Mechanism of 3-halogenoaniline photolysis in methanol

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The photolysis of 3-fluoro-, 3-chloro- and 3-bromoaniline (3-FA, 3-ClA, 3-BrA) in methanol leads to the formation of 3-anisidine and aniline with quantum yields depending on the nature of the halogen. Photosubstitution is the major reaction in the case of 3-FA, but photoreduction also occurs. The latter is more important with 3-BrA than with 3-FA and 3-ClA. Oxygen does not affect the formation of 3-anisidine but reduces that of aniline. Several transients are observed by laser flash photolysis. With each derivative, a broad absorption band with a maximum around 410 nm appears at the end of the pulse. Based on the quenching of oxygen, these bands are assigned to the triplet–triplet absorptions. The anilino radical cation $\mathrm{PhNH_2^{\cdot+}}$ ($\lambda_{\max} = 410$ and 430 nm) is produced by excitation of the three halogenoanilines. Its formation is not influenced by oxygen. The characteristic absorption of $\mathrm{Br_2^{\cdot-}}$ is observed by irradiation of 3-BrA in the presence of $\mathrm{Br^-}$ (5×10^{-3} M). The solvated electron and the long-lived halogenoanilino radical cations ($\mathrm{XPhNH_2^{\cdot+}}$) are detected. From the quantum yields of aniline, 3-anisidine, $\mathrm{PhNH_2^{\cdot+}}$ and $\mathrm{Br_2^{\cdot-}}$ formation in the absence and presence of oxygen, the following mechanism can be proposed: 3-anisidine is produced after heterolytic cleavage of the C–X bond from the excited singlet state and addition of MeOH. Aniline is also yielded from the excited singlet state, after heterolytic and/or homolytic cleavage of the C–X bond. In the former case $\mathrm{PhNH_2^{\cdot+}}$ is formed as an intermediate. With 3-BrA, the homolytic cleavage of the C–Br bond is proved by the formation of $\mathrm{Br_2^{\cdot-}}$.

Mécanisme de la phototransformation des 3-halogénoanilines en solution méthanolique. La photolyse des 3-fluoro-, 3-chloro- et 3-bromoaniline (3-FA, 3-ClA et 3-BrA) en solution dans le méthanol conduit à la formation de 3-anisidine et d'aniline avec des rendements quantiques qui dépendent de la nature de l'halogène. Dans le cas de la 3-FA la photosubstitution est la principale réaction, mais il se produit également une photoréduction. Cette dernière est plus importante avec la 3-BrA qu'avec les 3-FA et 3-ClA. La présence d'oxygène est sans effet sur la formation de 3-anisidine mais elle défavorise la formation d'aniline. Plusieurs espèces transitoires ont été observées en photolyse laser. Avec les 3 composés une large bande d'absorption ayant un maximum vers 410 nm apparaît juste après l'éclair. Cette bande disparaît en présence d'oxygène; elle est attribuée à l'absorption triplet–triplet. Le radical cation aniline $\mathrm{PhNH_2^{\cdot+}}$ ($\lambda_{\max} = 410$ et 430 nm) apparaît lors de l'irradiation des 3 dérivés. Sa formation n'est pas influencée par l'oxygène. L'absorption caractéristique du radical anion $\mathrm{Br_2^{\cdot-}}$ est observée lorsque la 3-BrA est irradiée en présence de $\mathrm{Br^-}$ (5×10^{-3} M). L'électron solvaté et les radicaux cations halogénoaniline de relative longue durée de vie sont détectés dans tous les cas. La comparaison entre les rendements quantiques de formation d'aniline, de 3-anisidine et des espèces transitoires $\mathrm{PhNH_2^{\cdot+}}$ et $\mathrm{Br_2^{\cdot-}}$ permet d'expliquer le comportement photochimique des 3-halogénoanilines de la façon suivante: la formation de 3-anisidine résulte d'une coupure hétérolytique de la liaison C–X à partir de l'état excité singulet, suivie de l'addition de méthanol, et celle d'aniline d'une coupure hétérolytique ou d'une coupure homolytique de la liaison C–X. Dans le premier cas, il se forme intermédiairement le radical cation $\mathrm{PhNH_2^{\cdot+}}$. L'homolyse a été mise en évidence avec la 3-BrA par détection de radicaux $\mathrm{Br_2^{\cdot-}}$ en présence d'ions bromure.

