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Pulse radiolysis and flash photolysis studies of arylalkylamines in aqueous solutions — primary photoprocesses

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Abstract

The photophysical processes leading to photoionization and photodissociation in the arylalkylamines benzylamine and benzhydrylamine were examined as a function of pH in aqueous solution using a KrF excimer laser. The main photolytic reaction observed for the amines is photoionization. The hydrated electron subsequently reacts with the amine leading to deamination when the amino group is in the protonated form, whereas, at pH ≈ 11.0, e_{aq}^- adds to the benzene ring. Photodissociation processes occurring via C–H and C–C bond rupture are also observed and various transient intermediates can be identified by generation in appropriate pulse radiolysis experiments under suitable conditions. The two-step photoionization occurs via the triplet excited state as indicated by the heavy atom effect. In contrast, photodissociation occurs via a monophotonic process. © 1997 Elsevier Science S.A.

Keywords: Aqueous solution; Arylalkylamines; Flash photolysis; Primary photoprocesses; Pulse radiolysis

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1. Introduction

Various studies on the absorption and luminescence of benzyl derivatives of the type $C_6H_5CH_2X$ have been carried out [1], and different mechanisms have been suggested for the photochemical processes taking place in the phenylalkyl compounds [2,3], including the formation of benzyl radicals and hydrated electrons via photoionization. Some data also indicate the nature of the excited state precursor involved. However, the photochemistry of benzylamine [4] is not yet clearly understood. An effort is made in this work to clarify the laser flash photolysis results of benzylamine, and to study aminodiphenylmethane in which the α-H atom of benzylamine is substituted by a phenyl group. In addition, the effects of pH, light intensity and heavy atoms on the photophysical and photochemical processes have been studied. The intermediates observed in the laser photolysis (248.4 nm) studies are identified and characterized using the fast reaction technique of pulse radiolysis.

2. Experimental details

The photochemical experiments were conducted using an excimer laser photolysis apparatus with pulses (248.4 nm, 20 ns, 25 mJ per pulse) from a KrF excimer laser system. A description of the computer-controlled apparatus, including the kinetic spectrophotometer with a nanosecond response, is given elsewhere [5]. The solutions were saturated with N_2 or N_2O for the removal of oxygen. Cells with a path length of 20 mm were used for photolysis. A conventional analysis system with a pulsed Xe flash lamp was used to monitor the transient absorption. Neutral density filters were used to vary the laser pulse intensity. Actinometry was performed by monitoring the absorption of naphthalene triplet at 414 nm in oxygen-free cyclohexane solution. The absorption spectra of the solutions before and after irradiation were obtained with a Cary 219 UV–visible spectrophotometer.

The pulse radiolysis experiments were carried out with an ARCO LP-7 linear accelerator supplying 5 ns electron pulses. The doses were 1 krad per pulse which produced approximately $(3–6) \times 10^{-6}$ M of radicals. The transient absorption spectra and kinetics were measured by computer-controlled pulse radiolysis as described elsewhere [6,7].

The $O^{\bullet -}$ reactions with arylalkylamines in the pulse radiolysis studies were carried out in 1 M KOH solutions where OH is over 99% dissociated into $O^{\bullet -}$. Water was purged with N_2O for at least 30 min before KOH was added. The absolute data for reactions of $O^{\bullet -}$ with arylalkylamines were determined by following the growth in absorption of the product radicals.

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In the absence of side reactions of e_{aq}^- and H atoms with the solutes present in solution, the $O^{\bullet -}$ radical yield in N_2O-saturated solution is $G = 6.6$ [8].

Dosimetry for pulse radiolysis experiments was carried out to obtain accurate radical concentrations using KCNS solution [9]. The optical absorption spectra before and after irradiation were recorded on a Cary 219 spectrophotometer.

Benzylamine and aminodiphenylmethane were obtained from Aldrich. Tertiary butyl alcohol (tert-BuOH) and other inorganic reagents used to adjust the pH were ''Baker Analysed Reagents''.

3. Results and discussion

3.1. Benzylamine

The transient absorption spectra produced on laser photolysis of oxygen-free solutions of 7.5 mM benzylamine ($pK = 9.3$) in 20% tert-BuOH at pH 7.2 are shown in Fig. 1. A band with a maximum at approximately 290 nm, a shoulder at about 303 nm, another sharp absorption at approximately 314 nm and a broad absorption in the visible region were observed. On saturating the above solution with N_2O and photolysing under the same conditions, the broad absorption in the visible region almost disappeared, the absorption peak at 290 nm remained and no sharp peak was observed at 314 nm.

The broad absorption in the visible region observed for an N_2-saturated solution of benzylamine is due to the hydrated electrons produced via the photoionization of benzylamine. Similar photoionization processes have been observed in the photolysis of aromatic amino acids [10–12] and arylalkyl carboxylic acids [12,13]. From the optical density (OD) of the photoionized electrons obtained on flash photolysis of 7.5 mM benzylamine, the concentration of the electrons produced was calculated to be 3.6×10^{-5} M based on the known extinction coefficient of e_{aq}^- [14]. In the presence of N_2O, these hydrated electrons are scavenged by the following reaction

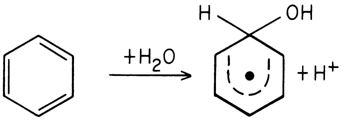
$$e_{aq}^- + N_2O \rightarrow {}^{\bullet}OH + N_2 + OH^- \qquad (1)$$

The OH radicals react with tert-BuOH to give rise to ${}^{\bullet}CH_2C(CH_3)_2OH$ radicals which absorb [15] below 300 nm and are relatively unreactive.

