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ULTRASONIC AND PHOTOCHEMICAL DEGRADATION OF CHLORPROPHAM AND 3-CHLOROANILINE IN AQUEOUS SOLUTION

B. DAVID[1]*, M. LHOTE[1], V. FAURE[2] and P. BOULE[2]

[1]Laboratoire de Chimie Moléculaire et Environnement, ESIGEC, Université de Savoie, 73376 Le Bourget du Lac Cedex, France and [2]Laboratoire de Photochimie Moléculaire et Macromoléculaire, URA CNRS 433, Université Blaise Pascal (Clermont–Ferrand), 63177 Aubiere Cedex, France

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Abstract—Sonolysis and photolysis are compared for the transformation of chlorpropham, a systemic herbicide belonging to the carbamate group, and 3-chloroaniline, the main intermediate often observed in the degradation of chlorpropham. In both cases the ultrasonic degradation is much more efficient at 482 kHz than at 20 kHz. The main identified sonoproducts formed in the degradation of chlorpropham are 3-chloroaniline, formic acid, carbon monoxide and dioxide and chloride ions. The degradation of 3-chloroaniline also leads to Cl^-, CO and CO_2 but chlorohydroquine was also detected as an intermediate. Two different mechanisms are involved in the ultrasonic transformation: pyrolysis resulting from the implosion of cavitation microbubbles and oxidation by hydroxyl radicals formed by sonolysis of water. Photolysis is more specific: 3-chloroaniline is initially quantitatively transformed into 3-aminophenol. A heterolytic mechanism is suggested. Resorcinol and some unidentified photoproducts are formed in a second stage. The same type of reaction is involved in the photo-transformation of chlorpropham, but the reaction is not so specific. In both cases the photolysis at 254 nm leads to a complete disappearance of phenolic and quinonic compounds.

Key words—ultrasound, photolysis, herbicide, chlorpropham, CIPC, 3-chloroaniline, mineralization

INTRODUCTION

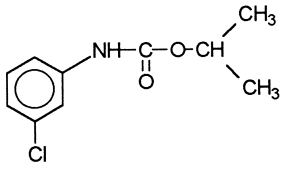
Several studies have already demonstrated that ultrasound is an efficient method for the degradation of organic pollutants in aqueous solution (Kotronarou *et al.*, 1992; Serpone *et al.*, 1994; Petrier *et al.*, 1992b, 1994). The applied pressure field induces the formation of microbubbles which oscillate and collapse. The implosion of the cavitation bubbles generates high energy reactions due to the local increase of temperature and pressure, that is the hot spot theory (Suslick and Hammerton, 1986; Suslick, 1988). The high energy phenomena can also be attributed to electrical discharges (Margulis, 1990) and/or corona effect (Lepoint and Mullie, 1994). In these conditions the homolytic cleavage of water yields $^{\bullet}OH$ and $H^{\bullet}$ which recombine or diffuse in the bulk.

$$H_2O[\longrightarrow^{)))}]H^{\bullet} + {}^{\bullet}OH$$

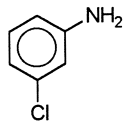
Hydroxyl radicals lead to the oxidation of most of the organic compounds present in the solution. Besides, if the vapour pressure of substrates is sufficient for their diffusion in the short lived bubbles, a thermal degradation, assisted or not by electric discharges and/or corona effect also occurs.

If the ultimate purpose of sonochemistry is water treatment, photodegradation is one of the main natural processes of elimination of xenobiotic pollutants. It can also be used for the decontamination of polluted waters, in association with other processes: UV/H_2O_2, UV/O_3 and photo-Fenton. The photolysis consists in exciting the substrate by absorption of a photon. Then several processes may be involved according to the structure of the compound. With chloroaromatic derivatives in dilute aqueous solution, photooxidation and heterolytic scission of the C–Cl bond with formation of the corresponding hydroxylated product and hydrochloric acid, are the most frequent reactions (Boule *et al.*, 1982, 1985; Lipczynska-Kochany and Bolton, 1991).

The aim of the present work is to compare the ultrasonic degradation with the photodegradation of chlorpropham (also called CIPC) and 3-chloroaniline.



chlorpropham
(CIPC)



3-chloroaniline

*Author to whom all correspondence should be addressed.

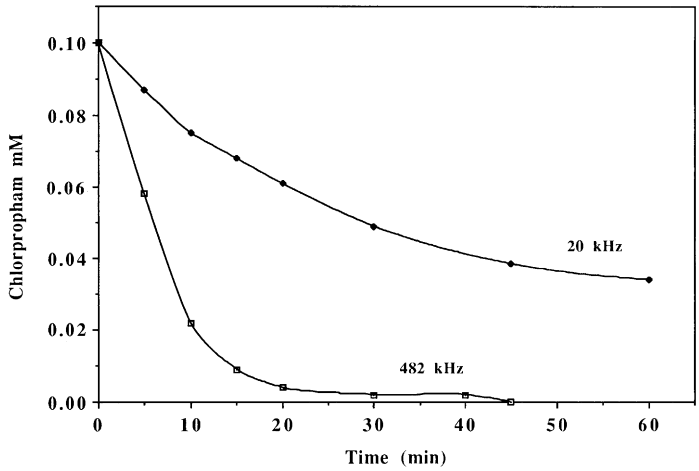


Fig. 1. Kinetics of ultrasonic transformation of chlorpropham (CIPC) at 20 and 482 kHz in air-equilibrated solution (100 ml).