Halogenoanilines can be easily transformed by UV light and analogies with the photoreactivity of halogenophenols are generally observed. So far, only the mechanism of 4-halogenoaniline photolysis has been clarified[1,2] with the help of the results previously obtained in the case of 4-chlorophenol.[3] The carbene 4-iminocyclohexa-2,5-dienylidene cation produced by photo-elimination of $\mathrm{X^-}$ was shown to be the key intermediate.[1,2] The irradiation of 2-halogenoaniline in water yields 1,3-cyclopentadiene carbonitrile after ring contraction[4] and 2-aminophenol by photohydrolysis, but no transient was observed. The intermediate formation of a nitrene was proposed upon irradiation of 2-chloroaniline in the gas phase.[5,6] Photohydrolysis was reported to be almost quantitative with 3-chloroaniline[7] and 3-chlorophenol[8] in aqueous solution with the formation of 3-aminophenol and resorcinol, respectively. No transient was detected. This reaction was assumed to be heterolytic.

In alcohol and in alcohol–water mixtures, halogenoaromatic compounds are known to undergo photosubstitution and photoreduction.[9–16] However, the mechanisms of the reactions have been the subject of some controversy. The photosubstitution was reported to be unaffected by oxygen in the case of chlorobenzene,[9] chloro- and fluoroanisole[10] and naphthylmethyl halides.[11] It was deduced that this reaction results from the heterolytic cleavage of the C–X bond from the excited singlet state. Photoionization was also suggested to be the preliminary step in the substitution of chlorobenzene.[12] A very different mechanism was proposed in the case of chloromethoxybenzene: formation of a radical cation *via* the triplet excimer and subsequent nucleophilic attack of the radical cation by the solvent.[13]

Photoreduction was generally assumed to result from the homolytic scission of the C–X bond from both the excited singlet and triplet states.[10,11,13,14] The increase in phenol formation in the series *m*-chloro-/*m*-bromo-/*m*-iodophenol with decreasing strength of the C–X bond is consistent with the homolytic cleavage.[15] The lack of formation of reduction products upon irradiation of fluoromethoxybenzene in MeOH–H$_2$O (1 : 1)[16] is in accordance with the high energy of the C–F bond ($\approx$523 kJ mol^{-1}), making the homolysis energetically prohibitive.

The aim of the present work is a better understanding of the mechanism of the phototransformation of *meta*-halogenoanilines in methanol, using nanosecond laser flash photolysis and product studies. The photochemical behaviour of fluoro-, chloro- and bromo-derivatives are compared.

Experimental

Materials

The 3-halogenoanilines were purchased from Aldrich (purity 98–99%) and used as received. Methanol was from Carlo Erba (HPLC grade, 99.9%). Aniline and 3-anisidine were of the highest grade commercially available. 3,3′-Dichloroazobenzene was synthesized from 3-chloronitrobenzene and lithium aluminium hydride.[17] Acetonitrile used for HPLC analysis was from Carlo Erba (HPLC grade, 99.9%). Water was purified by a Milli-Q device (Millipore). Ammonium acetate used as buffer, was Aldrich 98%. Potassium peroxodisulfate used as actinometer, was Aldrich 99%.

Irradiation

For the determination of quantum yields, solutions were irradiated at 282 nm in the parallel beam obtained from a Schoeffel monochromator equipped with a xenon lamp (1600 W). Band width at mid-height was about 10 nm. The photon flow was evaluated by means of classical ferrioxalate actinometry. For preparative purposes, solutions were irradiated at 254 nm in a quartz reactor using six germicidal lamps surrounded by a cylindrical mirror.

Analysis

UV spectra were recorded on a Varian Cary 3 spectrophotometer. Irradiated solutions were analysed by HPLC using a Waters 996 apparatus equipped with a photodiode array detector. A water–acetonitrile gradient was generally used as the eluent, and a 1.8 g L^{-1} ammonium acetate solution was added to water to prevent ionization in the column (C$_{18}$ 250 mm × 4.6 mm). GC-MS spectra were recorded on a Hewlett–Packard 5985 mass spectrometer. The column was Optima 5 (Machery–Nagel, 25 m, i.d. 0.25 mm). Transient absorption experiments were carried out using a frequency-quadrupled Nd : YAG laser (Quanta-Ray GCR 130-1, $\lambda_{\text{exc}} = 266$ nm, pulse width 9 ns). Experimental procedures have been described elsewere.[18] Potassium peroxodisulfate was used as the chemical actinometer. The formation of sulfate radicals was monitored at 450 nm ($\varepsilon = 1400 \pm 100$ M^{-1} cm^{-1} and $\Phi = 1.4$[19–21]). To measure the $\varepsilon \times \Phi$ product of the transients formed from 3-XA, we used solutions with the same optical densities at 266 nm as that of K$_2$S$_2$O$_8$.

