed within minutes and the solution turned pale yellow. The resulting suspension was stirred for 1 h at room temperature and then water (50 ml) was added. Upon vigorous stirring a white precipitate formed. The product was washed with water (10 ml) and collected by suction filtration. The crude material was recrystallized twice from (1:1) cyclohexane:dichloromethane to give 2-bromo-2′-acetylphenanthrene (**2**) as pale yellow crystals. Yield: 0.79 g, 53% MP: 143°C.

2.1.1.4. Preparation of 2-bromo-9′acetylanthracene (3)

Small portions of phenyltrimethylammonium tribromide (1.88 g, 5.00 mmol) was added in small portions over 10 min to a stirred solution of 9-acetylanthracene (1.10 g, 5 mmol) in anhydrous THF (10 ml). The reaction mixture turned deep orange and within minutes a precipitate formed.

The solution subsequently turned pale yellow. The reaction mixture was stirred for 1 h at room temperature and then water (50 ml) was added dropwise, via an addition funnel. The product oiled out. The reaction mixture was extracted with EtOAc (3×20 ml). Organic layers were combined, anhydrous $MgSO_4$ and charcoal (0.20 g) were added and the suspension was stirred for 30 min at room temperature. The reaction mixture was filtered through a pad of celite and the celite pad was washed with EtOAc (2×20 ml). A brown oil was obtained after concentration of the filtrate and it solidified upon placing under high vacuum. The crude material was recrystallized twice from cyclohexane (10 ml) to give 2-bromo-9′-acetylanthracene (**3**) as pale yellow crystals. Yield: 0.84 g, 56% MP: 95°C.

2.2. *Laser flash photolysis*

The laser flash photolysis system has been described in detail elsewhere [20]. Briefly, for kinetic studies and transient absorption spectra, solutions of **1**–**3** were prepared at concentrations sufficiently large to give absorbances in the range 0.6–0.8 at the excitation wavelength. Unless otherwise noted, the solutions contained in a reservoir were continuously purged with a stream of nitrogen and were caused to flow through a specially constructed quartz cell (7 mm× 7 mm) by means of a peristaltic pump. This ensured that a fresh volume of solution was exposed to each laser pulse, thereby avoiding accumulation of photoproducts. Samples were irradiated with the pulses of a Lumonics EX 510 excimer laser (308 nm; ~20 mJ pulse^{-1}; 8 ns pulse duration) or the frequency-tripled output of a Continuum Nd/YAG laser (355 nm, ~30 mJ pulse^{-1}, 5 ns). In two-laser studies [21], the 308 (or 355) nm pulse was followed, after a period of 1–2 μs, by the pulse from a flashlamp-pumped dye laser (output tuned to the T–T absorption maxima of **1**–**3**; ~70 mJ; 400 ns).

2.2.1. *Debromination quantum yields*

Debromination quantum yields, $\Phi_{\cdot Br}$, were determined using the bromine atom–benzene π-complex as a transient debromination probe and α-bromoacetophenone (BrACP) as a standard ($\Phi_{\cdot Br}=0.40$) [6]. Yields were determined by measuring the transient absorbance at the π-complex absorption maximum (550 nm) immediately after laser excitation (308 nm) of air-saturated solutions of BrACP and **1**–**3**. The solutions were matched in absorbance at the laser wavelength.

2.3. *Phosphorescence measurements*

Phosphorescence spectra were obtained with a Perkin-Elmer LS 50 Spectrofluorimeter. Spectra of nitrogen-saturated solutions of **1**–**3** in 1:1 ethanol:methanol were measured at 77 K.