Chlorpropham (isopropyl-3-chlorocarbanilate) is a selective systemic herbicide and growth regulator. It is also used as a sprouting inhibitor for ware potatoes and sucker control agent in tobacco (Metcalf, 1971; Tsumura-Hasegawa *et al.*, 1992; Tomlin, 1994). As its solubility in water is 80 mg l^{-1} and it is resistant to hydrolysis and oxidation, the bacterial degradation of chlorpropham is probably the dominant elimination pathway in the environment. It leads to the formation of the toxic 3-chloroaniline (Wolfe *et al.*, 1978) listed on the European Community priority pollutant Circular No 90–55 (1990). So it is important to study and compare different processes to eliminate these compounds from water and analyse the intermediate products involved in their degradation.

EXPERIMENTAL SECTION

Reagents

Chlorpropham (99%) was provided by Chem Service and used as received, 3-chloroaniline (>99%) by Aldrich, 3-aminophenol (>98%) and resorcinol (>99%) by Merck. Water used for solutions and HPLC was purified with a Milli-Q apparatus. Methanol was of HPLC grade.

Analyses

UV spectra of solutions were recorded on a CARY 13, Varian Spectrophotometer.

Separations and titrations of products were carried out on HPLC chromatographs (Waters 600E model and Beckman 420 model) equipped with C_{18} columns, 5 μm 250 mm × 4.6 mm. The eluent was a mixture MeOH/H_2O (usually 60/40). Acetic acid (0.1%) was added to water to prevent ionisation of phenolic derivatives. Nitrate, nitrite and chloride ions were analysed by ionic liquid chromatography on a Waters ILC1 apparatus equipped with a conductimeter 430.

Identification of the main sonoproducts was obtained by GC-MS (Carlo Erba Instruments QMD 1000) on a CP-SIL8 column. Photoproducts were identified by ^{1}H NMR on a Bruker AC400 spectrometer and by mass spectrometry on Fison type EB (70E) or Nermag R10-10C spectrometers; GC-MS (Hewlett-Packard 5985 with capillary column Supelco SE 52) was used for the identification of some of the products.

Carbon dioxide and monoxide analyses were carried out after head space sampling on an Intersmat I.G.16 chromatograph equipped with a Porapak Q 2 m × 2 mm id. column. Identification and calibration were obtained with gas standards.

Ultrasonic treatments

Degradation was performed at two frequencies. At low frequency, 20 kHz, a commercial titanium probe system of 35 mm diameter was connected to a Branson Sonifier 450 generator. High frequency was obtained with a transducer emitting at 482 kHz. Both reactors have been previously described (Petrier *et al.*, 1994). They were calibrated by determination of the calorimetric power which was 20 W for the two frequencies corresponding to 40 W electric. Most of these experiments were carried out in air-equilibrated solutions at 20°C and constant pressure.

Photochemical irradiations

Several devices were used to study the photochemical transformations. Solutions were irradiated at 254 nm with a low pressure mercury lamp germicide Mazda TG-15 W surrounded by an elliptical mirror, the lamp being located along one focal axis and the reactor in quartz along the other. A device in which the reactor was surrounded by 6 lamps in a cylindrical mirror was used to study the complete phototransformation of substrates. In the latter, the incident photon flow in 25 ml was evaluated at about 2×10^{-6} Einstein s^{-1} using uranyl oxalate actinometry (Calvert and Pitts, 1966).

A monochromator Schoeffel equipped with a xenon lamp (1600 W) was used for irradiations at 270 nm, and a monochromator Bausch and Lomb with a high pressure mercury lamp (Ushio USM-200 DP) at 296 nm. For the isolation of photoproducts, solutions were irradiated in the range 290–340 nm with 6 low pressure UVB lamps Duke GL 20 W.

Photochemical reactions were carried out in unbuffered solution at room temperature.

RESULTS

Ultrasonic transformation of chlorpropham

The disappearance of chlorpropham at 20 and 482 kHz is compared in Fig. 1.