Results

Continuous irradiation

3-Chloroaniline. A methanolic solution of 3-ClA (8.5×10^{-4} M) was irradiated at 282 nm under different oxygenation conditions (air-saturated, oxygenated or argon-purged solutions). Irradiated solutions were analysed by HPLC as described in the experimental section. The two main products were assigned to aniline and 3-anisidine by comparison with the HPLC retention time and UV spectrum of authentic commercial compounds. However, to ensure their identification a larger volume of solution was irradiated at 254 nm. The reaction mixture was then evaporated to dryness, dissolved in a small volume of methanol and analysed by GC-MS. Only two products were found: product 1: $m/z = 93$ (M$^{\cdot+}$, 100%); 66 (42) and product 2: $m/z = 123$ (M$^{\cdot+}$, 62%); 94 (25); 93 (21%); 80 (15%); 66 (10%); 53 (18%). These results confirm the identification of product 1 as aniline and product 2 as 3-anisidine. We evaluated the quantum yields of formation of both products using commercial standards. These quantum yields, as well as the quantum yield of 3-ClA disappearance, are given in Table 1. Oxygen has no influence on the disappearance of 3-ClA and on the formation of 3-anisidine, but disfavours the formation of aniline. Aniline and 3-anisidine together represent 85% of converted 3-ClA in deoxygenated or aerated medium and 61% in oxygen-saturated solution.

It was verified that under our experimental conditions there is no detectable formation of nitrosobenzene, 3-chloronitrosobenzene, 3-chloronitrobenzene, azobenzene or 3,3′-dichloroazobenzene.

3-Fluoro- and 3-bromoaniline. Aniline and 3-anisidine were also found in irradiated solutions of 3-FA (7.4×10^{-4} M) and 3-BrA (7.6×10^{-4} M). The quantum yield values are reported in Table 1. As in the case of 3-ClA, oxygen has no effect on the formation of 3-anisidine, but reduces the formation of aniline. The quantum yields of 3-FA and 3-BrA disappearance are significantly higher than that of 3-ClA. An inhibiting effect of oxygen on the substrate disappearance is only observed in the case of 3-FA.

Laser flash photolysis. Identification of transients

3-Bromoaniline. The irradiation of 3-BrA (4.6×10^{-4} M) in deoxygenated methanol gives the transient spectra shown in Figs. 1(*A*) and 1(*B*). By taking the difference between the absorbances measured at 0.1 and 0.5 μs after the end of the pulse ($A_{0.1\,\mu\text{s}}$ and $A_{0.5\,\mu\text{s}}$), we obtained the spectrum drawn in the inset of Fig. 1(*A*). The presence of at least two species is revealed. The first has a broad absorption band with a

Table 1 Quantum yields for the disappearance of 3-halogenoanilines (Φ_{disp}) and quantum yields for the formation of aniline and 3-anisidine at 282 nm

	$C/10^{-4}$ M	Solution	$100 \times \Phi_{\text{disp}}$	$100 \times \Phi_{\text{aniline}}$	$100 \times \Phi_{\text{3-anisid}}$
3-FA	7.4	O$_2$ satd	3.4 ± 0.4	0.31 ± 0.06	2.5 ± 0.5
		Air satd	4.1 ± 0.4	0.54 ± 0.10	2.5 ± 0.5
		Ar purged	5.2 ± 0.5	1.2 ± 0.25	2.8 ± 0.5
3-ClA	8.5	O$_2$ satd	1.3 ± 0.2	0.13 ± 0.03	0.66 ± 0.15
		Air satd	1.2 ± 0.2	0.42 ± 0.08	0.64 ± 0.15
		Ar purged	1.4 ± 0.2	0.52 ± 0.10	0.64 ± 0.15
3-BrA	7.6	O$_2$ satd	5.1 ± 0.5	1.4 ± 0.3	2.3 ± 0.5
		Air satd	5.7 ± 0.6	2.3 ± 0.5	2.4 ± 0.5
		Ar purged	5.5 ± 0.6	3.6 ± 0.7	2.3 ± 0.5
3-BrA + Br$^-$ (5×10^{-3} M)	7.5	Ar purged	6.6 ± 0.6	4.3 ± 0.8	2.6 ± 0.5