3. Results and discussion

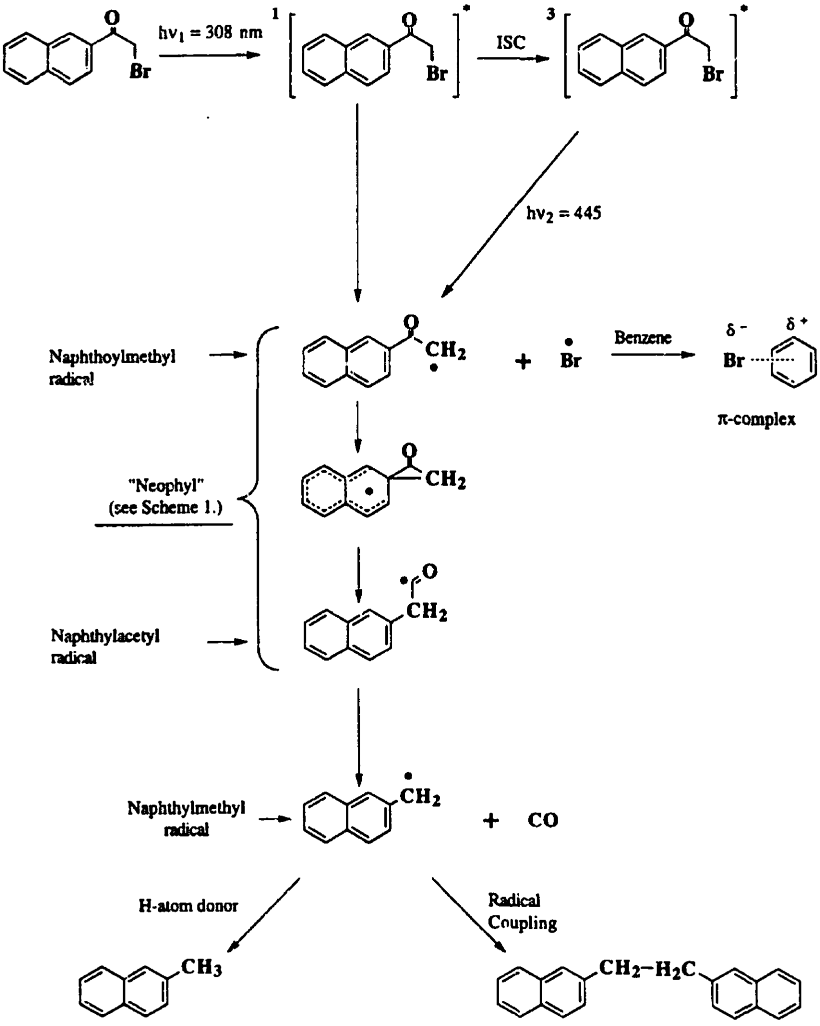
Scheme 3 shows the photoinduced debromination of **1** in room-temperature solution as supported by the following fluorescence and phosphorescence data measured under CW conditions as well as the transient absorption spectra and decay kinetics obtained upon 308 nm pulsed-laser irradiation. The mechanism shown also applies to **2** and **3**. (Note that in this scheme, we have not considered the possible participation of dissociative upper triplet states. While we have obtained evidence for such a state formed following photoexcitation of the T_1 state in two-color experiments, there is no direct evidence for the formation of such a state by ISC from the singlet. Therefore, in rationalizing the results, we have considered only singlet, S_1, and triplet, T_1, states. However, we cannot rule out the participation of such a dissociative upper triplet state formed by ISC.)

Table 1 provides fluorescence quantum yield data, singlet and triplet energies as obtained from absorption and luminescence measurements, as well as from literature sources, for **1**–**3**, the non-brominated ketones **4**–**6** and the parent aromatics **7**–**9**, and debromination quantum yields for **1**–**3**. The fluorescence quantum yields for **1**–**6** were measured relative to the corresponding parent aromatics, the values for which were taken from the literature [22,23]. Due to the low quantum yields for **1**, **2** and **5**, the singlet energies were estimated from the onset of the $S_0 \rightarrow S_1$ absorption band. The value for **4** was taken from the literature [22].

