

## Photocatalytic degradation of chlorobenzoic isomers in aqueous suspensions of neat and modified titania

Halima Tahiri<sup>a,b</sup>, Yahia Ait Ichou<sup>b</sup>, Jean-Marie Herrmann<sup>a,\*</sup>

<sup>a</sup> *Laboratoire de Photocatalyse, Catalyse et Environnement (CNRS), Ecole Centrale de Lyon, B.P. 163, 69131 Ecully-cedex, France*

<sup>b</sup> *Laboratoire de Chimie-Physique, Université Ibnou Zohr, Agadir, Morocco*

Received 15 December 1997; accepted 27 January 1998

### Abstract

The three isomers of chlorobenzoic acid (CBA) have been degraded using photocatalysis. The three pollutants disappeared from water in the following order: 3-CBA < 2-CBA < 4-CBA, the para position being the most reactive. The zeroth kinetic order was interpreted by a Langmuir–Hinshelwood mechanism involving a saturation of the adsorption sites. The chemisorption of CBA molecules involves the carboxylic group linked to the surface with the aromatic ring possibly oriented perpendicularly to the surface. The initial step of CBA disappearance was the decarboxylation of the molecule (photo-Kolbe reaction) with an initial rate of CO<sub>2</sub> formation equal to that of the disappearance of CBA. The mass balance could be established for all the final products. All the intermediate products found correspond to successive hydroxylations of the corresponding chlorophenol obtained after the initial photo-Kolbe reaction. They all disappeared within less than 2 h of UV irradiation. In 2-CBA degradation, a transient condensation product (4'-chloro,3,4-dihydroxy-(1,1')biphenyl) could be identified before its degradation. Modification of titania by doping with Cr<sup>3+</sup> ions or by depositing 1 wt.% Pt was detrimental for the activity, the best catalyst remaining neat titania. The present study illustrates the difference in the kinetics of photodegradation of various isomers for one compound. © 1998 Elsevier Science S.A. All rights reserved.

**Keywords:** Photocatalytic degradation; Chlorobenzoic isomers; Decarboxylation; Titania

### 1. Introduction

Among the new oxidation methods under development denoted advanced oxidation processes (AOP), heterogeneous photocatalysis appears as an emerging nonbiological technology for destroying and totally mineralizing most organic pollutants [1–6]. A general list of various families of organic pollutants which can be treated by photocatalysis has been given in Ref. [7]. In our laboratory, various types of contaminants were studied. The different isomers of mono-, di- and trichlorophenols were totally converted into CO<sub>2</sub> and Cl<sup>-</sup> with illuminated suspensions of titania [8–10]. Nitrogen-containing compounds such as benzamide and nitrobenzene were converted into CO<sub>2</sub> and mainly NO<sub>3</sub><sup>-</sup> or NH<sub>4</sub><sup>+</sup> depending on the initial oxidation state of nitrogen [11–13]. Other aromatic pollutants containing other heteroatoms such as oxygen in dimethoxybenzene [14] or sulfur and phosphorus in pesticides [15,16] have been also

successfully mineralized into innocuous products (CO<sub>2</sub>, H<sub>2</sub>PO<sub>4</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup>).

Among the numerous water pollutants, which can be treated by heterogeneous photocatalysis, organic acids constitute an important group. The photo-assisted degradation of various organic acid molecules has been reported. They were either aliphatic, such as formic acid [17,18], acetic acid [19–22], propionic and butyric acids [21,22], polychloroacetic acids [22–25], oxalic acid [26], or aromatic such as benzoic acid [27–30] and its mono- and polysubstituted derivatives [27,28] such as salicylic [28,31–33] and chlorosalicylic acids [34]. More complex chlorinated aromatic acids could be mineralized in TiO<sub>2</sub> aqueous suspensions. They were 2,4-D (2,4-dichlorophenoxyacetic acid) [35] and 2,4,5-T (trichlorophenoxyacetic acid) [36], both compounds being known as herbicides.

