

Photochemical behaviour of 2-halogenoanilines in aqueous solution

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Abstract

The main photoproducts formed in aqueous solutions of 2-chloro-, 2-bromo- and 2-fluoroaniline (2-CIA, 2-BrA and 2-FA) are 2-amino-phenol, aniline and 1,3-cyclopentadiene-1-carbonitrile. They result from a heterolytic mechanism more efficient with 2-FA than for the two other congeners. Quantum yields of disappearance are in the range 0.02–0.04 for 2-CIA and 2-BrA and 0.10–0.13 for 2-FA, according to the conditions. The formation of aniline occurs only in the absence of oxygen. In the presence of oxygen 2-aminophenol initially formed is phototransformed into 2-aminophenoxazin-3-one.

Three isomers of diaminobromobiphenyls were identified in the photolysis of 2-BrA. Similar products are formed with 2-CIA but with a lower yield. This formation of biphenyl derivatives is attributed to the reactivity of the excited triplet state. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Halogenoanilines; Photohydrolysis; Photoreduction; Photocontraction; Dihalogenobiphenyls

1. Introduction

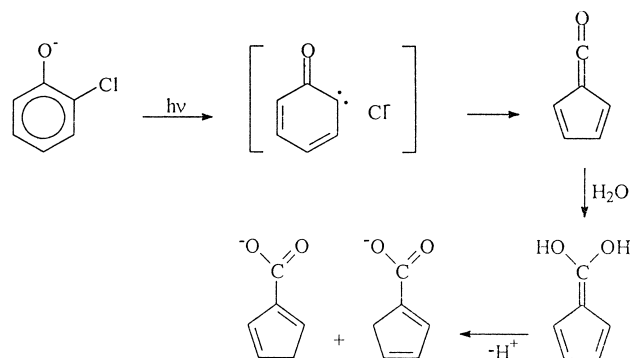
Halogenoanilines are toxic compounds listed by the EC as priority pollutants. Their solubility in water is not negligible. They absorb up to about 320 nm and their photodegradation is a possible route for their elimination as it is experimentally proved.

It was previously reported that the main photochemical reaction of 3-chloroaniline in water is photohydrolysis [1]. It is almost specific. The phototransformation of 2-chloroaniline (2-CIA) was the subject of some controversies: according to Ishikawa et al. [2] 2-CIA is initially transformed into 2-chloronitrobenzene and then into phenol via 2-chlorophenol and chlorobenzene. This mechanism is surprising compared with the dechlorination observed with chlorophenols [3]. In a more recent paper it was reported that 1,3-cyclopentadiene-1-carbonitrile is formed by irradiation in the range 275–340 nm [4]. Similar photocontraction of the ring was reported in the case of 2-chlorophenolate [3,5] but with the latter, photoproducts are cyclopentadiene carboxylic acids that dimerize in concentrated solution.

Ishida et al. [6] observed the formation of cyclopentadienyl radical by excimer photolysis (supersonic jet cooled technique) of 2-CIA as it was observed with phenylisocyanate. The latter is first photolysed into phenylnitrene

that rearranges into cyclopentadiene-1-carbonitrile. They deduced that the photolysis of 2-CIA also involves the formation of phenylnitrene. Cullin et al. [7] suggested that singlet phenylnitrene initially formed in the photolysis of phenyl azide can, according to the conditions, rearrange into cyclopentadiene carbonitrile (in gas phase) or into azacycloheptatetraene (ambient temperature, fluid solution).

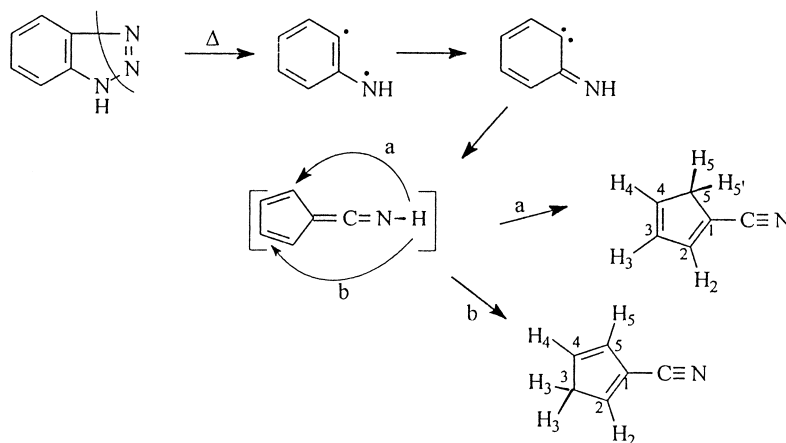
No data are available about the phototransformation of the other 2-halogenoanilines. However, some analogies were observed between halogenophenols and halogenoanilines, and the mechanism of 2-chlorophenol may be useful to interpret the photochemical transformation of 2-halogenoanilines. The first transient detected in the photolysis of 2-chlorophenolate is a ketene that is hydrolysed and rearranged into cyclopentadiene carboxylic acid [5]. The intermediate formation of a carbene was suggested but not proved.