Photoexcitation of **1**–**3** results initially in the formation of the lowest excited singlet state. From the luminescence and laser measurements (see below) we ascribe the decay of this singlet state to a combination of fluorescence, intersystem crossing and debromination, the relative efficiencies of which depend upon the derivative. For **1**, **2**, **4** and **5**, i.e. the naphthalene and phenanthrene derivatives, the fluorescence quantum yields were below the detection limit of our apparatus. Since both the brominated and non-brominated compounds exhibited low yields, the immediate conclusion can be made

Table 1
Photophysical data for excited singlet and triplet states of **1**–**9** and debromination quantum yields of **1**–**3**

Compound	Φ_F	E_S (kcal mol^{-1})	E_T (kcal mol^{-1})	$\Phi_{\cdot Br}$
1	$<10^{-4}$	~77	58.6	0.34
2-Acetylnaphthalene (**4**)	$<10^{-4}$	77.7	59.4	–
Naphthalene (**7**)	0.23	92.0	60.9	–
2	$<10^{-4}$	~78	62.0	0.27
2-Acetylphenanthrene (**5**)	$<10^{-4}$	~78	61.9	–
Phenanthrene (**8**)	0.13	82.8	62.0	–
3	3.6×10^{-3}	75.9	~42	0.06
9-Acetylanthracene (**6**)	2.8×10^{-3}	76.0	42.0	–
Anthracene (**9**)	0.29	76.3	42.0	–



Scheme 3.

that the addition of the ketone substituent dramatically enhances the ISC efficiency at the expense of the fluorescence yield. However, the transient evidence (see Table 1 and below) also indicates that a significant number of excitation events lead to debromination ($\Phi_{\cdot Br} = 0.34$ and 0.27 for **1** and **2**, respectively). It is clear then, that debromination competes effectively with formation of T_1.

From the standpoint of the energetics of debromination, it is not surprising that the relatively high singlet energies of **1** and **2** can promote this process. However, upon first inspection, the low efficiency of debromination in **3**, which is reflected in both the low value for the debromination quantum yield ($\Phi_{\cdot Br} = 0.06$) and the lack of effect of bromine substitution on the measurable fluorescence quantum yield, appears to be inconsistent with the singlet energy, which is similar to those of **1** and **2** and is significantly higher than the expected bond energy. We suggest that in **1** and **2**, the singlet states may have mixed nπ^* and $\pi\pi^*$ character. This is supported by the significant decrease in the singlet energy which is observed upon the introduction of the acetyl substituent on the parent aromatic (15 kcal mol^{-1} in naphthalene and 5 kcal mol^{-1} in phenanthrene). In contrast, methyl substitution of naphthalene (methylnaphthalene also has a $\pi\pi^*$ singlet) causes only a small decrease in singlet energy.

The nπ^* excited state of **1** or **2** can be visualized as an α-bromo-substituted radical. There is precedent from work on the debromination of vicinal dibromides that indicates such a radical would be prone to efficient thermal loss of bromine [24–27]. On the other hand, the singlet state of **3** likely has very little nπ^* character (there is virtually no effect on the singlet energy as a result of acetyl substitution), meaning that there is less likelihood of debromination.

Laser flash photolysis of **1** leads to the production of three transient species as shown in the transient absorption spectra in Figs. 1 and 2. In nitrogen-saturated benzene (Fig. 1, square symbols), the two absorption bands at λ_{max} ~ 430 and 550 nm decay with lifetimes of 9.2 and 1.1 μs, respectively, and are assigned to the T–T absorption and bromine atom–benzene π-complex absorption. The identity of the triplet is confirmed by the sensitivity of the 430 nm absorption to oxygen as well as its similarity to the T–T absorption spectra of **4** and **7**. Note that under air-saturated conditions (Fig. 1, round symbols) the 430 nm absorption band is absent. The decay of the 550 nm band is insensitive to oxygen and is absent when acetonitrile is used in place of benzene. (See Fig. 2.) This behavior, coupled with the spectral location of the band are consistent with the π-complex. The relatively long lifetime of the triplet T_1 state and the 'instantaneous' production of the π-complex rule out T_1 as a cleavage precursor. The triplet state energies measured by phosphorescence are very similar to those of the non-brominated and parent aromatics, i.e. they lie below the bond energy by at least 4 kcal mol^{-1}. It is not surprising, therefore, that the triplet states of **1** and **2** are unreactive towards debromination.