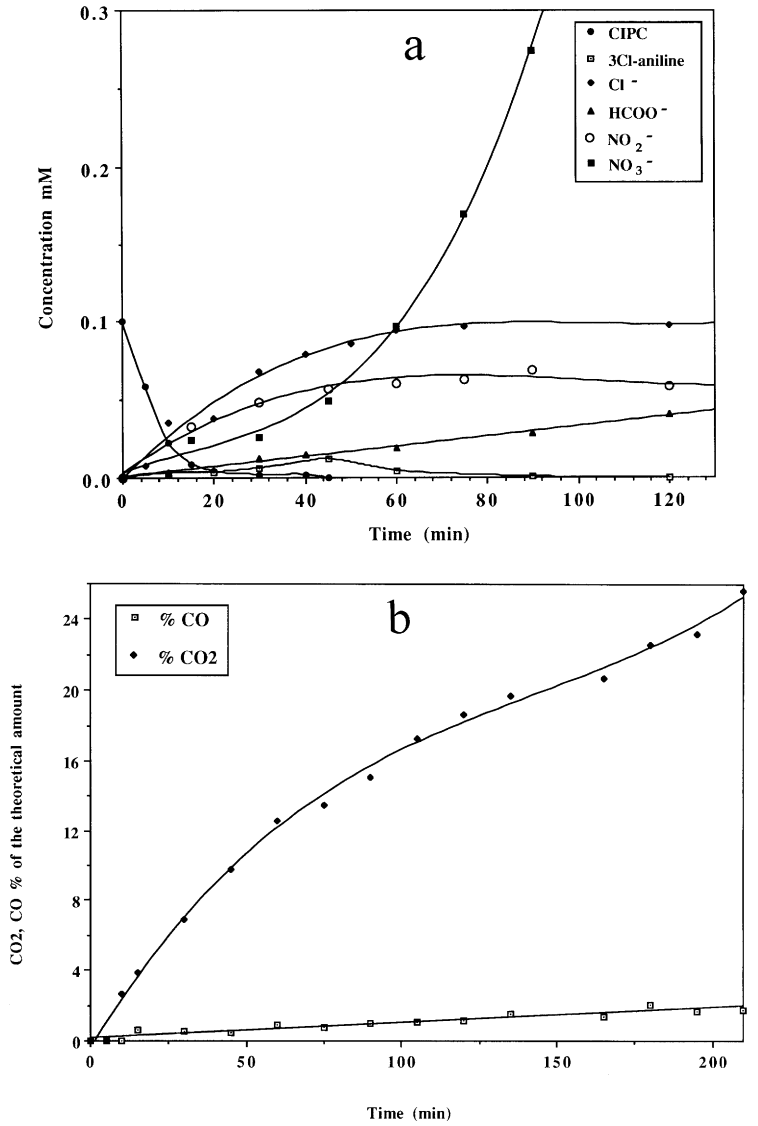


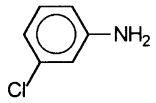
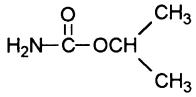
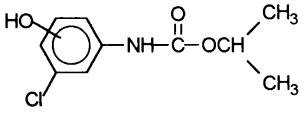
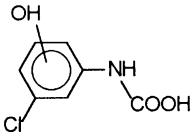
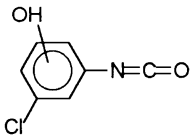
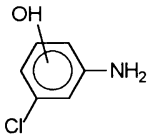
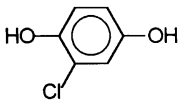
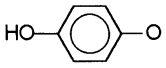
Fig. 2. Kinetics of formation of the main sonoproducts of chlorpropham at 482 kHz in air-equilibrated solution (100 ml, 0.1 mM). (a) Organic and ionic products; (b) carbon monoxide and dioxide.

The treatment at high frequency (initial rate 13.0×10^{-8} M s^{-1}) is much more efficient than at 20 kHz (initial rate 4.2×10^{-8} M s^{-1}). The complete degradation was obtained after 45 min at 482 kHz whereas about 1/3 of chlorpropham remained after 60 min at 20 kHz. The kinetics of formation of ionic species, 3-chloroaniline and formic acid at 482 kHz are reported in Fig. 2(a). Formation of 3-chlorohydroquinone has been observed on the HPLC chromatogram, but not quantified. It can be noted that the same sonoproducts were obtained at 20 kHz but in lower amounts.

The C–Cl bond cleavage is the major primary process. The yield of Cl^- is about 98% after 80 min at 482 kHz. Ultrasound does not only lead to a dechlorination but also to a drastic degradation of the herbicide. During the course of the reaction, nitrite and nitrate ions are formed. Both ions do not result from the sonication of chlorpropham because their formation was not observed when nitrogen was eliminated from the solution by oxygen purging whereas chloropropham was completely degradated. Moreover it appears in Fig. 2(a) that the sum of nitrite and nitrate ions formed is quite higher than the amount of chlorpropham converted.

Nitrite ions are formed as primary sonoproduct whereas nitrate ions appear as secondary product. This is consistent with the oxidation of nitrite by hydroxyl radicals formed in the sonolysis of water. In the first stage of the reaction, when the concentration of nitrite is too low to quench $^{\bullet}OH$, the formation of hydrogen peroxide was observed (iodometric test) and attributed to recombination of $^{\bullet}OH$.

Table 1. Main products of ultrasonic transformation of chlorpropham (482 kHz) identified by GC-MS

	Values of m/e (Dalton)	
	parent peak	fragments
	127-129	low fragmentation
	103 (unstable)	88, 62, 59, 45
 4 isomers	229-231	 187-189  169-171  143-145
	144-146	 109 80 51 low fragmentation

The pH decrease observed with unbuffered solutions results from the formation of HCl, HNO_2, HNO_3, formic and carbonic acids.

The main organic sonoproduct is 3-chloroaniline. It was identified by its HPLC retention time (comparison with a standard) and by GC-MS. The yield reached 12.5% after sonication at 482 kHz during 45 min and decreased afterwards. Other products were identified from GC-MS spectra by comparison with NBS library, namely carbamic acid isopropyl ester, the four isomeric 3-chlorohydroxyphenylcarbamic acid isopropyl esters and 3-chlorohydroquinone. The main values of *m/e* are given in Table 1. Isopropanol was also detected by GC on a Gaschrom 254 column at the end of the experiment, but it was not quantified.

The formation of hydroxylated products indicates that hydroxyl radicals are involved in the ultrasonic degradation of chlorpropham. Actually, it was observed that the transformation is 65% inhibited by addition of isopropanol 0.1 M.

Gases formed in the ultrasonic degradation of chlorpropham were analysed by the head space method. Kinetics are reported in Fig. 2(b). It appears that CO_2 is formed as both a primary and a secondary product.