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Similar mechanism was proposed by Sakaizumi et al. [8] for the pyrolytic transformation of 1H-benzotriazole into cyclopentadiene-1-carbonitriles.

266 nm, pulse width 9 ns). Potassium peroxydisulfate was used as the actinometer. Experimental procedures have been previously described [9].



The aim of the present work is to compare the photochemical transformation of 2-chloro, 2-bromo and 2-fluoroaniline (2-CIA, 2-BrA and 2-FA, respectively) in aqueous solution for a better understanding of the mechanism of reaction.

2. Experimental

2.1. Reactants

2-Chloroaniline Aldrich >98%, 2-bromoaniline Aldrich 98%, 2-fluoroaniline Aldrich >99%. Aniline 99% and 2-aminophenol 99% used as analytical standards were provided by Prolabo and Aldrich, respectively. Water was purified with Milli-Q device (Millipore) and its purity was controlled by its resistivity (>18 MΩ cm).

2.2. UV irradiation

For monochromatic irradiations at 285 nm a xenon lamp (1600 W) equipped with a Schoeffel monochromator was used. This device was used for the evaluation of the quantum yields and for the analysis of products in diluted solutions (5×10^{-4} M). But the photon flux was too low to irradiate solutions more concentrated than 2×10^{-3} M. For these solutions a device consisting of six low pressure mercury lamps (emission at 254 nm) surrounded with a cylindrical mirror was used. The reactor was a cylinder in quartz placed along the axis.

For the evaluation of quantum yields the photon fluxes were evaluated by chemical actinometries, at 285 nm with potassium ferrioxalate and at 254 nm with uranyl oxalate (irradiation times would be too short with ferrioxalate).

Laser flash photolysis was carried out with a frequency-quadrupled Nd:YAG laser (Quanta-Ray GCR 130-1, $\lambda_{exc} =$

2.3. Identification of photoproducts

When commercial standards were not available for the identification of photoproducts appearing on the HPLC chromatograms, products were isolated and identified by mass spectrometry on Hewlett–Packard 5985 or 5989B MS Engine, and by ¹H NMR in CD₃COCD₃ or CDCl₃ on Bruker AC 400. The precise value of the molecular mass of product P₃ was provided by *Service Central d'Analyse of Centre National de la Recherche Scientifique*.

2.4. Isolation and identification of product P₃ obtained from 2-CIA

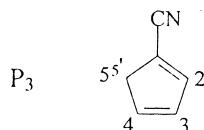
A solution 10^{-3} M of 2-CIA was irradiated in the range 275–340 nm in a quartz reactor by six lamps (Duke Sun Lamp GL20), up to about 80% of transformation. The solution was acidified to protonate the unreacted 2-CIA and distilled under reduced pressure. The distillate trapped at low temperature was an aqueous solution of a product termed P₃. It was extracted with diethyl ether and analysed by mass spectrometry. For ¹H NMR analysis, the solution collected in the trap was extracted with C₂Cl₃F₃. CDCl₃ was added to the solution in C₂Cl₃F₃, and then C₂Cl₃F₃ evaporated by a nitrogen flow [4]. (At the present time the use of this solvent cannot be recommended, but no alternative solvent was available when this work was engaged).

P₃ : $m/z = 91(M^{\bullet+}, 100\%), 64(55\%)$

Three formulae are consistent with the precise value of molecular mass 91.040300 obtained by MS analysis: C₆H₅N, C₃H₇O₃ and CH₅N₃O₂, but only the former is likely. The presence of five protons was confirmed by ¹H NMR shifts:

$^1\text{H NMR}$ (CDCl_3) δ (ppm): 7.30 (quint, $J=1.7$ Hz, 1H); 6.70 (d.quad, $J\approx 1.3$ and 5.4 Hz, 1H); 6.63 (m, 1H); 3.34 (quad, $J=1.5$ Hz, 2H). (quint: quintuplet; quad: quadruplet; m: multiplet; d.quad: double quadruplet).

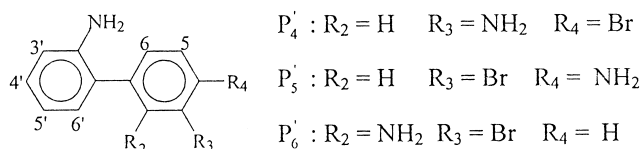
Three structures might be proposed: cyclopenta-1,3-diene-1-carbonitrile, cyclopenta-1,4-diene-1-carbonitrile and cyclopenta-1,3-diene-5-carbonitrile. The latter was ruled out since protons at 3.34 ppm are inconsistent with ethylenic protons. The second formula was also eliminated since both protons 2 and 5 should have similar NMR shifts higher than the shift of the third ethylenic proton 4. It was concluded that P_3 is cyclopenta-1,3-diene-1-carbonitrile.



This structure and NMR shifts reported here for P_3 are in good agreement with results of Chin-Hsing Chou et al. [11] for cyclopenta-1,3-diene-1-carbonitrile.

2.5. Identification of photoproducts P'_4 , P'_5 and P'_6 obtained from 2-bromoaniline

These products were isolated by preparative HPLC from a deoxygenated solution 10^{-2} M irradiated at 254 nm and identified as:



P'_4 : $m/z=264$ ($\text{M}^{\bullet+}$, 100%), 262 ($\text{M}^{\bullet+}$, 100%), main fragments: 182 (90%), 166 (42%), 91 (92%).