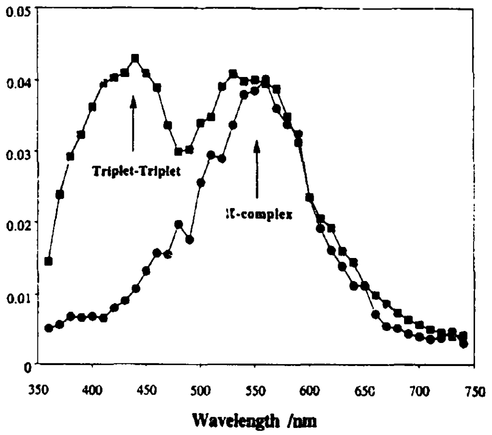


Fig. 1. Transient absorption spectra obtained 1 μs after 308 nm excimer laser irradiation of **1** in nitrogen- (square symbols) and air-saturated (round symbols) benzene.

In addition to these two transients, a third, long-lived, oxygen-insensitive absorption, λ_{max} ~ 370–380 nm, can be observed after the overlapping absorption due to the triplet state has decayed. This situation is shown in Fig. 2, where the spectra have been obtained 0.2 (round symbols) and 10 μs (square symbols) after the laser pulse. (The spectrum was obtained in acetonitrile to eliminate complications due to the π-complex absorption. However, a similar absorption is observed in benzene after the π-complex has decayed.) The 370 nm absorption band is assigned to the 2-naphthylmethyl radical, as its lifetime (> 100 μs) and spectral location are in accord with numerous previous reports of this radical (see, for example, Refs. [13–15]). The observation of this absorption in both benzene and acetonitrile lends further support to this assignment as does the fact that both **2** and **3** exhibit long-lived absorptions consistent with their respective arylmethyl radicals. While it could be argued that assignment of the radical to the low wavelength absorption shown in Fig. 2 is not indisputable due to the fact that this absorption is generally featureless, the spectrum obtained for **3** is much more distinctive and is identical to that reported previously for anthrylmethyl and anthrylethyl radicals [27,28]. This observation provides support for our assignment of arylmethyl radicals for all three compounds formed via the neophyl rearrangement. Fig. 3 shows the spectrum obtained for **3** in air-saturated benzene. (The negative ΔOD at λ < 400 nm is due to bleaching of the ground state.)

The kinetic decay profiles for **1** in benzene shown in Fig. 4 further support the above assignments. The decay at 410

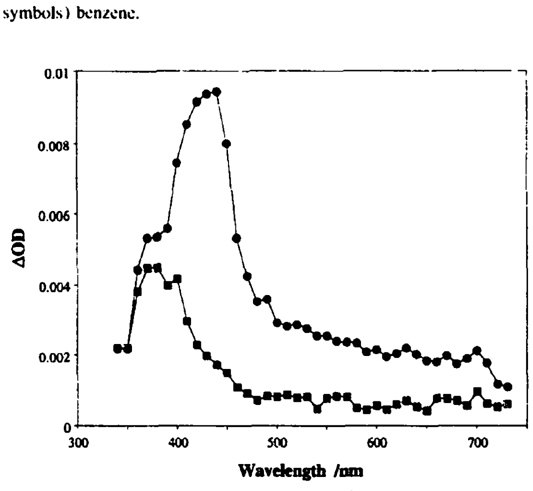


Fig. 2. Transient absorption spectra obtained 0.2 μs (round symbols) and 10 μs (square symbols) after 308 nm laser irradiation of **1** in air-saturated acetonitrile.

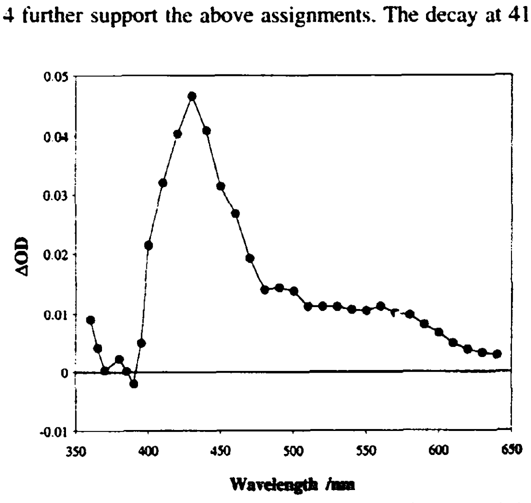


Fig. 3. Transient absorption spectrum obtained 4 μs after 308 nm irradiation of **3** in air-saturated benzene. The π-complex absorption has decayed prior to this time.