The radical cation of benzylamine seems to undergo hydrolysis in water

$$(PhCH_2\overset{+}{N}H_3)^{\bullet +} + H_2O \rightarrow H^+ + Ph(OH)CH_2\overset{+}{N}H_3 \qquad (2)$$

Similar results have been observed during the laser-induced photoionization of benzene in aqueous solution [16,17], where the benzene radical cation undergoes hydrolysis



(3)

Hydrated electrons have been shown, in pulse radiolysis experiments [18], to react with benzylamine at pH 7.2, leading to deamination of the molecule by the following dissociative electron capture reaction

$$e_{aq}^- + PhCH_2\overset{+}{N}H_3 \rightarrow Ph^{\bullet}CH_2 + NH_3 \qquad (4)$$

with $k = 1.5 \times 10^9\ M^{-1}\ s^{-1}$. We propose that the transient absorption band obtained in Fig. 1 with a sharp peak at 314 nm is due to the absorption of the benzyl radicals $Ph^{\bullet}CH_2$ produced by the reductive deamination reaction. From the difference spectrum obtained from the photolysis of N_2- and N_2O-saturated solutions, the OD of the benzyl radicals formed during the laser photolysis of benzylamine can be obtained after subtracting the absorption due to $Ph(OH)CH_2\overset{+}{N}H_3$ radicals; based on the known extinction coefficient of this radical [18], the concentration of the benzyl radicals formed was calculated to be approximately 2.6×10^{-5} M. This yield of benzyl radicals shows that 72% deamination takes place with the hydrated electrons formed. This agrees with the percentage deamination determined for benzylamine in the pulse radiolysis experiments. The second-order rate constant of the reaction of photoionized electrons with $PhCH_2\overset{+}{N}H_3$ was calculated from the pseudo-first-order rate of decay of the electrons measured during the photolysis of benzylamine by following the decay at 600 nm; this was found to be very close to the value obtained in the pulse radiolysis experiment [18].

The sharp absorption peak observed with $\lambda_{max} = 290$ nm may be due to the following photodissociation reaction

$$PhCH_2\overset{+}{N}H_3^+ \xrightarrow{h\nu} H + Ph\overset{+}{C}H\overset{+}{N}H_3\ (\text{C–H rupture}) \qquad (5)$$

$$H + PhCH_2\overset{+}{N}H_3 \rightarrow Ph(H)CH_2\overset{+}{N}H_3$$

$$(\text{H atom adduct to benzylamine}) \qquad (6)$$

In our earlier flash photolysis work on phenylglycine [13], the $Ph^{\bullet}CH\overset{+}{N}H_3$ radical was postulated to have been formed

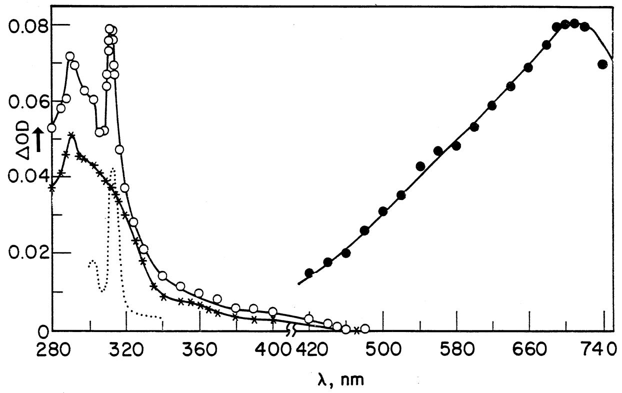


Fig. 1. Transient absorption spectrum observed on laser photolysis of oxygen-free 7.5 mM benzylamine in 20% tert-BuOH at pH 7.2 in the presence of N_2 (○); OD measured 2 μs after the laser pulse in the presence of N_2O (∗); OD measured 2 μs after the laser pulse in the presence of N_2 (●); OD measured 50 ns after the flash is the difference spectrum (· · ·).

by the decarboxylation reaction of phenylglycine at pH 3.3 in the presence of N_2O and tert-BuOH

$$\overset{+}{N}H_3CH(Ph)COO^- \xrightarrow{h\nu} e_{aq}^- + \overset{+}{N}H_3\overset{+}{C}H(Ph) + CO_2 \qquad (7)$$

and a transient spectrum with $\lambda_{max} = 290$ nm was observed. To identify and characterize the absorption spectrum of $Ph^{\bullet}CH\overset{+}{N}H_2$ conclusively, the $O^{\bullet -}$ reaction with benzylamine was studied during the pulse radiolysis of a 1 mM solution of $PhCH_2NH_2$ in the presence of 1 M KOH and N_2O. At this high pH, the hydroxyl radical produced in the irradiated aqueous solution is rapidly converted into its basic form, the oxide anion radical, to a degree controlled by the equilibrium [19]

$$^{\bullet}OH + OH^- \underset{pK=11.85}{\rightleftarrows} O^{\bullet -} + H_2O \qquad (8)$$

