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Phototransformation of 2-Chloroaniline in Aqueous Solution

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Chloroanilines are toxic substances listed as typical pollutants of the environment. Their photolysis in sunlight is a possible route for their elimination, and it is important to know the structure of their photoproducts.

The transformation of 2-chloroaniline (2-CA ; 95-51-2) was previously studied in aqueous solution (Ishikawa et al. 1989) and in gas phase (Cullin et al. 1990 ; Ishida et al. 1990). The main photoproducts identified in aqueous solution were 2-chloronitrobenzene, 2-chlorophenol and phenol. It was suggested that the former results from the initial photooxidation of the substrate and that the two others result from its photohydrolysis. This mechanism contrasts with the phototransformation of most halogenoaromatic derivatives which lead to an initial C-halogen scission (Boule et al. 1982 and 1985 ; Lipczynska-Kochany 1992). It is also quite different from the transformation of 2-chloroaniline in gas phase observed by means of excimer laser photolysis since the formation of 1,3-cyclopentadiene-1-carbonitrile was explained by the intermediate formation of a nitrene.

The aim of the present work is to analyse the main photoproducts formed in aqueous solution and to compare them with the photochemical behaviours previously published.

MATERIAL AND METHODS

Reactants : 2-chloroaniline Aldrich > 98%. Water was purified with Milli-Q device (Millipore) (purity controlled by resistivity ≥ 18 MΩ.cm).
Irradiations : solutions were irradiated at 253.7 nm or 285 nm. At short wavelength with 6 low pressure mercury lamps (15 w) placed in a cylindrical mirror ; at 285 nm with a Schoeffel monochromator equipped with a xenon lamp (1600 w).

For preparative purposes solutions 10^{-3} M or 10^{-2} M were irradiated in the range 275-340 nm with 6 lamps Duke Sunlamp GL20 (reactor in quartz) or at wavelengths longer than 300 nm (reactor in Pyrex) to minimize further

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phototransformation of the main product (see spectrum on Fig. 2) and minor phenolic products.

Irradiated solutions were analysed in HPLC on a Waters chromatograph equipped with a photodiode array detector and a column C_{18} 250 mm x 4 mm ; eluent : MeOH/H_2O mixture usually 55/45 (v/v).

The main photoproduct was identified by MS and NMR. GC-MS chromatogram and spectrum were obtained on Hewlett-Packard 5985. The column was OPTIMA 5 (Machery-Nagel) 25 m, internal diameter 0.25 mm, stationary phase siloxane (mainly methyl siloxane). The precise molecular mass was determined in Service Central d'Analyse du CNRS on VG ZAB2-SEQ. ^1H 400 MHz NMR spectrum was recorded in acetone D_6 on Bruker AC400.

RESULTS AND DISCUSSION

The pKa of the protonated form of 2-chloroaniline was evaluated at 2.6 from the variation of UV spectrum with pH. The neutral form has a maximum absorption at 285 nm with a molar absorption coefficient evaluated at 2035 $M^{-1} cm^{-1}$. The absorption of the protonated form is much lower so it can be neglected for irradiation at $\lambda>230$ nm.

An unbuffered $1.0x10^{-3}$ M solution was irradiated at 253.7 nm in air-equilibrated condition, after N_2 purging or after O_2 purging. No influence of oxygen was observed on the transformation rate.

After irradiation of 1 min, *i.e.* after about 22% conversion the solution was brownish, but only one main product (I) could be observed on the HPLC chromatogram (Fig. 1). The UV spectrum of (I) was obtained with the photodiode array detector. Its maximum is located at 268 nm (Fig. 2) but it is not identical to the UV spectrum of phenol. It was also noticed that product (I) and phenol have different HPLC retention times. The same product (I) was obtained by irradiating at 285 nm or in the range 275-340 nm.

The photoproduct (I) accumulates quite well and for identification a solution 10^{-3} M was irradiated in the range 275-340 nm up to about 80% conversion. It can be separated by HPLC but it was not possible to isolate since it evaporated during the concentration of the solution. However it was noted that it can be extracted by nitrogen flow or by distillation under reduced pressure and collected in a trap cooled in ice-salt mixture. Distillation under reduced pressure was preferred because it is more rapid than the other method. To minimize the simultaneous extraction of 2-CA, the irradiated solutions were strongly acidified with HCl in order to protonate the reactant.