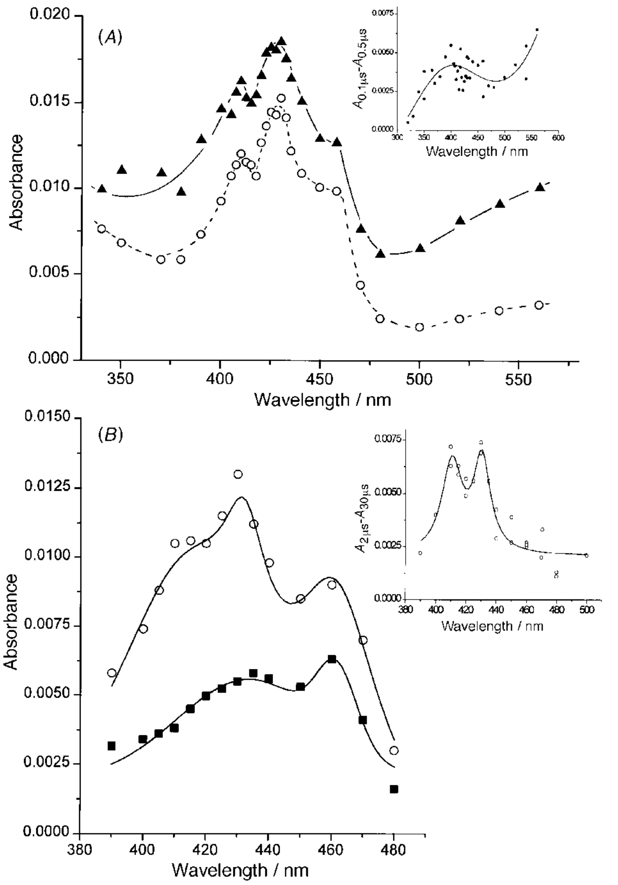


Fig. 1 Transient spectra measured in a deoxygenated methanolic solution of 3-BrA (4.6×10^{-4} M). (*A*) Absorbances measured 0.1 μs (▲) and 0.5 μs (○) after the end of the pulse. Inset: difference between $A_{0.1\,\mu s}$ and $A_{0.5\,\mu s}$. (*B*) Absorbances measured 2 μs (○) and 30 μs (■) after the end of the pulse. Inset: difference between $A_{2\,\mu s}$ and $A_{30\,\mu s}$.

maximum at *ca.* 410 nm and a decay time of *ca.* 0.5 μs (see Fig. 2A). Its lifetime is shortened to less than 0.1 μs when the solution is saturated with oxygen. This transient may be assigned to the triplet state. The second transient absorbs at $\lambda > 500$ nm. In argon-saturated solution, the decay follows first-order kinetics with $k = 6.2 \times 10^6$ s^{-1} (see Fig. 2B). This latter species, which is quenched by oxygen, is most likely the solvated electron.

The absorption spectrum of a third species was obtained by subtracting the absorbance measured at 30 μs ($A_{30\,\mu s}$) from that measured at 2 μs ($A_{2\,\mu s}$) [inset of Fig. 1(*B*)]. This species has a two-band structure with $\lambda_{max} = 410$ nm and 430 nm. It decays by first-order kinetics with $k = 6.0 \times 10^4$ s^{-1} [see Fig. 2(C)]. The difference $A_{2\,\mu s} - A_{30\,\mu s}$ at 430 nm increases linearly with the energy pulse, showing that the transient is formed *via* a monophotonic process (Fig. 3). Neither its formation nor its decay is affected by oxygen.

Another two-band structure species with $\lambda_{max} = 435$ nm and 455 nm can be observed 30 μs after the end of the pulse. This species is mainly produced by a monophotonic process (Fig. 3). It is a long-lived species that decays by second-order kinetics. The same transient is generated when 3-BrA is oxidized by $SO_4^{\cdot -}$, formed by photolysis of aqueous $K_2S_2O_8$ (0.1 M) (Fig. 4). The 435/455 nm absorption was therefore attributed to the 3-bromoanilino radical cation ($BrPhNH_2^{\cdot +}$), which is expected to be produced by photoionization along with solvated electrons.