After preliminary results on 2-chlorobenzoic acid [37], we report in the present paper the photocatalytic decomposition of the three isomers of chlorobenzoic acid (CBA) in relation with the nature and the position of both substituents on the aromatic ring and with the attempt of identifying the maximum of the intermediates formed.

\* Corresponding author. Tel.: +33-4-72-18-64-93; fax: +33-4-78-33-03-37; e-mail: herrmann@cc.ec-lyon.fr

## 2. Experimental

### 2.1. Materials

The chlorobenzoic isomers and the commercial intermediates of degradation mentioned hereafter were purchased from Aldrich (purity better than 99%) and were used as received. The photocatalyst was TiO<sub>2</sub> Degussa P-25, mainly anatase, nonporous with a specific area of 50 m<sup>2</sup> g<sup>-1</sup>, corresponding to a mean particle size of 30 nm.

### 2.2. Photoreactor

The reaction was carried out in water at room temperature in a static batch photoreactor of ca. 100 cm<sup>3</sup>, consisting of a Pyrex cylindrical flask, open to air, with a bottom optical window whose surface was approximately 11 cm<sup>2</sup>. UV light was delivered by a high-pressure mercury lamp (Philips HPK, 125 W) and filtered by a circulating-water cuvette (thickness 2.2 cm) and a 340 nm cut-off filter (Corning 0-52), except when otherwise indicated, to avoid a possible photolysis of CBA. The radiant flux was measured with a power meter (UDT, model 21 A) calibrated against a microcalorimeter. At the suspension level, it was ca. 50 mW cm<sup>-2</sup>. The corresponding number of photons per second potentially absorbable by TiO<sub>2</sub> was about 1.6 × 10<sup>17</sup>. It was calculated as indicated in Refs. [9,10]. In these calculations, no allowance was made for the light scattered by the photocatalyst particles.

### 2.3. Initial conditions

The volume of the aqueous solution introduced into the photoreactor was 20 cm<sup>3</sup> and the mass of catalyst was 70 mg. This mass corresponds to a total absorption of light by the suspended catalytic bed. The initial concentrations of CBA isomers were either 50 or 80 mg l<sup>-1</sup> (50 or 80 ppm). Before each photocatalytic test, the suspension was magnetically stirred for 40 min to reach the adsorption equilibrium in the dark prior to illumination.

### 2.4. Analyses

Centrifugation or millipore discs (0.45 μm) were used to separate titania before analysis of the solution. The organics (CBA and aromatic intermediates) were analysed by high-performance liquid chromatography (HPLC) using a UV detector at fixed wavelengths and a photodiode array detector. A good separation of the products was achieved within 25 min with the following eluent: 40% methanol/60% water buffered by acetic acid. Some of the intermediates were also identified by gas chromatography/mass spectrometry (GC/MS) after extracting the aqueous solutions with proper solvents. Chloride ions were analyzed by HPLC with a conductivity detector. The kinetics of the evolution of CO<sub>2</sub> formed was followed with a gas chromatograph connected to the

closed photoreactor whose gas phase was periodically renewed with fresh oxygen (or air).

## 3. Results and discussion

Experiments were made with cut-off filters at 290 and 340 nm for the three CBA isomers. The reaction rates were roughly in the same ratios as those of the numbers of efficient photons absorbable by TiO<sub>2</sub>. In the absence of TiO<sub>2</sub>, only negligible conversions were obtained at 340 nm. This indicates that the system is working in a pure photocatalytic regime.

### 3.1. Photocatalytic degradation of 2-CBA

The results are presented in Fig. 1 with normalized concentrations (initial concentration of 2-CBA: 80 ppm (or mg l<sup>-1</sup>), i.e., 5.11 × 10<sup>-4</sup> mol l<sup>-1</sup>). The concentration of 2-CBA decreases at first linearly with time during a period corresponding to a conversion of ca. 80%. 2-CBA practically disappears after 2 h of illumination and a prolonged irradiation leads to non detectable traces, which means that residual concentration of 2-CBA is smaller than a fraction of a ppm.