nm (Fig. 4(a)) (this wavelength was chosen so as to avoid the overlapping π-complex absorption) is given for both nitrogen- and air-saturated conditions. It is clear from both profiles that there are two transients present, one sensitive to oxygen (triplet) and one insensitive (2-naphthylmethyl radical). Fig. 4(b) shows the decay at 440 and 550 nm. While the decay kinetics appear to be very similar at both wavelengths, it is important to note that the 440 nm decay was obtained under nitrogen while that at 550 nm was in air-saturated solution. Thus these, profiles clearly indicate the presence of two transients — the triplet and π-complex.

To further support our suggestion of a neophyl rearrangement, we carried out product studies in which a solution of **1** in benzene with added benzenethiol was irradiated by 1000 pulses from the excimer laser. Benzenethiol has been shown to act as an efficient hydrogen atom donor for carbon-centered radicals [6,29]. The solutions were continuously stirred during the irradiation. Following irradiation, the solutions were evaporated and resolubilized in a small quantity of benzene and analyzed by GC. The results indicated that a significant concentration of 2-methylnaphthalene and a minor amount of 1,2-(bis-2-naphthyl)ethane were formed by the photolysis. Both products support the formation of the 2-naphthylmethyl radical, the neophyl product. 2-Methylnaphthalene forms when the 2-naphthylmethyl radical abstracts a H-atom from benzenethiol and 1,2-(bis-2-naphthyl)ethane forms via a radical–radical coupling reaction. Similar results were obtained for **2** and **3** with the exception that the formation of the radical coupling product could not be confirmed due to the lack of authentic standards for comparison.

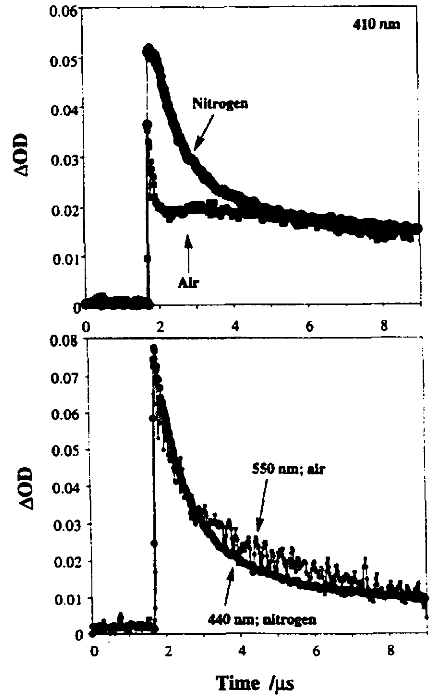


Fig. 4. (a) Transient decay kinetics monitored at 410 nm obtained for 308 nm irradiation of **1** in nitrogen- (round symbols) and air-saturated (square symbols) benzene solution. (b) Decay kinetics for 308 nm irradiation of **1**: monitored at 550 nm under air-saturated conditions and at 440 nm under nitrogen-saturated conditions.

The kinetic decay profile obtained at 410 nm under air-saturated conditions (shown in Fig. 4(a)) has a minor, resolvable growth component between 0 and 1.5 μs after the laser pulse. This was a small but consistent feature of all the experiments with **1** that were run under air-saturation. (The unquenched T–T absorption under nitrogen prevents the observation of this effect.) Previous studies [8] of benzoylalkyl radicals derived from acetophenone and α-substituted acetophenones indicated that the neophyl conversion from benzoylalkyl to phenylacetyl was relatively slow (the rate-determining step) and that subsequent decarbonylation was rapid. Based on these results, we suggest that the growth shown in Fig. 4, which ultimately represents the formation of the 2-naphthylmethyl radical, reflects the kinetics of the neophyl rearrangement, specifically the conversion from naphthoylmethyl radical to naphthylacetyl radical. (Decarbonylation is again expected to be rapid.) We were unable to observe a similar growth for the radicals derived from **2** and **3** due to stronger overlapping transient absorptions.