The 410/430 nm species differs spectrally from the 3-bromoanilino radical cation by a 25 nm blueshift, as expected for the unsubstituted anilino radical cation $PhNH_2^{\cdot +}$. This latter radical was produced and characterized by Szczepanik and Grabner by photolysis of 4-chloroaniline in water in the

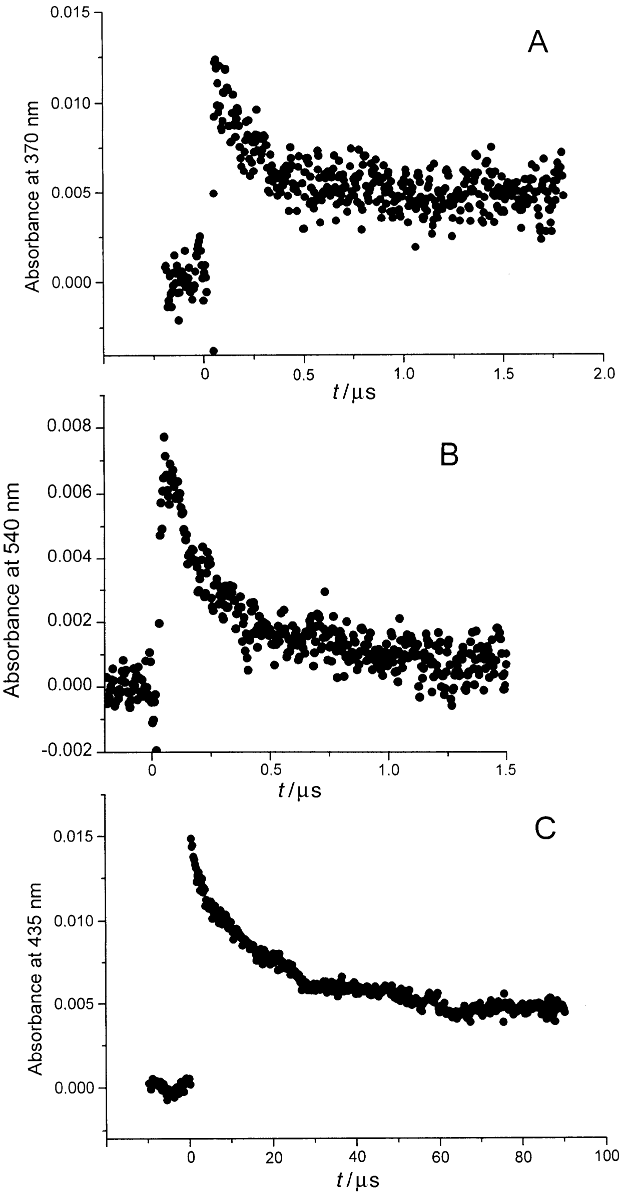


Fig. 2 Time evolution of absorbances measured at A 370, B 540 and C 435 nm in a deoxygenated methanolic solution of 3-BrA (4.6×10^{-4} M).

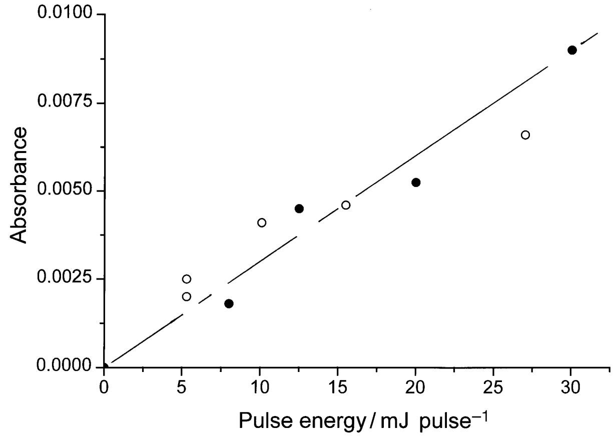


Fig. 3 Pulse energy dependence of transients measured in deoxygenated solutions of 3-BrA in methanol: (●) difference between the absorbances measured 2 and 30 μs after the pulse end at 430 nm, optical density at 266 nm equal to 0.85; (○) absorbance measured 30 μs after the pulse end at 460 nm, optical density at 266 nm equal to 0.93.