As shown in Fig. 1, Cl<sup>-</sup> ions are progressively released in the solution. The final amount is reached within 2 h and is equal to 90% of the value expected from the stoichiometry of a total decomposition. This discrepancy is not due to the existence of some chloro-organics refractory to decomposition since (i) all the intermediates identified disappear within approximately 2 h (see further) and (ii) the final carbon balance indicates a 100% conversion into CO<sub>2</sub> (see Fig. 1). The 10% difference in Cl<sup>-</sup> balance has to be rather ascribed to a partial adsorption of Cl<sup>-</sup> onto TiO<sub>2</sub>.

The kinetics of CO<sub>2</sub> evolution (Fig. 1) indicates that the final level is reached within 5 h under the conditions chosen and corresponds to the total mineralization of 2-CBA according to the equation:

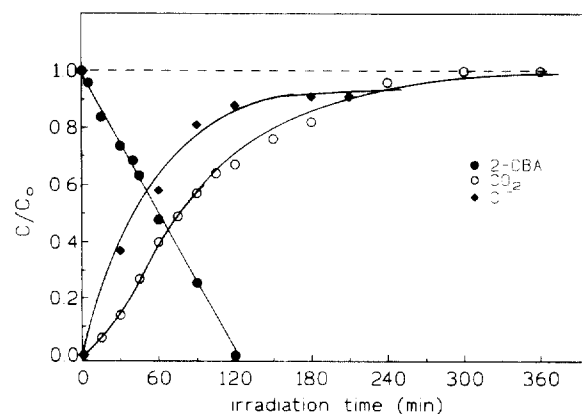
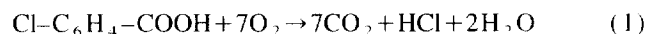


Fig. 1. Kinetics of 2-CBA disappearance and total mineralization.

The stoichiometry of Eq. (1) was checked by establishing the carbon balance with three different initial concentrations of 2-CBA (20, 50 and 80 ppm). The period of time necessary to reach the total mineralization is thus ca. 2.5 times longer than that necessary to eliminate 2-CBA and to reach the maximum of chloride formation. For a potential application, one will have to consider the stage where the treatment has to be stopped as a function of the cost and of the regulations.

2-CBA decreases with an apparent zero kinetic order with respect to time for conversions reaching 80%. This zeroth kinetic order can be accounted for by an adsorption with saturation of the corresponding adsorption sites. Assuming a Langmuir–Hinshelwood kinetic model, the reaction rate  $r$  is proportional to the coverage  $\theta$

$$r = \frac{-d[2\text{-CBA}]}{dt} = k\theta = kKC/(1+KC) \quad (2)$$

where  $k$  is the true rate constant of 2-CBA disappearance and  $K$  is the adsorption constant of 2-CBA on  $\text{TiO}_2$  in aqueous suspension. At saturation, unity is negligible with respect to  $KC$  in the denominator of Eq. (2), which becomes:

$$r = \frac{-d[2\text{-CBA}]}{dt} = kKC/(1+KC) \approx k \quad (3)$$

After integration, one gets:

$$C = C_0 - kt \quad (4)$$

The model of adsorption at saturation is in line with the important fraction of adsorbed molecules in the dark prior to illumination: the nominal concentration  $C_0$  decreased from 80 ppm to 60 ppm, which corresponded to a coverage of 0.42 molecule adsorbed per  $\text{nm}^2$ . This behaviour is different from that of other compounds such as chlorophenols [8], benzamide or nitrobenzene [11–13]. It can be accounted for by a strong adsorption at the surface of titania with the carboxylic group linked to the surface in interaction with the hydroxyl sites of titania. The aromatic ring is probably oriented perpendicularly to the surface, as already proposed for the adsorption of benzoic and terephthalic acids at the surface of alumina [38].