P'_5 : $m/z=264$ ($\text{M}^{\bullet+}$, 93%), 262 ($\text{M}^{\bullet+}$, 98%), main fragments: 182 (95%), 166 (48%), 154 (33%), 91 (100%).

$^1\text{H NMR}$ (CD_3COCD_3) δ (ppm): 7.42 (d, H_2 , $J=2$ Hz), 7.16 (dd, H_6 , $J=8.2$ Hz, $J=2$ Hz), 7.02 (td, H_4 , $J=8.0$ Hz, $J=1.5$ Hz), 6.96 (dd, H_6 , $J=7.5$ Hz, $J=1.5$ Hz), 6.92 (d, H_5 , $J=8.2$ Hz), 6.77 (dd, H_3 , $J=8.0$ Hz, $J=1.1$ Hz), 6.64 (td, H_5 , $J=7.5$ Hz, $J=1.1$ Hz), 5.01 (s, NH_2), 4.42 (s, NH_2).

P'_6 : $m/z=264$ ($\text{M}^{\bullet+}$, 100%), 262 ($\text{M}^{\bullet+}$, 100%), main fragments: 247 (46%), 245 (43%), 182 (79%), 167 (84%), 154 (27%), 91 (95%).

$^1\text{H NMR}$ (CD_3COCD_3) δ (ppm): 7.41 (dd, H_6 , $J=8$ Hz, $J=1.5$ Hz), 7.12 (td, H_4 , $J=8.0$ Hz, $J=1.5$ Hz), 7.01 (dd, H_6 , $J=7.5$ Hz, $J=1.5$ Hz), 6.98 (dd, H_4 , $J=7.5$ Hz, $J=1.5$ Hz), 6.85 (dd, H_3 , $J=8.0$ Hz, $J=1.0$ Hz), 6.70 (td, H_5 , $J=8.0$ Hz, $J=1.0$ Hz), 6.65 (t, H_5 , $J=7.5$ Hz), 4.51 (s, NH_2), 4.30 (s, NH_2).

Table 1
Physical-chemical properties of 2-halogenoanilines (spectrophotometric determination)

	Solubility in water (10^{-2} M)	$\text{p}K_a$	Neutral form	
			λ_{max} (nm)	ϵ ($\text{M}^{-1} \text{cm}^{-1}$)
2-CIA	5.0	2.6	285	2035
2-BrA	2.0	2.7	287	2170
2-FA	18	3.3	276	1660

3. Results

3.1. Physico-chemical properties

2-Chloroaniline described in Merck Index as practically insoluble in water. However, its solubility is not negligible at the photochemical point of view. Solubilities of 2-chloro-, 2-bromo- and 2-fluoroanilines were evaluated by comparison of the UV spectrum of a saturated solution with the spectrum of a solution obtained by diluting in water (ratio 1/100) a solution in methanol. It was shown that the addition of a few percent of methanol does not modify the spectrum. Results are gathered in Table 1.

UV spectrum of 2-chloroaniline in unbuffered solution is given in Fig. 1. The wavelengths of maximum absorption and corresponding molar absorption coefficients of halogenoanilines are given in Table 1. Halogenoanilines are protonated in very acidic solution. It can be noted that the protonated forms absorb very little in UV range (Fig. 1, dotted line). The $\text{p}K_a$ s were evaluated from the variation of UV spectrum as a function of pH. Results are reported in Table 1. There is only a little overlap between the UV spectrum of the molecular form and sunlight spectrum as it appears in Fig. 1. However, this overlap is sufficient to induce a photodegradation in sunlight. A solution 5×10^{-4} M of 2-CIA was exposed in sunlight (in February and July) in Clermont-Ferrand (latitude 46°N , altitude 420 m). It was deduced from the kinetics

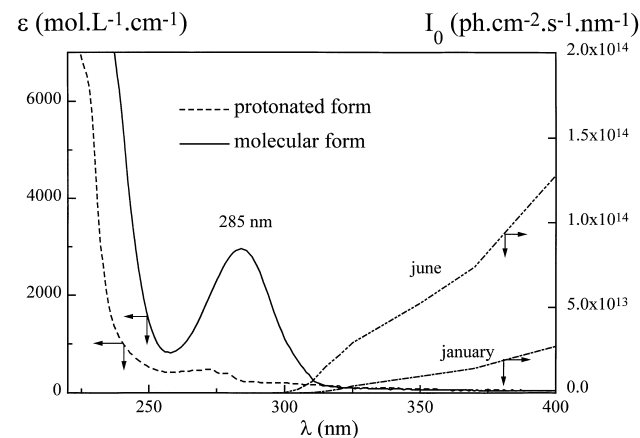


Fig. 1. UV spectra of aqueous solution of 2-chloroaniline compared to the sunlight spectrum according to Frank et Klöpffer [10].

of degradation that the half-life is about 2 days in summer and 1 month in winter.