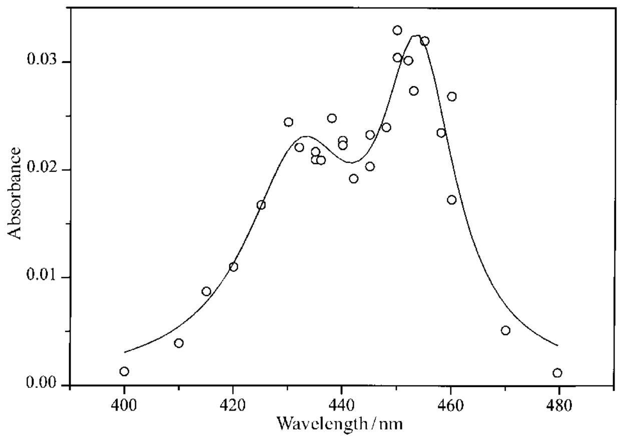


Fig. 4 Transient spectrum of 3-bromoanilino radical cation produced by photolysis of an acidic aqueous solution containing $K_2S_2O_8$ (0.1 M) and 3-BrA (8.5×10^{-4} M).

presence of H-donor molecules.[2] It exhibits an absorption spectrum with two maxima at 407 and 423 nm. The 410/430 nm transient that we observed in methanol is most likely the anilino radical cation, the small wavelength shift being attributed to a solvent effect.

When 3-BrA (7.3×10^{-4} M) is irradiated in the presence of Br^- (5×10^{-3} M) a new species is produced with $\lambda_{max} = 380$ nm (Fig. 5). Its build-up is at a maximum about 5 μs after the pulse end and not influenced by oxygen. Based on the literature data, this transient is assigned to the radical anion $Br_2^{\bullet -}$.[22] The formation of this species is evidence for the homolytic scission of the C–Br bond.

3-Chloroaniline. As in the case of 3-BrA, a short-lived transient exhibiting a maximum at about 410 nm and readily quenched by oxygen was observed. The two-band structure species ($\lambda_{max} = 410$ and 430 nm) was detected too. This feature confirms the assignment to the anilino radical cation ($PhNH_2^{\bullet +}$). A long-lived transient was also produced. Due to the very weak absorption (A around 0.001), it was not possible to measure the spectrum accurately. Nevertheless, the absorption maximum is located around 440–450 nm, as expected for the 3-chloroanilino radical cation, which was produced independently for comparison by photolysis of an acidic aqueous mixture of $K_2S_2O_8$ (0.1 M) and 3-ClA (10^{-3} M) (Fig. 6).

3-Fluoroaniline. The photolysis of an air-saturated solution of 3-FA (7.3×10^{-4} M) yields the anilino radical cation ($PhNH_2^{\bullet +}$) as in the case of 3-ClA and 3-BrA. A transient attributed to 3-fluoroanilino radical cation ($FPhNH_2^{\bullet +}$) was also observed, the same radical being obtained independently by irradiation of an aqueous solution containing $K_2S_2O_8$ and 3-FA (Fig. 6).

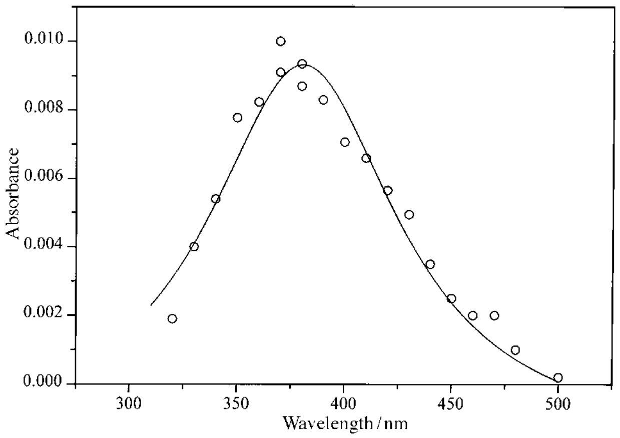


Fig. 5 Transient spectrum measured 5 μs after the pulse end in a methanolic solution of 3-BrA (7.3×10^{-4} M) containing Br^- (5×10^{-3} M).

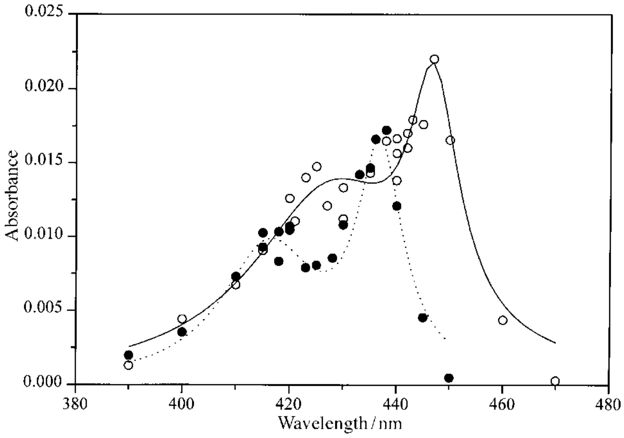


Fig. 6 Transient spectra of 3-fluoro- and 3-chloroanilino radical cations produced by photolysis of acidic aqueous solutions containing $K_2S_2O_8$ (0.1 M) and (●) 3-FA (10^{-3} M) or (○) 3-ClA (10^{-3} M).