$O^{\bullet -}$ radicals have been suggested [20] to be very useful reagents in the preparation of substituted benzyl radicals in aqueous solution. They can abstract a hydrogen atom from the alkyl chain of benzylamine to give rise to $Ph^{\bullet}CHNH_2$ as follows

$$O^{\bullet -} + PhCH_2NH_2 \rightarrow OH^- + Ph^{\bullet}CHNH_2 \qquad (9)$$

Fig. 2 shows the absorption spectrum of $Ph^{\bullet}CHNH_2$ observed during the pulse radiolysis of an aqueous solution of $PhCH_2NH_2$. This radical has a sharp absorption maximum at 290 nm with $\epsilon_{290} = 13\,000$ M^{-1} cm^{-1}. The hydrogen abstraction from the α position is very nearly quantitative [20]. The $Ph^{\bullet}CHNH_2$ radical is expected [18] to have acid–base properties

$$Ph^{\bullet}CH\overset{+}{N}H_3 \leftrightharpoons Ph^{\bullet}CHNH_2 + H^+ \qquad (10)$$

By following the kinetics of formation of the radical $Ph^{\bullet}CHNH_2$ by studying its optical absorption at 290 nm at varying substrate concentrations, the pseudo-first-order rate was determined, from which the absolute second-order rate constant for reaction (9) was calculated to be 2.4×10^9 M^{-1} s^{-1} (see inset in Fig. 2).

To determine the quantum requirement of the various processes involved, we studied the dependence of the concentration of the various intermediates produced during the laser photolysis of benzylamine at pH 7.2 on the intensity (I and I^2) of the excitation light. The OD values of the transients at various wavelengths (600 nm, 314 nm and 290 nm) in the presence of N_2 and N_2O were plotted as a function of I and I^2. Fig. 3(A) shows that photoionization is a two-step process, whereas photodissociation leading to the $Ph^{\bullet}CH\overset{+}{N}H_3$ radical is a monophotonic process (see Fig. 3(B)). The slope of the line obtained by plotting log OD_{314} vs. log I in N_2-saturated solution shows a value of 1.3 probably because, at this wavelength, more than one radical absorbs.

Fig. 4 shows the transient absorption spectrum obtained during the flash photolysis of N_2-saturated 7.5 mM benzylamine at pH 1.7 in 20% tert-BuOH. An absorption peak is observed at 314 nm and a shoulder at 288 nm. The 288 nm shoulder is assigned to the photodissociation process giving rise to $Ph^{\bullet}CH\overset{+}{N}H_3$, and the 314 nm peak may be due to the absorption of $Ph(OH)CH_2\overset{+}{N}H_3$ obtained by hydrolysis of the cation and the H atom adduct to the benzene ring of $PhCH_2\overset{+}{N}H_3$. The hydrated electron absorption spectrum could not be observed due to its fast reaction with H

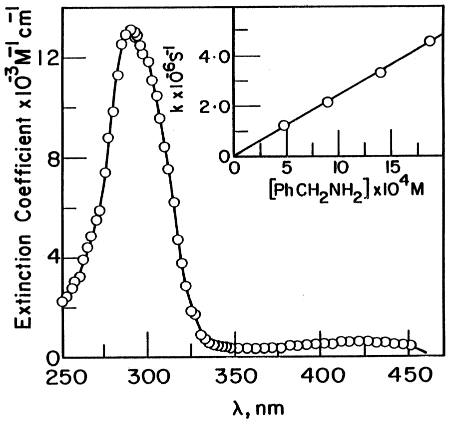


Fig. 2. Transient absorption spectrum produced by the reaction of $O^{\bullet -}$ with an oxygen-free 1 mM aqueous solution of benzylamine in the presence of N_2O and 1 M KOH. Inset shows the change in the pseudo-first-order rate of reaction of $O^{\bullet -}$ with benzylamine at different concentrations of the solute.

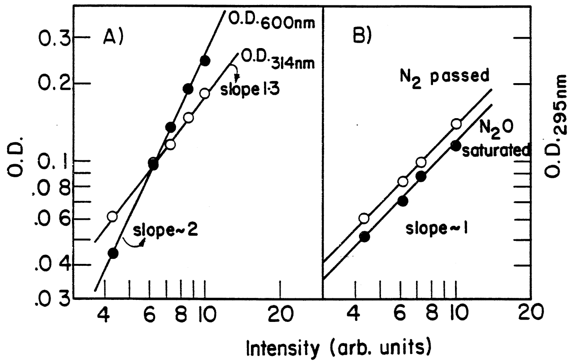


Fig. 3. (A) Dependence on the light intensity of the concentration of the transient species produced during the laser photolysis of 7.5 mM $PhCH_2NH_3$ in 20% tert-BuOH at pH 7.2 in N_2-saturated solution: ●, OD measured at 600 nm; ○, OD measured at 314 nm. (B) OD measured at 295 nm in N_2O-saturated solution (○) and N_2-saturated solution (●).

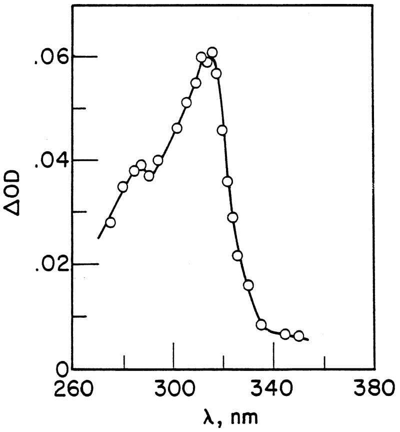


Fig. 4. Transient absorption spectrum produced during the laser photolysis of 7.5 mM $PhCH_2NH_3$ in 20% tert-BuOH at pH 1.7 in the presence of N_2. OD was measured 2 μs after the laser pulse.