Ultrasonic transformation of 3-chloroaniline

As it was observed with chlorpropham the degradation of 3-chloroaniline is more efficient at 482 kHz than at 20 kHz and this effect is much more important: the ratio of initial rates is about 8 as it appears in Fig. 3. The main sonoproducts are Cl^-, NO_2^-, NO_3^-, CO and CO_2. Kinetics are given in Fig. 4 for sonolysis at 482 kHz.

Another product formed was identified as chlorohydroquinone (*m/e* = 144) by means of GC-MS. The commercial compound was characterised by

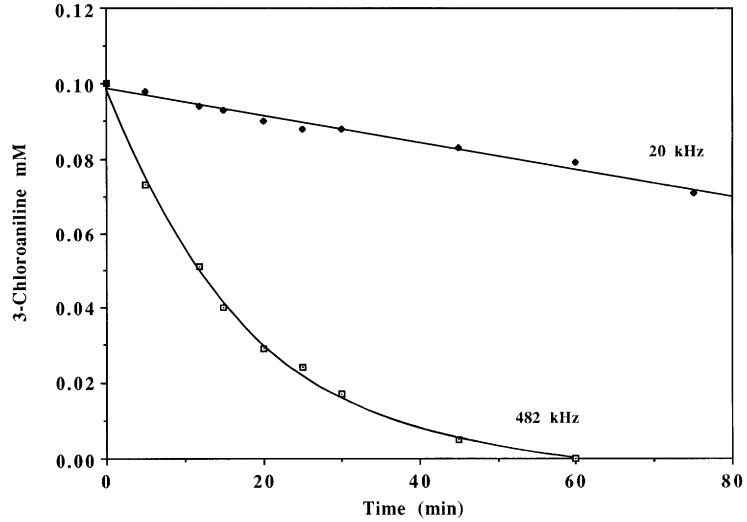


Fig. 3. Kinetics of ultrasonic transformation of 3-chloroaniline at 20 and 482 kHz in air-equilibrated solution (100 ml).

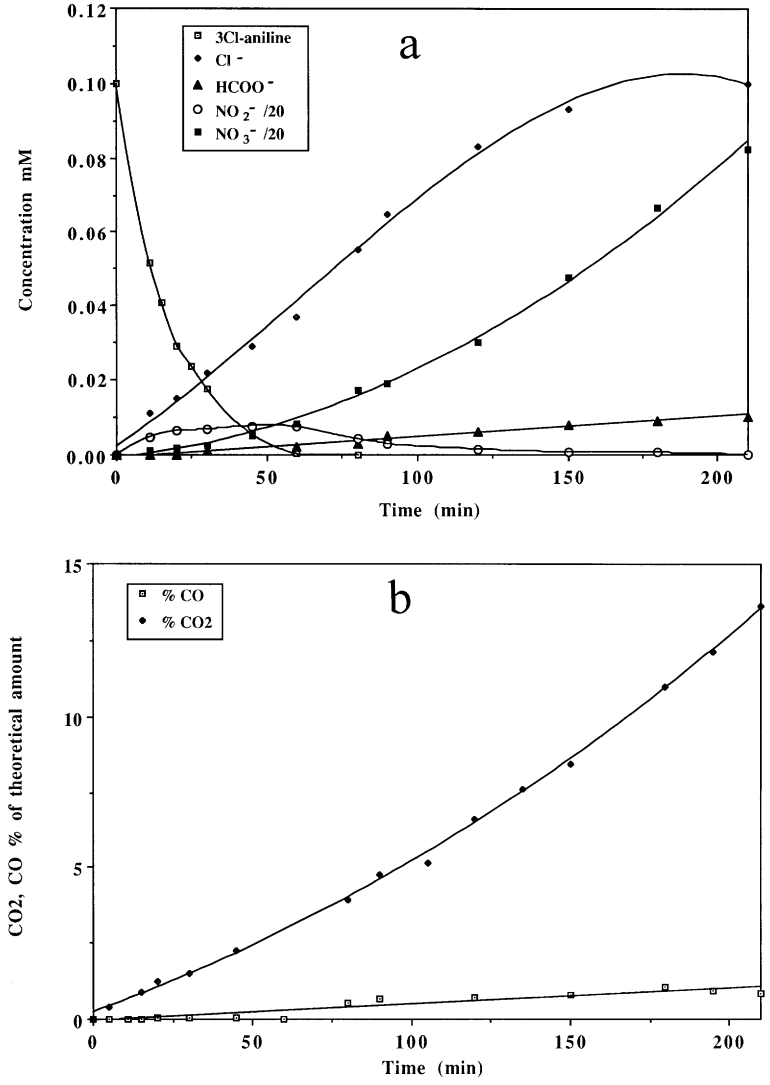


Fig. 4. Kinetics of formation of the main sonoproducts of 3-chloroaniline at 482 kHz in air-equilibrated solution (100 ml). (a) Organic and ionic products; (b) carbon monoxide and dioxide.