Laser flash photolysis. Quantum yield measurements

Using appropriate actinometries (see experimental section), we determined the $\varepsilon \times \Phi$ product for $PhNH_2^{\bullet +}$ at 430 nm by measuring the difference $A_{2\,\mu s} - A_{30\,\mu s}$. Taking for the extinction coefficient at 430 nm the value 4000 M^{-1} cm^{-1} given by Szczepanik and Grabner,[2] we computed Φ. Values are reported in Table 2. The quantum yield of $Br_2^{\bullet -}$ formation was evaluated at 0.019 ± 0.003 from the $\varepsilon_{430} \times \Phi$ product and the value of the extinction coefficient at 380 nm reported in the literature[22] ($\varepsilon_{430} = 9000$ M^{-1} cm^{-1}).

Discussion

We experimentally prove in this work that photosubstitution and photoreduction occur with 3-FA, 3-ClA and 3-BrA. If photosubstitution of halogenoaromatics was often reported in the literature, whatever the nature of the halogen, photoreduction of fluoroaromatic compounds, on the other hand, is not common.

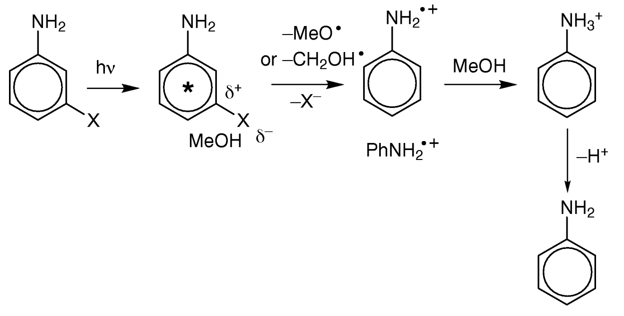
Several transients are detected by laser flash photolysis of the three halogenanilines: triplet excited states, $XPhNH_2^{\bullet +}$, solvated electrons and $PhNH_2^{\bullet +}$. Oxygen has no influence on the disappearance of 3-ClA and 3-BrA. This feature implies that the excited triplet states observed by laser flash photolysis are chemically unreactive and that the photochemistry is therefore likely to proceed from the singlet excited states. Photoejection takes place with formation of $XPhNH_2^{\bullet +}$ and solvated electrons. However, this reaction is expected to be a minor pathway, especially in steady-state irradiation. Among all the transients detected, the anilino radical cation $PhNH_2^{\bullet +}$, which is observed with all the derivatives, is the one that should contribute most significantly to the phototransformation; it is a logical precursor for aniline.

The photoreduction of halogenoaromatics is generally explained by the homolytic cleavage of the C–X bond and subsequent reduction of the organic radical through H-abstraction from the alcohol. Homolysis is not possible in the

Table 2 Quantum yields for the formation of the anilino radical cation $PhNH_2^{\bullet +}$ ($\varepsilon_{430} = 4000$ M^{-1} cm^{-1})[2]

	$A_{266\,nm}$	$\varepsilon_{430} \times \Phi$	$100 \times \Phi$
3-FA	0.69	25 ± 3	0.62 ± 0.12
3-ClA	0.70	20 ± 2	0.50 ± 0.10
3-BrA	0.70	48 ± 10	1.2 ± 0.25

$A_{266\,nm}$ is the absorbance of the solution at 266 nm.

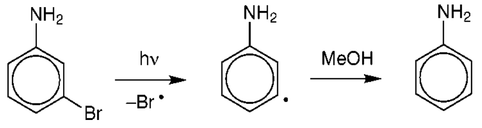


Scheme 1 Heterolytic photoreduction of 3-halogenoanilines.

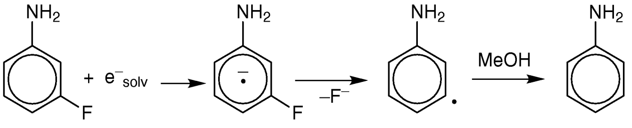
case of 3-FA because of the bond strength. The formation of aniline is therefore likely to involve the intermediate formation of PhNH$_2^{\bullet+}$, resulting from the heterolytic cleavage of the C–F bond and reduction of the carbocation by methanol (Scheme 1).