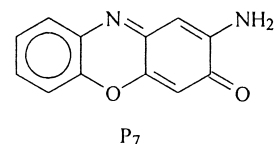
3.2. Irradiation of 2-chloroaniline

3.2.1. Analysis of photoproducts in diluted solution

Three photoproducts P_1 , P_2 , P_3 appear in the chromatogram of a deoxygenated solution 5×10^{-4} M irradiated at 285 nm (Fig. 2a). P_2 is a minor product compared to P_1 and P_3 and it was not detected in oxygenated solution. P_1 and P_2 were identified as 2-aminophenol and aniline respectively by comparison of their HPLC retention times and their UV spectra with those of commercial standards. A special procedure was used for the isolation of P_3 since it has a relatively high vapour pressure and it evaporates when solvent is eliminated (see Section 2.4). From the results of ^1H NMR and mass spectrometry it was concluded that P_3 is cyclopenta-1,3-diene-1-carbonitrile (see Section 2.4).

Another minor product P_7 was formed. Its HPLC retention time was 12 min in the conditions given in Fig. 2. Its

formation is enhanced in the presence of oxygen. This product has the same HPLC retention time and the same UV spectrum as 2-aminophenoxazin-3-one. The latter was identified by Ikekawa et al. [12], and by Nogami et al. [13] in the phototransformation of 2-aminophenol in aqueous solution. Moreover, such reactions were recently observed in the photolysis of dichloroanilines [14].

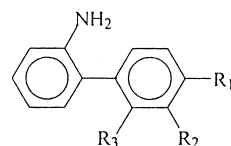


P_7

2-aminophenoxazin-3-one

3.2.2. Deoxygenated solution 2.15×10^{-3} M

Deoxygenated solutions 2.15×10^{-3} M of 2-CA were irradiated at 254 nm since the irradiation with the parallel beam of the monochromator would be too long. It was shown that the irradiation wavelength (285 or 254 nm) has not influence on the orientation of the reaction. Three new photoproducts P_4 , P_5 , P_6 were observed on the chromatogram (Fig. 2b). Their retention times are significantly longer than the retention times of P_1 – P_3 . They were formed with a very low yield, but they have HPLC retention times and UV spectra very similar with those of products obtained and isolated from irradiated solutions of 2-bromoaniline as described in Section 3.3. By analogy P_4 , P_5 and P_6 were assumed to be diaminochlorobiphenyls. These products were not observed in air-saturated solution.



P_4 : $R_1 = \text{Cl}$ $R_2 = \text{NH}_2$ $R_3 = \text{H}$

P_5 : $R_1 = \text{NH}_2$ $R_2 = \text{Cl}$ $R_3 = \text{H}$

P_6 : $R_1 = \text{H}$ $R_2 = \text{Cl}$ $R_3 = \text{NH}_2$

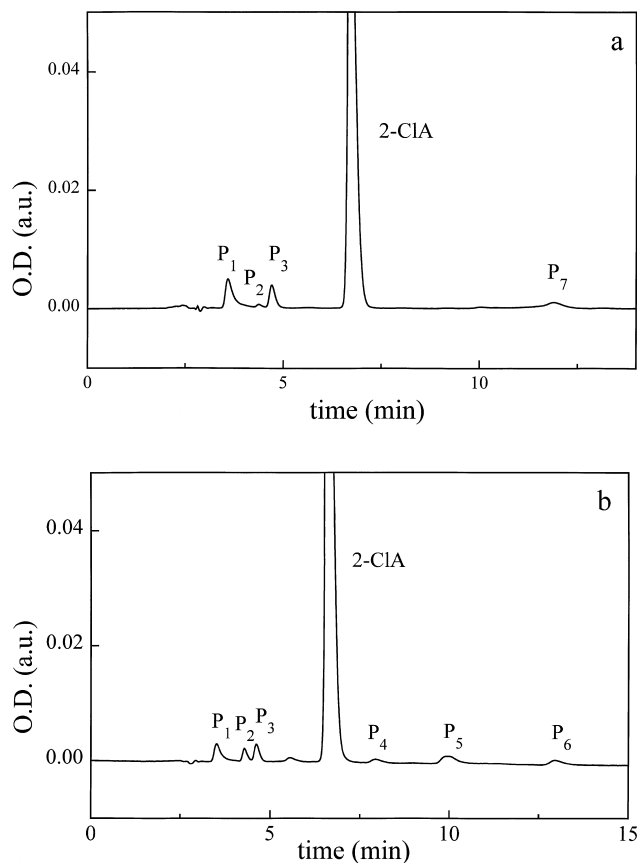


Fig. 2. HPLC chromatograms of irradiated deoxygenated solution of 2-CA. Eluent methanol–water (60–40 by volume). Water was buffered with ammonium acetate 1.8 g l^{-1} to prevent from ionisation of both amine and phenolic functions. Detection 280 nm. (a) Solution 5×10^{-4} M irradiated at 285 nm (conversion about 12%); (b) solution 2.15×10^{-3} M irradiated at 254 nm (conversion about 7%).