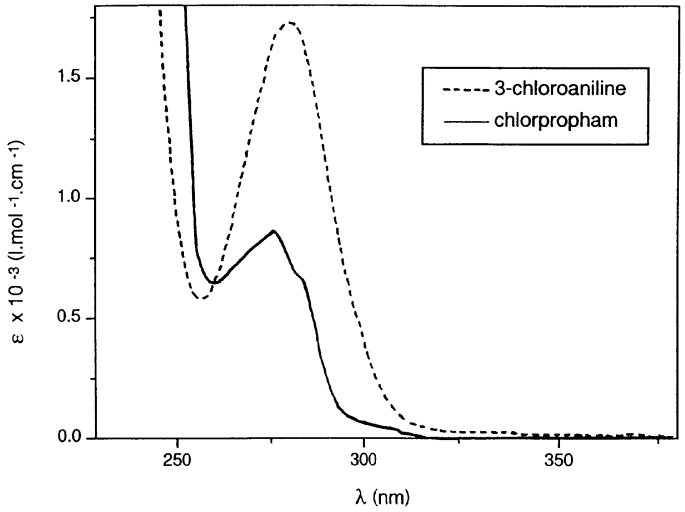


Fig. 5. UV spectrum of chlorpropham and 3-chloroaniline in aqueous solution.

the same retention time and the same fragmentation.

It was observed that the inhibition of the ultrasonic transformation of 3-chloroaniline by isopropanol (85% inhibition with isopropanol 0.1 M) is more efficient than the inhibition of chlorpropham. Thus it can be deduced that hydroxyl radicals play a major role in the degradation compared with direct pyrolysis.

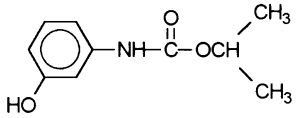
Phototransformation of chlorpropham

The UV spectrum of chlorpropham is given in Fig. 5. The maximum absorption is located at 277 nm with a molar absorption coefficient ε evaluated at $606 \pm 5\ M^{-1}\ cm^{-1}$. At 300 nm the absorption is rather low ($\varepsilon = 53.0 \pm 0.5\ M^{-1}\ cm^{-1}$), but sufficient to induce a photochemical transformation in summer sunlight. It was experimentally observed that a solution 1.7×10^{-4} M is about 80% transformed after 53 days in summer sunlight (latitude 46°N, 420 m over sea level).

Unbuffered aqueous solutions 5.7×10^{-4} M were irradiated at 254 and 270 nm. The quantum yield at 254 nm was evaluated at 0.14 ± 0.02 in both air-saturated and deoxygenated solutions, and at 0.10 ± 0.02 at 270 nm. The difference is not significant because of the error due to the sharp decrease of absorption in this range.

Three photoproducts appear on the HPLC chromatogram of a solution of chlorpropham irradiated at 254 nm (Fig. 6).

The main product (III) was extracted with ethyl ether from a solution irradiated until complete transformation. The parent peak in the mass spectrum obtained by electron impact was located at $m/z = 195$. It corresponds to a non-chlorinated compound. The main fragments correspond to $m/z = 153$ and 109. Four aromatic protons are located at δppm: 6.63 (dd); 6.99 (dd); 7.20 (s) and 7.23 (t) in the ^{1}H 400 MHz NMR spectrum in CD_3OD. The protons of isopropyl group are at 5.2 ppm (1H) and 1.5 ppm (6H). From these results the product can be identified as isopropyl 3-hydroxycarbanilate (HIPC). The fragment at $m/z = 153$ corresponds to the loss of the isopropyl group and $m/e = 109$ corresponds to aminophenol.



A few mg of this product was isolated and a solution of known concentration was used to calibrate the HPLC chromatogram. The initial yield was evaluated at more than 70%. The formation of the chloride ion was experimentally proved using a specific electrode.

A device with 6 germicide lamps was used to study the final photodegradation at 254 nm. As it appears in Fig. 7, chlorpropham is almost completely transformed after about 20 min and the main photoproduct (HIPC) after about 80 min. No organic species absorbing at 250 nm were detected in the chromatogram after 90 min.

Phototransformation of 3-chloroaniline

The formation of 3-chloroaniline was not observed in the direct photolysis of chlorpropham but it occurs in its biotransformation. So it is useful to study its photochemical behaviour. Figure 5 shows that 3-chloroaniline absorbs at longer wavelengths than chlorpropham. The maximal absorption of the neutral form is located at 286 nm with a molar absorption coefficient evaluated at $1730 \pm 15\ M^{-1}\ cm^{-1}$. The protonated form of 3-chloroaniline has only a very low absorption in the