The non-reactivity of the lowest triplet states of **1–3** towards debromination is consistent with the triplet energies as compared with the expected bond energy. It is also consistent with the observations reported previously for a variety of systems including bromoarenes such as bromonaphthalene and bromophenanthrene [6], bromo- and iodothiophene derivatives [18], and arylmethyl halides (see, for example, [17]). In the latter systems, a dissociative upper triplet state ($\sigma\sigma^*$) was implicated as the immediate precursor of bond cleavage. In the bromoarenes [6] it was possible to demonstrate directly by a two-color experiment that the upper triplet is responsible. Given this previous work and the non-reactivity of the triplets, we undertook a two-color study of **1–3**. These experiments involved generation of the lowest triplet state by the excimer laser and subsequent excitation of the triplet by a tunable flashlamp-pumped dye laser (445 nm for **1** and **3** and 488 nm for **2**) to an upper triplet state. The transient consequences of the two-laser excitation of **3** in nitrogen-saturated benzene are shown in Fig. 5. It is clear that the dye laser pulse causes permanent depletion of the triplet absorption. (Fig. 5(a)) This indicates that some of the upper triplet states formed by excitation do not relax back to the lowest triplet, but rather, undergo some other decay process or processes. In itself, this observation does not confirm debromination. However, the decay profile obtained at 550 nm (Fig. 5(b)) clearly shows the formation of π-complex concurrent with the dye laser pulse. A transient absorption spectrum obtained following the dye laser pulse further supports the formation of the π-complex. Similar results were obtained for **1** and **2**.

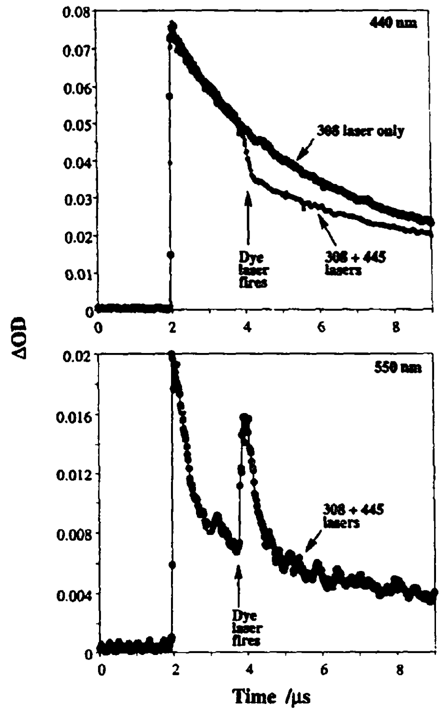


Fig. 5. (a) Transient decay kinetics monitored at 440 nm for one-laser (308 nm) (round symbols) and two-laser (308+445 nm) (square symbols) irradiation of 3 in nitrogen saturated benzene. (b) Two-laser kinetics monitored at 550 nm.

4. Summary

UV excitation of 1-3 results in debromination via the excited singlet state, as evidenced by low fluorescence quantum yields, unreactive, long-lived triplet (T_1) states and 'instantaneous' production of the bromine atom-benzene π-complex. While no evidence was obtained for the participation of a dissociative upper triplet state formed directly by ISC, we do not rule out this possibility, especially in light of the fact that the upper triplet states produced by two-color irradiation undergo debromination. The debromination process and its yield were measured using the bromine atom-benzene π-complex as a transient probe. The debromination yields decreased in the order 1 > 2 > 3. For 1 and 2, the singlet states have significant $n\pi^*$ character, as indicated by the substantial decrease in singlet energy upon acetyl substitution of the parent aromatic. This, in turn, facilitates debromination and results in a relatively high quantum yield for this process. On the other hand, the singlet energy of 3 is virtually the same as for anthracene, indicating substantial $\pi\pi^*$ character. This is reflected in the debromination yield for 3, which is low despite the fact that the singlet energy is comparable to the singlet energies of 1 and 2. Following debromination the initially formed aroylmethyl radical undergoes a 'neophyl-type' rearrangement and subsequent decarbonylation, producing the arylmethyl radical. Support for the formation of the latter radical is provided by transient spectral observation and the results of product studies.

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