3.2.3. Kinetic study

The kinetics of transformation of 2-CA and formation of the main primary photoproducts were studied under various conditions. Fig. 3 is given as an example. Both aniline and 2-aminophenol have kinetics of primary photoproducts. The disappearance is slightly inhibited by oxygen that is consistent with the formation of other photoproducts (biphenyl derivatives) in deoxygenated solution. The formation of aniline is only observed in the absence of oxygen, but the formation of 2-aminophenol is not influenced by O_2 .

The quantum yields are gathered in Table 2.

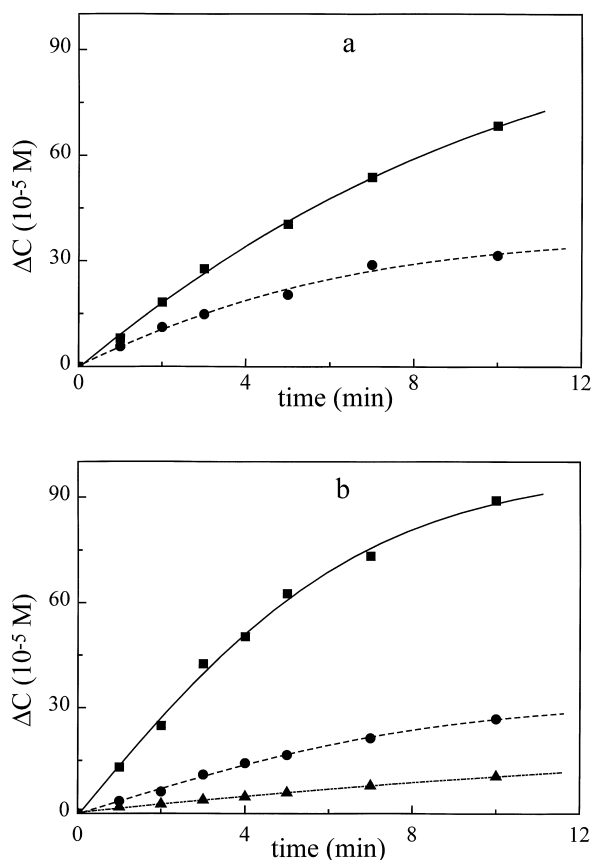


Fig. 3. Kinetics of transformation of 2-CIA 2.15×10^{-3} M irradiated at 254 nm and kinetics of formation of 2-aminophenol and aniline. (■): 2-chloroaniline transformed; (●): 2-aminophenol formed; (▲): aniline formed. (a) air-saturated solution; (b) deoxygenated solution.

3.3. Irradiation of 2-bromoaniline

3.3.1. Analytical study

The HPLC chromatogram of a deoxygenated solution of 2-BrA 6×10^{-4} M irradiated at 285 nm is given in Fig. 4a. It is very similar to the chromatogram obtained with 2-CIA. Photoproducts P_1 , P_2 , P_3 and P_7 were identified as 2-aminophenol, aniline, cyclopenta-1,3-diene carbonitrile and 2-aminophenoxazin-3-one, respectively,

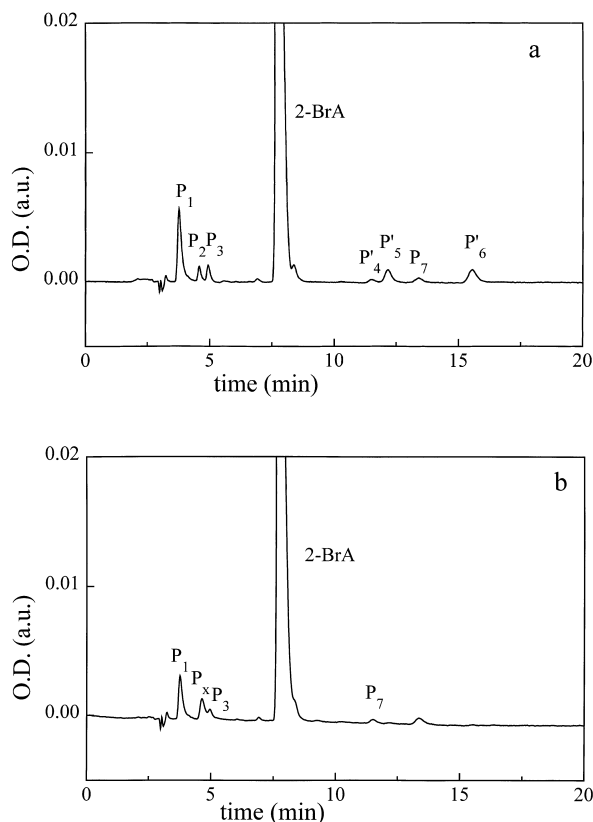


Fig. 4. HPLC chromatograms of irradiated solution of 2-BrA 6×10^{-4} M irradiated at 285 nm. (conversion about 10%). (a) deoxygenated solution; (b) air-saturated solution.