For MS and GC-MS analyses the mixture was extracted with diethyl ether. The parent peak on the MS spectrum was localized at m/e=91 ; a fragment was

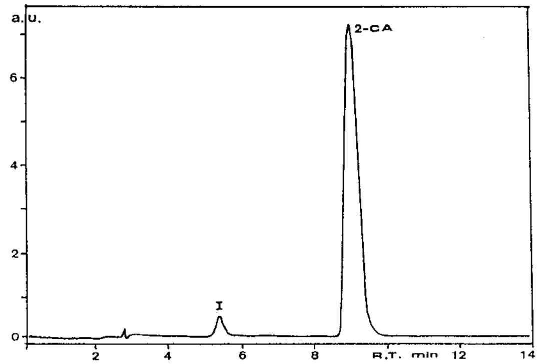

Figure 1. HPLC chromatogram of an air-saturated solution of 2-CA (1.0×10^{-3} M) irradiated up to 22% transformation at 253.7 nm. Eluent MeOH/H_2O 55:45 (v/v) λ_{detec}=270 nm.

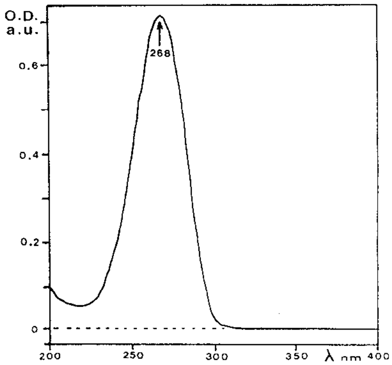

Figure 2. UV spectrum of photoproduct (I) obtained with the photodiode array detector of HPLC chromatograph.

observed at m/e=64. The following value was obtained for the precise determination of the molecular mass : m/e=91.0403000. It is consistent with $C_3H_7O_3$, C_6H_5N and $CH_5N_3O_2$ but only C_3H_5N is likely. It corresponds to none of the products reported by Ishikawa et al. (1989).

To obtain the NMR spectrum the following procedure was used : the solution collected in the trap was extracted with $C_2Cl_3F_3$ (B.P.=45.8°C). Most of the fluorinated solvent was evaporated to about 1 ml. Deuterated chloroform was added and evaporation continued to almost complete elimination of the fluorinated solvent. The ^{1}H NMR spectrum is summarized in Table 1. It is consistent with the following structure :

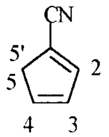

Table 1. ^{1}H NMR spectrum of the main photoproduct formed by irradiation of 2-CA in aqueous solution (NMR solvent $CDCl_3$ - Ref. $CHCl_3$ at 7.27 ppm)

δ ppm	Relative size	Multiplicity	Attribution	Coupling constants
7.30	1 H	quintuplet	2	$J_{2\text{-}X} = 1.7$ Hz
6.70	1 H	double-quadruplet	4	$J_{4\text{-}2} = J_{4\text{-}5} = J_{4,5'} \approx 1.3$ Hz
6.63	1 H	multiplet	3	$J_{4\text{-}3} = 5.4$ Hz
3.34	2 H	quadruplet	5,5'	$J_{5\text{-}X} = J_{5'\text{-}X} = 1.5$ Hz

From the NMR spectrum it can be deduced that the ring lies in a plane and that protons 5 and 5' are equivalent. The other possible structure (1,4-cyclopentadiene-I-carbonitrile) was ruled out since protons 2 and 5 should have similar shifts significantly higher than the shift of proton 4.

The formation of 1,3-cyclopentadiene-1-carbonitrile was previously observed in the gas phase phototransformation of 2-CA (Cullin et al. 1990, Ishida et al. 1990) but not in the aqueous photolysis probably because of its high vapour pressure that makes difficult its extraction and its detection in GC-MS.

The analysis of minor photoproducts was carried out with GC-MS. A solution 10^{-2} M was irradiated in the range 300-350 nm (reactor in Pyrex) to minimize photolysis of phenolic photoproducts. The irradiated solution was filtered on Millipore 0.45 µm to eliminate insoluble oligomers and extracted with ether for injection in GC-MS. In addition to product I, 2-chlorophenol, 2-aminophenol and phenol were detected as minor photoproducts, but no formation of chloronitrobenzene was observed.

It can be concluded that in aqueous solution 2-chloroaniline behaves as a 2-chlorophenolate that leads to a photocontraction of the ring (Guyon et al. 1984). The study of the mechanism of this reaction is still in progress. It needs laser flash photolysis experiments to determine if the reaction involves the intermediate formation of a nitrene as suggested in gas phase or if the mechanism is similar to that which was experimentally proved in the photolysis of 2-chlorophenolate.

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