($H^+ + e_{aq}^- \rightarrow H$ atom). The H atom adduct to $PhCH_2\overset{+}{N}H_3$ absorbs [18] at 315 nm with $\epsilon_{max,315} \simeq 4100\ M^{-1}\ cm^{-1}$. Therefore the 314 nm absorption maximum is a combination of the absorptions of the OH and H atom adducts to the benzene ring.

The transient absorption spectrum obtained on photolysis of 7.5 mM $PhCH_2NH_2$ at pH 11.2 in the presence of N_2 and 20% tert-BuOH is different from that obtained in the case of $PhCH_2\overset{+}{N}H_3$. Fig. 5 shows a broad absorption band at 700 nm, a sharp peak at 290 nm and a shoulder at 312 nm obtained during the photolysis of $PhCH_2NH_2$. The band at 700 nm disappears on passing N_2O. The only absorption peak left is at 290 nm and the OD at 290 nm decreases considerably from 0.087 to 0.067. The following processes may be taking place

$$PhCH_2NH_2 \xrightarrow[h\nu]{} e_{aq}^- + (PhCH_2NH_2)^+ \qquad (11)$$

$$e_{aq}^- + PhCH_2NH_2 \rightarrow \text{electron adduct to ring} \qquad (12)$$

$$PhCH_2NH_2 \xrightarrow[h\nu]{} PhCHNH_2 + H \qquad (13)$$

$$H + PhCH_2NH_2 \rightarrow Ph(H)CH_2NH_2 \qquad (14)$$

Support for reaction (12) was obtained in the pulse radiolysis experiments [18] of benzylamine, and it was observed that e_{aq}^- at pH 11.2 preferentially adds to the aromatic ring with $k = 8 \times 10^7\ M^{-1}\ s^{-1}$ giving rise to a transient absorption spectrum with $\lambda_{max} = 312$–315 nm. The pseudo-unimolecular rate of decay of the photoionized electrons observed at 600 nm gives a rate constant of $k = 0.1 \times 10^7\ s^{-1}$ for N_2-saturated 7.5 mM benzylamine on photolysis, which is slightly higher than expected. The cation may undergo hydrolysis to give rise to a hydroxyl adduct to the benzene ring as shown previously.

The photoionization proceeds via a two-step process, whereas the formation of $Ph^{\bullet}CHNH_2$ takes place through a monophotonic reaction as clearly indicated in Fig. 6. The plot of log OD_{290} vs. log I gives a slope of 1.17 in the photolysis of an N_2-saturated solution of $PhCH_2NH_2$. This may be due to the fact that, at 290 nm, we do not have exclusively $Ph^{\bullet}CHNH_2$ radicals in the N_2-saturated solution, but also the electron adduct to benzylamine, which is produced via a biphotonic process and absorbs in this region to some extent.

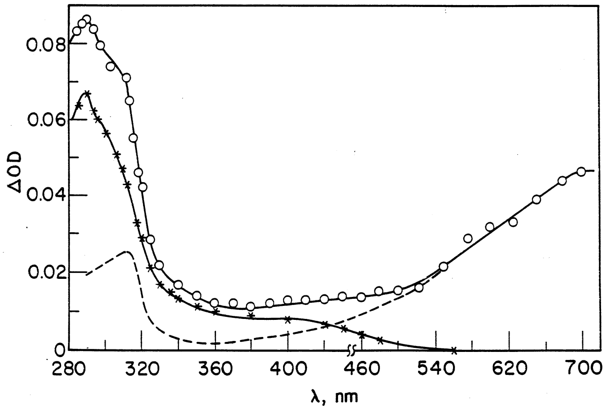


Fig. 5. Transient absorption spectrum obtained during the laser photolysis of O_2-free 7.5 mM $PhCH_2NH_2$ in 20% tert-BuOH at pH 11.2. OD measured 1.75 μs after the laser pulse in the presence of N_2 (○) and N_2O (∗). The difference spectrum is shown by · · ·.

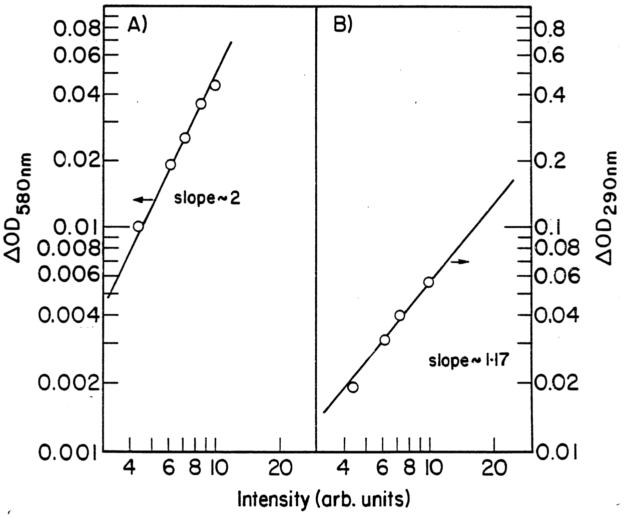


Fig. 6. Dependence on the light intensity of the concentrations of the transient species produced during the laser photolysis of 7.5 mM $PhCH_2NH_2$ in 20% tert-BuOH at pH 11.2 in N_2-saturated solutions at different wavelengths.