P_1 and P_2 by comparison with commercial standards, P_7 by comparison with the product formed by irradiation of 2-aminophenol. The formations of P'_4 , P'_5 and P'_6 are favoured by increasing concentration. These photoproducts were isolated from an irradiated solution $\approx 10^{-2}$ M and identified as 2',3-diamino-4-bromobiphenyl; 2',4-diamino-3-bromobiphenyl and 2,2'-diamino-3-bromobiphenyl, respectively, by MS and ^1H NMR 400 MHz after isolation (see Section 2.5). To corroborate this identification it can be noted that the irradiation of solutions of P'_5 and P'_6 leads to the formation of P''_5 to P''_6 , respectively. Products P''_5 and

Table 2

Quantum yields of disappearance of 2-chloroaniline and quantum yields of formation of 2-aminophenol and aniline under various conditions^a

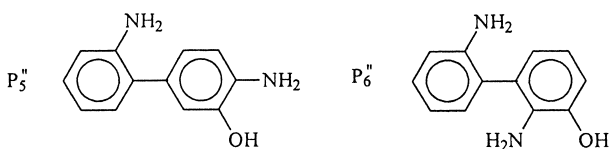
C (10^{-3} M)	λ_{irr} (nm)	pH	Oxygenation	ϕ_{disap}	$\phi_{2\text{ap}}$ (yield)	ϕ_{aniline} (yield)
2.15	254	6.5	O ₂	0.030	0.013 (0.43)	<0.001 (<0.03)
			Air	0.033	0.018 (0.54)	<0.001 (<0.03)
			N ₂	0.048	0.020 (0.41)	0.007 (0.14)
2.15	254	3.5	Air	0.032	0.013 (0.40)	<0.001 (<0.03)
		9.5	Air	0.034	0.011 (0.32)	<0.001 (<0.03)
0.50	285	6.5	O ₂	0.019	0.008 (0.42)	Traces
			Air	0.018	0.010 (0.55)	<0.001 (<0.06)
			N ₂	0.020	0.011 (0.55)	0.01 (≈ 0.5)

^a The chemical yields are given in parentheses.

P_6'' were identified as 2',4-diamino-3-hydroxybiphenyl and 2,2'-diamino-3-hydroxybiphenyl, respectively, from their mass spectra.

P_5'' : $m/z=200$ ($M^{\bullet+}$, 23%), main fragments: 184 (57%), 167 (17%), 166 (17%), 154 (17%), 91 (46%),... 43 (100%), 28 (97%).

P_6'' : $m/z=200$ ($M^{\bullet+}$, 87%), main fragments: 184 (27%), 183 (44%), 169 (17%), 154 (43%), 91 (23%),... 43 (76%), 28 (100%).



Only P_1 , P_3 and P_7 are formed in the presence of oxygen (Fig. 4b). A new unstable photoproduct P_x is also formed. It was tentatively identified as 2-amino-1,4-benzoquinone [$\lambda_{\max}=270$ nm (strong), 480 nm (weak)].

3.3.2. Kinetic study

It was observed that 2-aminophenol, aniline, cyclopenta-1,3-diene-1-carbonitrile and diaminobromobiphenyls have kinetics of primary photoproducts. In contrast P_5'' and P_6'' appear as secondary photoproducts, that is consistent with their identification.

The quantum yield of 2-BrA disappearance and of formation of the main photoproducts (2-aminophenol and aniline) were evaluated. They are reported in Table 3. As in the case of 2-CIA, solution 6×10^{-4} M were irradiated in parallel beam at 285 nm (monochromator) and solutions 1.7×10^{-3} M at 254 nm with six germicide lamps, because irradiations times would be too long with the monochromator.

Oxygen has no influence on the disappearance of 2-BrA in diluted solution but it slightly inhibits its transformation in solution 1.7×10^{-3} M. This phenomenon can be related to the formation of biphenyl derivatives. The presence of bromide ions reduced the quantum yield of disappearance and inhibited the formation of biphenyl derivatives. The formation of 2-aminophenol was not influenced by oxygen, but the formation of aniline was inhibited, that it is not surprising since it is a product of reduction. These data will be useful to discuss mechanisms.

3.4. Irradiation of 2-fluoroaniline

The photochemical behaviours of 2-FA and 2-CIA are very similar with this difference that no biphenyl derivative was obtained with 2-FA. The main photoproducts are 2-aminophenol, aniline and cyclopenta-1,3-diene-1-carbonitrile. The quantum yield of disappearance and of formation of 2-aminophenol and aniline are reported in Table 4. It was not possible to quantify the formation of the third photoproduct.

Oxygen has no influence on the disappearance nor in the formation of 2-aminophenol, but it inhibits the formation of aniline. The formation of 2-aminophenol is more efficient than with 2-BrA and 2-CIA. It corresponds to more than 50% of 2-FA transformed.