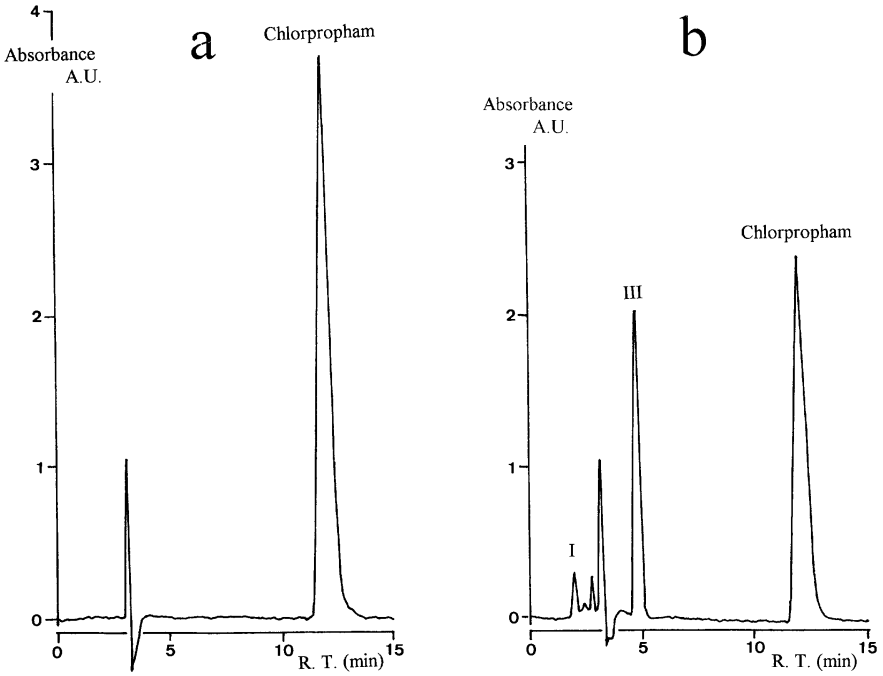


Fig. 6. HPLC chromatogram of an unbuffered air-saturated solution of chlorpropham 1.7×10^{-4} M. (a) Non-irradiated; (b) irradiated during 1 min at 254 nm (photon rate 1.6×10^{-7} Einstein s^{-1} in 10 ml, conversion 36%) eluent $MeOH/H_2O$, 68/32, detection 270 nm.

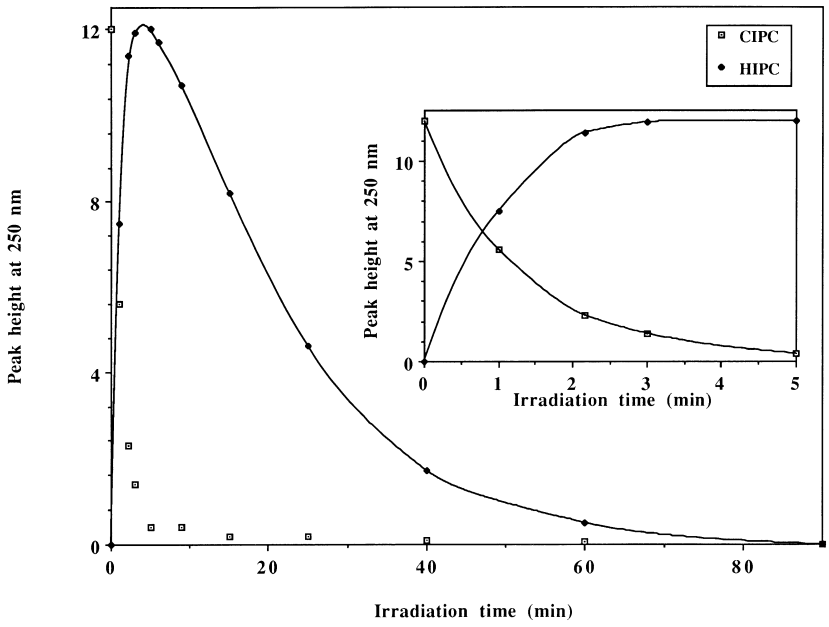


Fig. 7. Kinetics of phototransformation of a solution of chlorpropham 1.45×10^{-4} M, irradiated at 254 nm (detection at 250 nm, photon rate received in 25 ml $\approx 2 \times 10^{-6}$ Einstein s^{-1}).

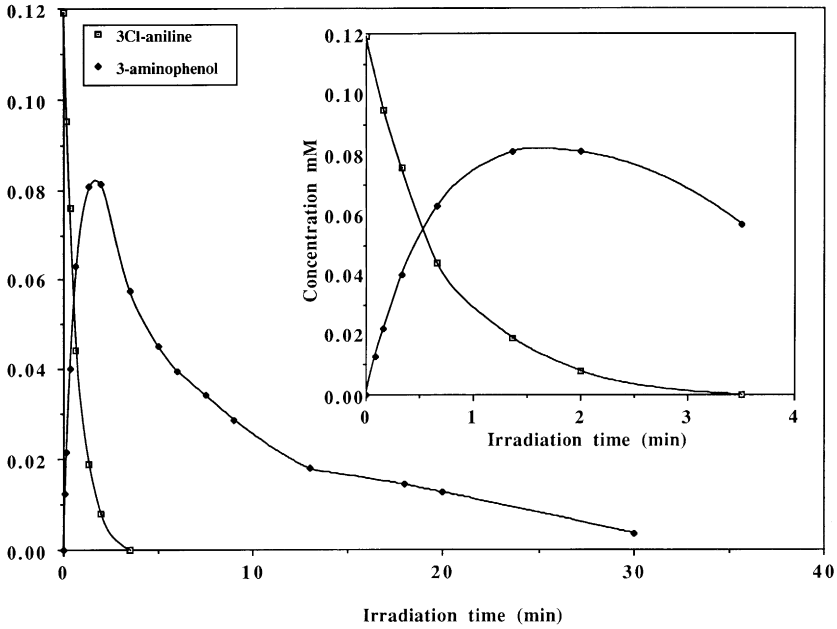


Fig. 8. Kinetics of transformation of 3-chloroaniline 1.2×10^{-4} M and formation of the main photoproducts by irradiation at 254 nm (detection at 270 nm, photon rate received in 25 ml 1.8×10^{-6} Einstein s^{-1}).

UV. It plays a minor role in environmental conditions, since the pK_a was evaluated at 3.2 by spectrophotometric measurements.