3.2. *Aminodiphenylmethane*

Laser photolysis of an N_2-saturated solution of 2.2 mM aminodiphenylmethane in 20% tert-BuOH at pH 11.2 gives rise to a transient absorption spectrum measured 1.5 μs after the laser pulse with a maximum absorption at 330 nm and a shoulder at 300 nm; another broad, but weaker, band is observed around 555 nm. On passing N_2O through the same solution followed by photolysis, two absorption maxima are observed, one at 290 nm and the other at 330 nm, and the peak at 555 nm remains the same. The OD at 330 nm decreases by approximately 12% in the photolysis of an N_2O-saturated solution, but there is not much change in the OD at 555 nm (see Fig. 7). A broad absorption due to hydrated electrons is also observed in the visible region, when the transient absorption is measured 50 ns after the laser pulse.

The photoionization of this molecule gives rise to solvated electrons whose concentration can be calculated to be approximately 3.3×10^{-5} M. Earlier work [18] on the pulse radiolysis of aminodiphenylamine conclusively indicated that solvated electrons attack the aromatic ring of aminodiphenylmethane and add to the ring to give rise to a radical anion; no reductive deamination is possible when the amine contains an NH_2 group

$$e_{aq}^- + Ph_2CHNH_2 \xrightarrow[k = 3.3 \times 10^8\ M^{-1}\ s^{-1}]{} (Ph_2CHNH_2)^- \qquad (15)$$

This reaction gives rise to a transient having an absorption band with $\lambda_{max} \sim 325$ nm which decays by second-order kinetics ($2k = 1.47 \times 10^9\ M^{-1}\ s^{-1}$) [16]. In N_2O-saturated solution, the solvated electrons are scavenged and two absorption peaks can clearly be seen, one at 330 nm and the

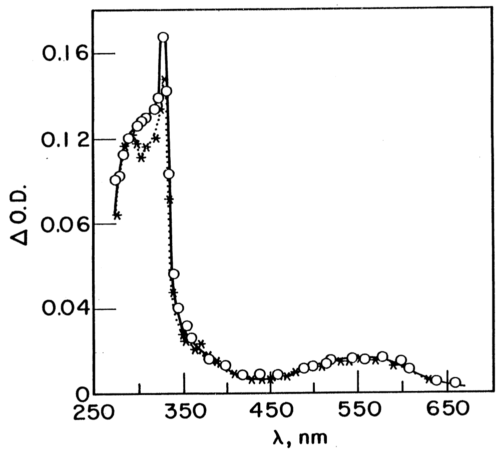


Fig. 7. Transient absorption spectrum obtained during the laser photolysis of oxygen-free 2.2 mM aminodiphenylmethane in 20% tert-BuOH at pH 11.0. OD was measured 1.5 μs after the laser pulse in the presence of N_2 (○) and N_2O (*).

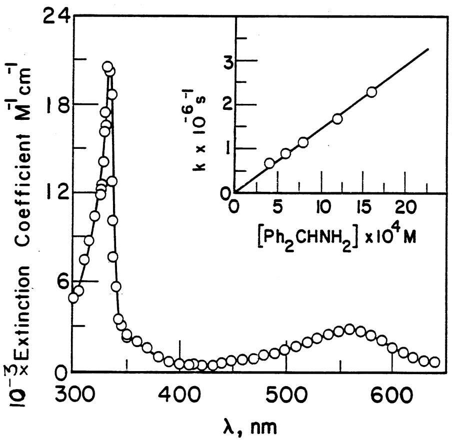


Fig. 8. Absorption spectrum of the $Ph_2^{\bullet}CNH_2$ radical obtained during the pulse radiolysis of a 1 mM aqueous solution of aminodiphenylmethane in the presence of N_2O and 1 M KOH. Inset shows a plot of the pseudo-first-order rate of the reaction of $O^{\bullet -}$ with aminodiphenylmethane as a function of the solute concentration.

other at 290 nm. The 330 nm peak may be due to the absorption of the $Ph_2^{\bullet}CNH_2$ radical formed by the following C–H rupture

$$Ph_2CHNH_2 \xrightarrow{h\nu} Ph_2^{\bullet}CNH_2 + H \qquad (16)$$

$$H + Ph_2CHNH_2 \rightarrow \text{H atom adduct to the ring} \qquad (17)$$

The $Ph_2^{\bullet}CNH_2$ radical has been obtained by the reaction of the $O^{\bullet -}$ radical with a 1 mM solution of aminodiphenylmethane in the presence of 1 M KOH and N_2O in the pulse radiolysis of aqueous solutions of this amine (Fig. 8)

$$Ph_2CHNH_2 + O^{\bullet -} \rightarrow Ph_2^{\bullet}CNH_2 + OH^- \qquad (18)$$

This radical shows a maximum absorption at 330 nm with $\epsilon_{330} = 23\,000\ M^{-1}\ cm^{-1}$ (Fig. 8) and a weaker, broad absorption at 560 nm with $\epsilon_{560} = 2900\ M^{-1}\ cm^{-1}$. The concentration of $Ph_2^{\bullet}CNH_2$ formed during laser photolysis was calculated to be 2.9×10^{-5} M. Thus the photoionization process seems to be slightly more efficient than C–H bond rupture (11 : 10).