3.5. Flash photolysis

To complement analytical studies laser flash experiments at 266 nm were carried out. No transient species was observed with 2-CIA either because the quantum yield is too low (0.02) or because transients have a too short life-time

Table 3
Quantum yields of disappearance of 2-bromoaniline and of formation of 2-aminophenol and aniline under various conditions^a

C (10^{-3} M)	λ_{irr} (nm)	Oxygenation	ϕ_{disap}	$\phi_{2\text{ap}}$, (yield)	ϕ_{aniline} , (yield)
1.7	254	O ₂	0.044	0.015 (0.34)	<0.001 (<0.02)
		Air	0.038	0.014 (0.37)	0.002 (0.05)
		N ₂	0.070	0.018 (0.26)	0.004 (0.06)
Br ⁻ 10^{-2} M added		N ₂	0.052	0.015 (0.29)	0.004 (0.08)
0.60	285	O ₂	0.043	0.006 (0.14)	<0.001 (<0.02)
		Air	0.042	0.008 (0.19)	0.001 (0.02)
		N ₂	0.040	0.009 (0.22)	0.003 (0.07)

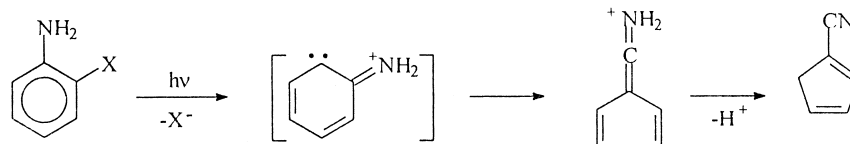
^a The chemical yields are given in parentheses.

Table 4
Quantum yields of disappearance of 2-fluoroaniline and formation of 2-aminophenol and aniline under various conditions^a

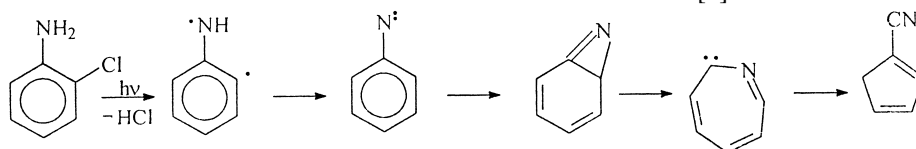
C (10^{-3} M)	λ_{irr} (nm)	Oxygenation	ϕ_{disap}	$\phi_{2\text{ap}}$, (yield)	ϕ_{aniline} , (yield)
2.86	254	O ₂	0.11	0.067 (0.61)	<0.001 (<0.01)
		N ₂	0.10	0.058 (0.58)	0.003 (0.03)
0.11	285	O ₂	0.13	0.067 (0.52)	<0.001 (0.008)
		Air	0.10	0.064 (0.64)	0.001 (0.01)
		N ₂	0.13	0.070 (0.54)	0.003 (0.02)

^a The chemical yields are given in parentheses.

compared to the duration of the flash (9 ns). In contrast several transients absorbing at $\lambda > 300$ nm were detected upon irradiation of 2-FA, two of them being long lived ($\tau_{1/2} \approx 16 \mu\text{s}$ and $\tau_{1/2} > 0.3$ ms). Unfortunately, it was not possible to characterise these transients.



1H-benzotriazole into cyclopentadiene-1-carbonitriles (see Section 1). Another argument is that the intermediate formation of a carbene was recently experimentally proved [16] in the photochemical transformation of 2-chlorophenolate into cyclopentadiene carboxylic acids.



B: formation of a nitrene rearranged into a seven membered carbene and then into carbonitrile, as suggested by Ishida et al. [6].

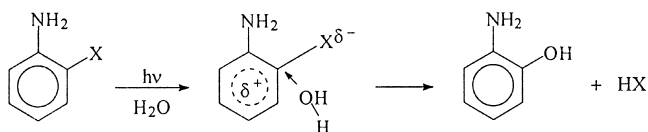
In order to point out a possible formation of Br^\bullet , solutions were irradiated in the presence of $\text{Br}^- 10^{-2}$ M. No formation of $\text{Br}_2^{\bullet-}$ was observed in spite of the high absorptivity of $\text{Br}_2^{\bullet-}$ ($\epsilon \approx 9000 \text{ M}^{-1} \text{ cm}^{-1}$) [15] that make possible to detect the formation Br^\bullet with a quantum yield as low as ca. 0.005.

Titled compound is formed with the three congeners chloro-, bromo-, and fluoroaniline. So it results from a heterolytic mechanism. Its formation is not influenced by concentration, by pH nor by oxygen. No definitive conclusion can be given about the mechanism, but mechanism A seems to be more likely than B, by analogy with the photochemical behaviour of 2-chlorophenolate in aqueous solution. Besides according to Cullin et al. [7], the formation of cyclopenta-1,3-diene-5-carbonitrile from nitrene in gas phase does not involve the intermediate formation of azacycloheptatetraene.

4. Discussion and mechanisms

4.1. Formation of 2-aminophenol

Formation of 2-aminophenol is the main reaction with the three congeners of 2-halogenoanilines. It results from a heterolytic process since it is more efficient with 2-FA than with 2-ClA and 2-BrA. A homolytic scission is not allowed with 2-FA for energetic reason, the energy of a photon at 285 nm (420 kJ mol^{-1}) being lower than the bond strength (523 kJ mol^{-1}). The reaction is not a substitution of Cl^- by OH^- , but it involves a molecule of water since it is not influenced by pH in the range 3–10. Same results were previously obtained with 3-chlorophenol [3] and 3-chloroaniline [1]. So similar mechanism is proposed. It is likely that both transients are not involved in this reaction since no transient was observed in the photohydrolysis of 3-chlorophenol.