An unbuffered solution (1.1×10^{-3} M, pH = 5.5) was irradiated at 254 and 296 nm. The quantum yield was evaluated at 0.12 ± 0.02 at these two wavelengths. This value and the data about the sunlight spectrum (see, for instance, Frank and Klöpffer, 1988), make it possible to evaluate the photochemical half-life in sunlight using the relationship proposed by the European Chemical Industry Ecology and Toxicology Centre (ECETOC, 1984).

$$\tau_{1/2} = \frac{\ln 2}{2300\phi \int_{\lambda_1}^{\lambda_2} I(\lambda)\varepsilon(\lambda)\, d\lambda}$$

where $\tau_{1/2}$ is the half-life in seconds, ϕ the quantum yield, λ_1–λ_2 the absorption range (nm) and $I(\lambda)$ and $\varepsilon(\lambda)$ the incident photon rate (Einstein cm^{-2} s^{-1} nm^{-1}) and molar absorption coefficient (l mol^{-1} cm^{-1}) at wavelength λ (nm).

The half-life was evaluated at a few hours in summer and a few days in winter. Actually it was experimentally observed that in a solution of 7.2×10^{-4} M, 3-chloroaniline was 98% transformed after 8 days in summer sunlight. This calculation is not very accurate with chlorpropham which absorbs only a very low percentage of sunlight.

The main photoproduct initially formed from 3-chloroaniline was identified as 3-aminophenol by comparison of HPLC retention times and UV spectra of irradiated solution and authentic sample. The transformation was quantified by calibration of HPLC. It clearly appears in Fig. 8 that the transformation is initially almost quantitative. Resorcinol and several unidentified photoproducts are formed in a second stage of the reaction. The phototransformation of 3-aminophenol is slower and not so specific as the transformation of 3-chloroaniline. Under the conditions given in Fig. 8, i.e. 25 ml of solution of 1.2×10^{-4} M irradiated with 6 germicide lamps, 3-chloroaniline disappeared in 3 min, 3-aminophenol in 30 min and no aromatic or quinonic compound could be detected after 3 h. In sunlight irradiation (summer time) most of photoproducts absorbing at 280 nm disappeared after 40 days.

Efficiency of both processes

The devices used in the present work for the degradation of chlorpropham and 3-chloroaniline were not optimised for practical application since the aim of this study was focused on the comparison of the mechanisms involved. However, the energy efficiencies were approximately evaluated for both techniques. For complete degradation of chlorpropham in aqueous solution (0.1 mM), ultrasonic treatment needs ca. 0.4 kWh for 1 L. The photolysis of the same solution needs about 0.15 kWh for the elimination of chlorpropham, but about 9 times more energy for the transformation of aromatic products. The efficiencies of both devices could be greatly increased by designing them for applied purposes. For the sonolysis treatment: optimisation of geo-

metrical parameters of the reactor and ultrasonic frequency; for photochemical treatment: insertion of the lamp into the contaminated solution to minimise photonic losses.

DISCUSSION AND MECHANISMS

Ultrasonic transformation

Two mechanisms are involved in the ultrasonic transformation of chlorpropham and 3-chloroaniline. With chlorpropham, the initial formation of CO_2 is too high to result only from the cleavage of carbamate function. Moreover, the transformation is partly inhibited by isopropanol. With 3-chloroaniline, the efficiency of the inhibition is higher than with chlorpropham and CO_2 formed appears as a secondary sonoproduct.

The first mechanism involves hydroxyl radicals formed by sonolysis of water. It is inhibited by alcohols and it explains the formation of hydroxylated compounds as primary products and the formation of CO_2 in the last stage of the reaction. Both compounds are concerned by this oxidative pathway which leads to the complete mineralisation in many steps. The final one is the oxidation of formic acid according to the following reactions:

$$HCOOH + {}^{\bullet}OH \rightarrow HCOO^{\bullet} + H_2O$$

($k = 1.3 \cdot 10^8\ mol^{-1}\ l$) (Buxton *et al.*, 1988),

$$HCOO^{\bullet} + {}^{\bullet}OH \rightarrow CO_2 + H_2O \text{ (minor pathway)}$$

$$\text{or } HCOO^{\bullet}; + O_2 \rightarrow CO_2 + HO_2^{\bullet}$$

But oxidation by hydroxyl radicals does not explain the initial formation of CO_2 (see Fig. 2).

The second mechanism which provides CO_2 as a primary product is most likely a thermal degradation. Actually it was shown that chlorpropham was degraded into 3-chlorophenyl–isocyanate and isopropanol at 250°C (Somda, 1986). It was observed that in aqueous solution 3-chlorophenylisocyanate is completely hydrolysed into 3-chloroaniline and CO_2. The following mechanism is proposed:

The amount of isopropanol formed is too low ($\leq 10^{-4}$ M) to significantly inhibit the degradation.

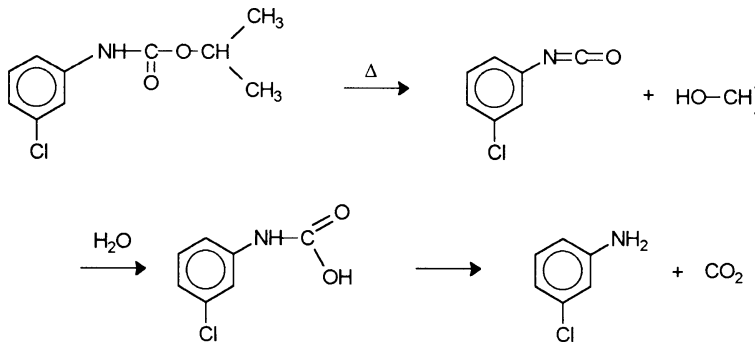
A similar mechanism has been suggested for the transformation of other carbamates, particularly on TiO_2 (Pramauro *et al.*, 1993) and bentonite (Sabadie and Coste, 1985). The thermal degradation could be attributed to the local increase of temperature resulting from the implosion of the cavitation bubble. This means that some molecules of chlorpropham are surrounding the cavitation bubbles in a layer of 250 nm thickness (Suslick and Hammerton, 1986). This bubble jacket can be considered as an intermediate region where temperature goes down from several thousand degrees Kelvin to the ambient liquid temperature.