The transient absorbing at 290 nm may be formed by the following reaction arising from C–C rupture in benzhydrylamine

$$Ph_2CHNH_2 \xrightarrow{h\nu} Ph + Ph^{\bullet}CHNH_2 \qquad (19)$$

The phenyl radical does not absorb [21] in the region of our observation, but $Ph^{\bullet}CHNH_2$ has a maximum absorption at 290 nm with $\epsilon_{290} = 13\,000\ M^{-1}\ cm^{-1}$ as shown earlier by the reaction of $O^{\bullet -}$ with $PhCH_2NH_2$. On the basis of the ϵ_{300} value of $Ph^{\bullet}CHNH_2$ of 12 000 $M^{-1}\,cm^{-1}$, it can be calculated that 3.02×10^{-5} M of $Ph^{\bullet}CHNH_2$ radicals are formed. Although, in the laser photolysis of benzylamine, a similar process could be taking place

$$PhCH_2NH_2 \xrightarrow{h\nu} {}^{\bullet}Ph + {}^{\bullet}CH_2NH_2 \qquad (20)$$

the radicals $^{\bullet}$Ph and $^{\bullet}CH_2NH_2$ are not expected to absorb in the region of our observation, and we cannot evaluate the efficiency of this process in benzylamine.

Fig. 9 shows the effect of the intensity of the excitation pulse on the relative yields of the transients absorbing at 600 nm and 330 nm during the photolysis of Ph_2CHNH_2 at pH 11.2. The non-linear dependence observed for e^-_{aq} absorbance at 600 nm implies that it is formed mainly in a two-step process (Fig. 9(B)). The plots of log OD_{290} and log OD_{330} (Fig. 9(A) and Fig. 10) vs. the intensity indicate that the C–C and C–H ruptures occur via monophotonic processes.

The transient absorption spectrum obtained during the laser photolysis of 2.2 mM aminodiphenylmethane in 20% tert-BuOH at pH ~ 6.0 is given in Fig. 11. The ODs of the transients were measured at different times as indicated in Fig. 11. The sharp absorption maximum observed at 327 nm is due to the $Ph_2^{\bullet}CH$ radical produced by the reductive deamination [18] of aminodiphenylmethane by the electrons produced via photoionization. The transient absorption spectra consist of a shoulder at 520 nm in addition to the broad spectrum of solvated electrons in the visible region

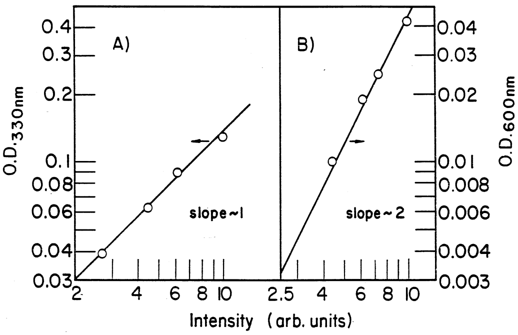


Fig. 9. Dependence on the light intensity of the concentration of the transient species produced during the laser photolysis of 2.2 mM aminodiphenylmethane: (A) at pH 11.0, OD was measured at 330 nm; (B) at pH 11.0, OD was measured at 600 nm.

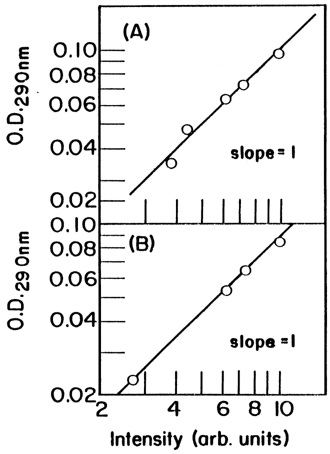


Fig. 10. Dependence on the light intensity of the concentration of the transient species produced during the laser photolysis of 2.2 mM aminodiphenylmethane. OD was measured at 290 nm at pH 11.0 in N_2O-saturated solutions (A) and N_2-saturated solutions (B).

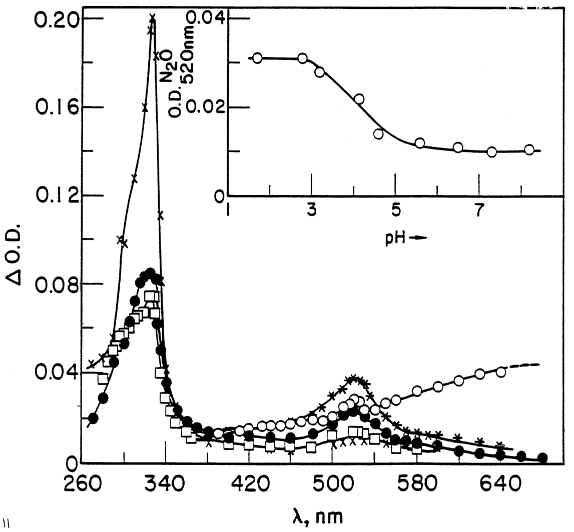


Fig. 11. Transient absorption spectra produced during the laser flash photolysis of 2.2 mM aminodiphenylmethane in 20% tert-BuOH: ×, N_2-saturated, pH 6.0, OD measured 4 μs after the laser pulse; ○, pH 6.0, N_2-saturated, OD measured 0.4 μs after the laser pulse; ●, pH 6.0, N_2O-saturated, OD measured 0.4 μs after the laser pulse; □, pH 1.7, N_2-saturated, OD measured 4 μs after the laser pulse; *, pH 1.7, N_2-saturated, OD measured 0.4 μs after the laser pulse. Inset shows the change in OD_{520} measured during the photolysis of N_2O-saturated solutions at different pH values.