Quantitative measurements show a very good agreement between the quantum yields of anilino radical cation and aniline formations in the case of 3-ClA (see Tables 1 and 2). With 3-BrA, the quantum yield of aniline formation is significantly higher, indicating that an additional reaction pathway takes place. The difference is explained by homolysis of the C–Br bond (Scheme 2). Indeed, the quantum yield of aniline formation is very close to the sum of the quantum yields of the formation of Br$_2^{\bullet-}$ and the anilino radical cation. As shown in Table 1, the addition of Br$^-$ (5×10^{-3} M) increases the formation of aniline because of the trapping of Br$^\bullet$ by Br$^-$.

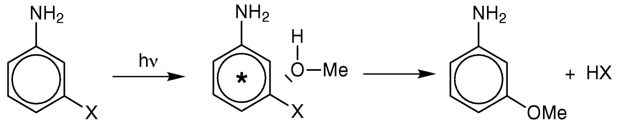
With 3-FA, Φ_{aniline} is higher than the quantum yield of anilino radical cation formation and this difference cannot be explained by homolysis. As an alternative pathway, it can be proposed that the solvated electrons produced by photoionization are trapped by 3-FA, thus inducing loss of F$^-$ and the formation of a dehalogenated radical, which is further reduced into aniline (see Scheme 3). Such a reaction is expected to be less efficient with the chloro and bromo derivatives because chlorine and bromine atoms are less electron withdrawing than fluorine. This assumption is consistent with the inhibiting effect of oxygen on the formation of aniline, with oxygen acting as electron quencher (see Table 1).



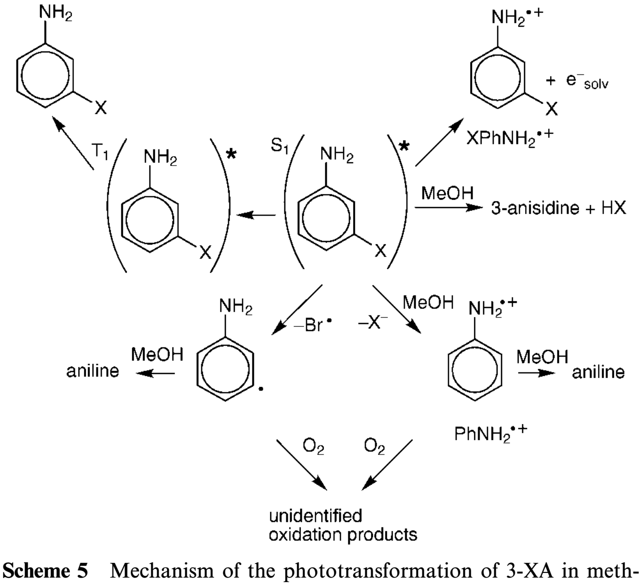
Scheme 2 Homolytic photoreduction of 3-bromoaniline.



Scheme 3 Formation of aniline *via* reduction of 3-FA by e_{solv}^-.



Scheme 4 Formation of 3-anisidine.



Scheme 5 Mechanism of the phototransformation of 3-XA in methanol.

The formation of 3-anisidine implies heterolytic cleavage of the C–X bond in the singlet excited state and addition of methanol. This reaction may be concerted as it was suggested for photohydrolysis[8] (Scheme 4). The formation of 3-anisidine is not affected by oxygen; in contrast, the production of aniline is significantly reduced in oxygenated solutions. It can be deduced that both the anilino radical cation PhNH$_2^{\bullet+}$ and aminophenyl radical are quenched by oxygen.

The photochemical behaviour of 3-halogenoanilines is summarized in Scheme 5.

Conclusions

Aniline and 3-anisidine are the main photoproducts in the photolysis of 3-halogenoanilines in methanolic solution. Several transients were observed in laser flash photolysis: anilino radical cation PhNH$_2^{\bullet+}$, halogenoanilino radical cation XPhNH$_2^{\bullet+}$, solvated electron and Br$_2^{\bullet-}$ in the case of 3-bromoaniline irradiated in the presence of Br$^-$.

The formation of 3-anisidine results from a heterolytic methanolysis. Quantum yields are similar with 3-BrA and 3-FA. The highest quantum yield of aniline formation is observed with 3-BrA. With 3-BrA, 65% of aniline formation is due to homolysis of the C–Br bond. Photoreduction proceeds also from heterolysis *via* the intermediate formation of the anilino radical cation, which is observed with the three derivatives. This latter pathway explains the unexpected photoreduction of 3-FA.

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