Comparing Figs 2 and 4 it can be noticed that the disappearance is slower with 3-chloroaniline than with chlorpropham. This phenomenon is attributed to a higher thermal stability of 3-chloroaniline. It was also observed that the inhibiting effect of alcohols is more significant with 3-chloroaniline than with chlorpropham. Thus the oxidation by hydroxyl radicals plays a more important role with 3-chloroaniline. Moreover, the thermal degradation into CO_2 is much lower with 3-chloroaniline than with chlorpropham. In both cases, the minor formation of carbon monoxide can be attributed either to the thermal degradation of formic acid (Tsang and Lifohitz, 1990) or to a possible reduction of CO_2 (Henglein, 1985).

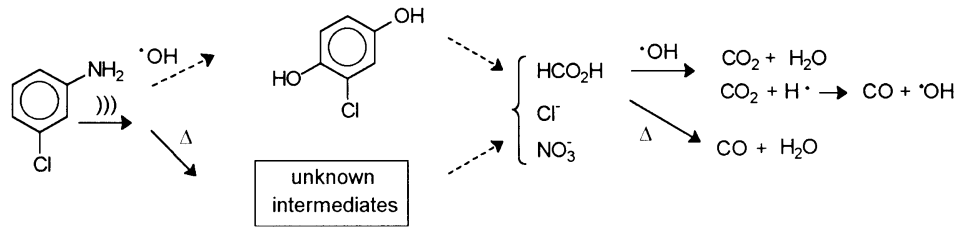
$$HCOOH \longrightarrow CO + H_2O$$

$$CO_2 + H \longrightarrow CO + OH$$

The following mechanism is proposed for the



ultrasonic degradation of 3-chloroaniline:



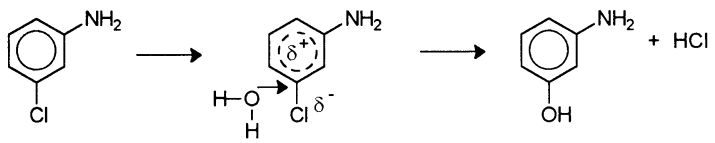
The influence of ultrasonic frequency on the efficiency of chlorpropham and 3-chloroaniline degradation may be mainly related to the $^{\cdot}OH$ production. Actually it was reported that the formation of $^{\cdot}OH$ is more efficient at 482 kHz than at 20 kHz (Petrier *et al.*, 1992a). At high frequency the collapse of microbubbles is too fast to allow the recombination:

$$H^{\bullet} + {}^{\bullet}OH \longrightarrow H_2O$$

so diffusion of radicals in the bulk is favoured.

Phototransformation

The transformation of 3-chloroaniline into 3-aminophenol is very specific and does not depend on the presence of oxygen. Such a behaviour was previously observed with 3-chlorophenol (Boule *et al.*, 1982) and chlorobenzene (Boule *et al.*, 1985). The reaction cannot result from a radical mechanism since the formation of 3-aminophenol is formed in the absence of oxygen. Moreover, oxidation products resulting from the oxidation by oxygen or chlorine atom should be expected. As it was suggested for chlorobenzene and 3-chlorophenol the reaction is explained by a heterolytic scission of the C–Cl bond, concerted or not with hydrolysis:



A similar mechanism can be applied to the transformation of 3-aminophenol into resorcinol and to the transformation of chlorpropham into the hydroxylated product (HIPC).

The photolysis involves the transformation of organic chlorine into hydrochloric acid which leads to a decrease of pH. Consequently, in unbuffered solutions, the protonation of 3-chloroaniline involves a decrease in the fraction of absorbed radiation specially at $\lambda \geq 275$ nm, but this effect is not significant in dilute solution (concentration around 10^{-4} M). Chlorinated substrates disappear in a few minutes when solutions are irradiated with the device equipped with 6 germicide lamps. Photoproducts are transformed more slowly, but after a few hours no quinonic or aromatic derivatives remain.

CONCLUSIONS

Ultrasound and light can transform chlorpropham and 3-chloroaniline, but the intermediates are different.

The ultrasonic degradation is more efficient at 482 kHz than at 20 kHz for both compounds. With chlorpropham, intermediates are hydroxylated products and 3-chloroaniline. Two pathways are involved, the oxidation by $^{\cdot}OH$ and pyrolysis near the cavitation bubbles. 3-chloroaniline, which is a toxic intermediate, does not accumulate and is mineralised.

Ultrasonic treatment at 482 kHz appears to be an efficient method for the elimination of both compounds.

Photolysis is initially more specific. The main initial reaction is a photohydrolysis of the C–Cl bond leading to hydroxylated products. This reaction is quantitative with 3-chloroaniline in the first stage of the transformation. With chlorpropham some unidentified minor by-products are also formed.

Irradiation at 254 nm can be used to eliminate 3-chloroaniline and chlorpropham from water. In the first stage hydroxylated products are rapidly formed. They may be more oxidable or biodegradable than the starting material. For example 3-aminophenol is easily oxidised in basic solution. In

both cases aromatic or quinonic intermediate photoproducts can be completely photodegradated in a few hours.

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