$$Ph_2CH\overset{+}{N}H_3 \xrightarrow{h\nu} e_{aq}^- + (Ph_2CH\overset{+}{N}H_3)^{\bullet +} \qquad (21)$$

$$e_{aq}^- + Ph_2CHNH_3 \rightarrow Ph_2^{\bullet}CH + NH_3 \qquad (22)$$

From the OD value of e_{aq}^- measured soon after the laser pulse, the concentration of the electrons produced was calculated to be 2.75×10^{-5} M, i.e. very close to the concentration of $Ph_2^{\bullet}CH$ radicals formed (calculated from the difference in OD_{328} obtained for the photolysis of N_2O- and N_2-saturated solutions). The deamination of aminodiphenylmethane was almost complete (95% ± 5%), which agreed with an earlier pulse radiolysis result of the reductive deamination of arylalkylamines [18]. The pseudo-first-order rate of decay of electrons in N_2-saturated 1 mM solutions of aminodiphenylmethane, measured from the OD value at 600 nm in laser photolysis experiments and the results of pulse radiolysis experiments, was calculated to be 3×10^6 s^{-1}, indicating that $k_{e_{aq}^- + Ph_2CHN + H_3} = 3 \times 10^9$ M^{-1} s^{-1}. The rate of formation of the radical $Ph_2^{\bullet}CH$ was also calculated to be 3.09×10^9 M^{-1} s^{-1}.

The shoulder of the transient absorption spectrum observed at 300 nm should be due to the photodissociation of benzhydrylamine by C–C rupture

$$Ph_2CH\overset{+}{N}H_3 \xrightarrow{h\nu} Ph + Ph^{\bullet}CH\overset{+}{N}H_3 \qquad (23)$$

On passing N_2O followed by photolysis, the OD_{328} value of the transient decreases significantly together with the disappearance of the visible band at 700 nm, but λ_{max} still remains at 328 nm. This spectrum was assigned to the absorption of $Ph_2^{\bullet}CNH_3$ formed by C–H rupture in benzhydrylamine

$$Ph_2^{\bullet}C\overset{+}{N}H_3 \rightleftharpoons H^+ + Ph_2^{\bullet}CNH_2 \qquad (24)$$

The acid–base properties of this type of radical [4] have been reported.

During the photolysis of an N_2-saturated solution of 2.2 mM benzhydrylamine at pH 6.0, it is observed that the decay kinetics of the transients at 328 nm and 520 nm are very different. The transient absorbing at 328 nm decays by second-order kinetics, whereas the transient absorbing in the 520 nm region decays with a pseudo-first-order rate of 5.3×10^5 s^{-1}. The optical absorption of the transient at 520 nm increases slightly when an N_2O-saturated solution of $Ph_2CH\overset{+}{N}H_3$ is photolysed. It increases further when the same solution is photolysed after changing the pH to 1.7 and saturating it with N_2. In the N_2-saturated solution at pH 1.7, the transient absorbing at 328 nm decays by second-order kinetics, whereas the transient absorbing at 520 nm decays with a pseudo-first-order rate constant of $k = 3.6 \times 10^5$ s^{-1}. The higher pseudo-first-order rate observed during the photolysis of an N_2-saturated solution at pH 6.0 for the 520 nm band may be due to the interference of absorption of e_{aq}^- in this region. During laser photolysis of an air-saturated solution of 2.2 mM $Ph_2CH\overset{+}{N}H_3$ at pH 1.7, a transient with $\lambda_{max} = 520$ nm is observed. The absorption spectra obtained during the laser photolysis of air-saturated solutions of 2.2 mM benzhydrylamine show an absorption maximum below 270 nm (Fig. 12). This spectrum is typical of the absorption spectrum of peroxyl radicals $RO_2^{\bullet}$, which usually exhibit absorption maxima [22] at 240–250 nm. The $HO_2^{\bullet}$ radical absorbs in the same wavelength region [23].

The fact that the absorption of the transient at 520 nm increases with decreasing pH suggests that it may be due to the absorption of the radical cation which is more stable in acid solution. The inset in Fig. 11 shows the increase in OD_{520} in N_2O-saturated solutions of $Ph_2CH\overset{+}{N}H_3$ with decreasing pH. Alternatively, the absorption at 520 nm may be due to triplet–triplet absorption. To check this point, the decay kinetics of the species absorbing at 520 nm were studied by

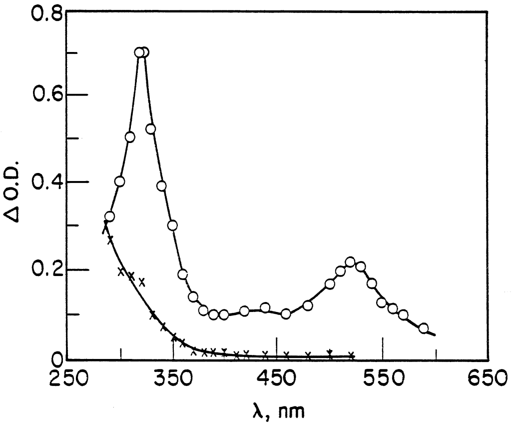


Fig. 12. Transient absorption spectrum produced during the laser photolysis of 2.2 mM aminodiphenylmethane in 20% tert-BuOH in air at pH ~ 1.7: ○, OD measured 2 μs after the laser pulse; ×, OD measured 13 μs after the laser pulse.

photolysing N_2-saturated and air-saturated solutions of $Ph_2CH\overset{+}{N}H_3$. In air-saturated solutions, these species were found to decay six times faster than in N_2-saturated solutions, showing that oxygen reacts with these species at diffusion-controlled rates.