4.3. Formation of aniline

Aniline is formed with similar efficiencies from the three congeners (2-ClA, 2-BrA, 2-FA). Consequently, a heterolytic mechanism is necessarily involved. A radical mechanism is excluded as the main pathway even in the case of 2-BrA since $\text{Br}_2^{\bullet-}$ was not detected in laser flash photolysis when 2-BrA was irradiated in the presence of Br^- . It is unlikely that nitrene resulting from the elimination of two atoms of hydrogen from nitrogen leads to aniline. Formation of aniline probably results from reduction of carbene. In the case of 4-chloroaniline it was reported that the carbene initially formed may be reduced by methanol [17]. However, in the case of 2-BrA we cannot exclude an alternative minor radical mechanism.

4.2. Formation of cyclopenta-1,3-diene-1-carbonitrile

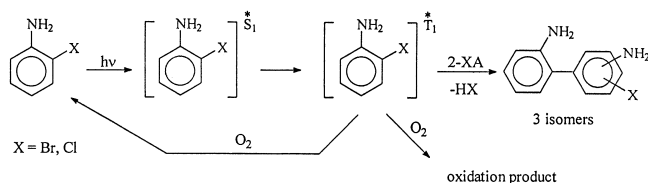
Two mechanisms may be written for the formation of cyclopenta-1,3-diene-1-carbonitrile:

A: formation of an iminocarbene rearranged into ketene imine and then into carbonitrile, as is was proposed by Sakaizumi et al. [5] for the pyrolytic transformation of

4.4. Formation of biphenyl derivatives

The formation of biphenyl derivatives was mainly observed with 2-BrA and, with a lower efficiency, with 2-ClA. It does not occur with 2-FA. A radical mechanism is excluded since no $\text{Br}_2^{\bullet-}$ was detected as indicated before. Moreover, if a radical mechanism was involved, the formation of aniline by reduction should be probably

more efficient with 2-BrA than with 2-FA, that was not observed. The absence of biphenyl derivatives in the presence of oxygen let us deduce that the reaction involves the excited triplet state. Then the formation of biphenyl derivatives may be attributed to the elimination of hydrogen halide from two molecules, one of them being in the excited triplet state. The suggested mechanism is presented below:



5. Conclusion

The three congeners 2-ClA, 2-BrA, 2-FA have similar photoreactivities except for the formation of biphenyl derivatives mainly observed with 2-BrA and with 2-ClA in concentrated solutions.

The quantum yield of disappearance is higher with 2-FA than with the two other congeners. C–F scission is necessarily a heterolytic process for energetic reason.

The main products (2-aminophenol, 1,3-cyclopentadiene-1-carbonitrile and aniline) formed with the three congeners result from a heterolytic mechanism.

The formation of biphenyl derivatives is attributed to the reactivity of the excited triplet state of 2-halogenoanilines more efficiently formed with 2-BrA than with 2-ClA.

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References

- [1] B. David, M. Lhote, V. Faure, P. Boule, *Water Res.* 32 (1998) 2451.
- [2] S. Ishikawa, K. Baba, Y. Hanada, Y. Uchimura, K. Kido, *Bull. Environ. Contam. Toxicol.* 42 (1989) 65.
- [3] P. Boule, C. Guyon, J. Lemaire, *Chemosphere* 11 (1982) 1179.
- [4] K. Othmen, P. Boule, *Bull. Environ. Contam. Toxicol.* 59 (1997) 924.
- [5] C. Richard, G. Grabner, *Communication at XVth IUPAC Symposium on Photochemistry, Prague, July 1994.*
- [6] T. Ishida, H. Abe, A. Nakajima, K. Kaya, *Chem. Phys. Lett.* 170 (1990) 425.
- [7] D.W. Cullin, N. Soundararajan, M.S. Platz, T.A. Miller, *J. Phys. Chem.* 94 (1990) 8890.
- [8] T. Sakaizumi, U. Kikuchi, O. Ohashi, I. Yamaguchi, *Bull. Chem. Soc. Jpn.* 60 (1987) 3903.
- [9] F. Bonnichon, C. Richard, *J. Photochem. Photobiol. A: Chem.* 119 (1998) 25.
- [10] R. Frank, W. Klöpffer, *Chemosphere* 17 (1988) 985.
- [11] Chin-Hsing Chou, Cheng-Chang Wu, Wey-Kao Chen, *Tetrahedron Lett.* 36 (1995) 5065.
- [12] T. Ikekawa, N. Uehara, T. Okuda, *Chem. Pharm. Bull.* 16 (1968) 1705.
- [13] T. Nogami, T. Hishida, M. Yamada, H. Makawa, Y. Shiota, *Bull. Chem. Soc. Jpn.* 48 (1975) 3709.
- [14] K. Othmen, P. Boule, *J. Photochem. Photobiol. A: Chem.* 121 (1999) 161.
- [15] G.L. Hug, *Optical Spectra of Nonmetallic Inorganic Transient Species in Aqueous Solution*, NSRDS-NBS 69 Washington, DC, 1981.
- [16] F. Bonnichon, C. Richard, personal communication.
- [17] K. Othmen, P. Boule, B. Szezeponik, K. Rotkiewicz, G. Grabner, *J. Phys. Chem.*, in press.