At pH ~ 1.7, in N_2-saturated solutions, e_{aq}^- is converted to H atoms which will add to the aromatic ring of aminodiphenylmethane. Earlier pulse radiolysis results [18] have shown that the H atom adduct to aminodiphenylmethane absorbs at 317 nm with $\epsilon_{317} = 5900\ M^{-1}\ cm^{-1}$. Some H atoms may also be produced by direct homolytic cleavage of the C–H bonds as follows

$$Ph_2CH\overset{+}{N}H_3 \xrightarrow{h\nu} Ph_2\dot{C}\overset{+}{N}H_3 + H \qquad (25)$$

Therefore the transient absorption observed at 330 nm may be due to the H atom adduct and the $Ph_2\dot{C}\overset{+}{N}H_3$ radical produced by reaction (25).

The effect of the laser intensity on the radical absorption at 600 nm and 328 nm during the photolysis of saturated solutions of benzhydrylamine at pH 6 shows that the photoionization is a two-step process. The slope of the plot of log OD_{328} vs. log I (see Fig. 13) is equal to 1.3. This may be due to the fact that, during the photolysis of N_2-saturated solutions, both $Ph_2\dot{C}H$ (biphotonic origin) and $Ph_2\dot{C}\overset{+}{N}H_3$ (formed by direct monophotonic rupture of the C–H bond) radicals are present. The monophotonic origin of C–H rupture is indicated by the slope (0.9) obtained during the photolysis of benzhydrylamine at pH 1.7.

To throw light on the excited state involved, the influence of Cs^+ ions on the formation of the intermediate transients was studied. Cs^+ is unreactive towards e_{aq}^-, as confirmed [24] by a pulse radiolysis experiment yielding $k(Cs^+ + e_{aq}^-) = 2 \times 10^4\ M^{-1}\ s^{-1}$. The transient optical absorption at 600 nm almost doubles in the presence of 1 M CsCl during the laser photolysis of both benzylamine and benzhydrylamine at pH 6 and 11, but no such effect is observed with 1 M NaCl. This indicates that, in these photophysical processes, the triplet states are involved as the introduction of CsCl is expected to enhance intersystem crossing [24–26] in aromatic molecules.

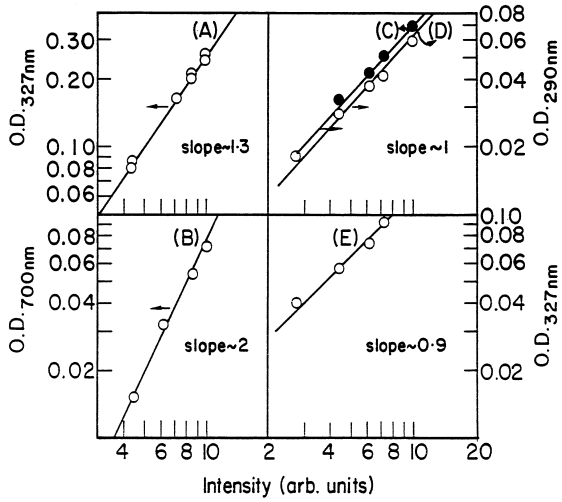


Fig. 13. Dependence on the light intensity of the concentration of the transient species produced during the laser photolysis of 2.2 mM Ph_2CHNH_3 at pH 6 and 1.7 at different wavelengths. A, B and C refer to N_2-saturated solutions of pH 6, whereas D shows the results obtained in N_2O-saturated solution at pH 6. E refers to pH 1.7 and N_2-saturated solution.

The involvement of a triplet excited state precursor in the laser photolysis of arylalkylamines is also indicated by the sensitization of the triplet state of all-*trans*-retinol [25] in a methanol solution of 1 mM retinol containing 7.5 mM benzhydrylamine. Care was taken to ensure that no retinol triplet could be produced by direct laser photolysis.

It is interesting to note that, in both of these amines, the C–N rupture takes place only by reductive deamination of the amines by photoionized electrons and not by direct bond rupture. From the bond energies [27,28] of the C–H and C–N bonds, we would expect that the C–N bond would be the easiest to rupture. It is probable that the nitrogen atom, which can form a positively charged tetravalent group, can labilize [29] the adjacent C–H bonds for chemical attack. Moreover, the factors which are important in explaining the photolysis in solution and rigid solvents at low temperature may be very different from those which are considered in the gas phase [30]. Photolysis in the gas phase may occur in accordance with bond energy considerations, but the bond dissociation energies are almost unknown in solution and may be very different from those in the vapour phase (due to the differences in the solution energies of the parent molecules as well as the radical products). Also, additional energy may be required to separate the dissociation products in the presence of solvent molecules. Therefore the activation energy of dissociation may exceed the bond energy. The first ionization energy of the aliphatic amines, as in the case of NH_3, essentially involves the production of an electron–hole pair in the lone pair region. Therefore it may be expected that the first ionization energies of benzylamine (8.6 eV) [30] and aminodiphenylmethane may be of the same order of magnitude. For both of these compounds, photoionization occurs via a two-step process involving the triplet excited state. The triplet excited state absorbs at about 520 nm and decays by first-order kinetics for benzhydrylamine.

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