### 3.2. Comparison of the degradation of the three isomers

In Fig. 2 are given the kinetics of CBA disappearance with a nominal initial concentration  $C_0$  of 80 ppm ( $5.11 \times 10^{-4} \text{ mol l}^{-1}$ ) except for 4-CBA ( $C_0 = 65 \text{ ppm}$  or  $4.15 \times 10^{-4} \text{ mol l}^{-1}$ ) because of its poor solubility in water. For a better comparison between acids, another experiment was carried out with  $C_0$  equal to 50 ppm for all the three compounds (Fig. 3). It can be observed that all the reactants exhibit a zero kinetic order according to Eq. (3) from which a true rate constant  $k$  could be determined. The values indicated in Table 1 clearly demonstrate that, as expected, they are independent of the initial concentration. This confirms the true kinetic character of this rate constant. Additionally, they provide a good classification of the reactivity of the three isomers.

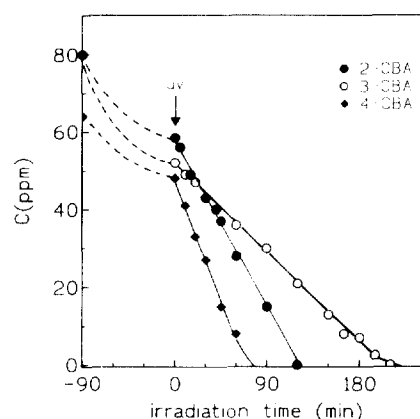


Fig. 2. Kinetics of CBA isomer disappearance at  $C_0 = 80 \text{ ppm}$  except for 4-CBA ( $C_0 = 65 \text{ ppm}$ ) for solubility reasons.

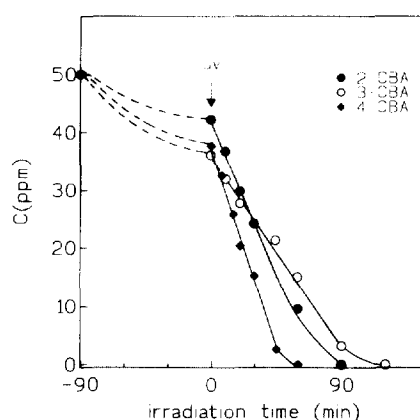


Fig. 3. Kinetics of CBA isomer disappearance at  $C_0 = 50 \text{ ppm}$ .

### CBA > 2-CBA > 3-CBA

The same reactivity order was found for the total mineralization followed by  $\text{CO}_2$  evolution. The effect of Cl-substitution on the reactivity will be discussed further in Section 3.5 (Reaction mechanism).

### 3.3. Identification of the intermediates

No aromatic acids could be detected during the photo-degradation of the three CBA isomers. In particular no hydroxybenzoic acids, such as salicylic acid in the case of

Table 1  
Rate constants (in  $\text{ppm h}^{-1}$  and in  $\mu\text{mol h}^{-1}$ ) of CBA disappearance at two different initial concentrations ( $C_0 = 50$  and  $80 \text{ ppm}$ )

Acid	$C_0 = 50 \text{ ppm}$		$C_0 = 80 \text{ ppm}$	
	$k$ ( $\text{ppm h}^{-1}$ )	$k$ ( $\mu\text{mol h}^{-1}$ )	$k$ ( $\text{ppm h}^{-1}$ )	$k$ ( $\mu\text{mol h}^{-1}$ )
2-CBA	32	4.1	29	3.7
3-CBA	18.7	2.4	15.2	1.95
4-CBA	41.5	5.3	43.2*	5.5*

\*Values obtained for (4-CBA) = 65 ppm instead of 80 ppm because of solubility limit.

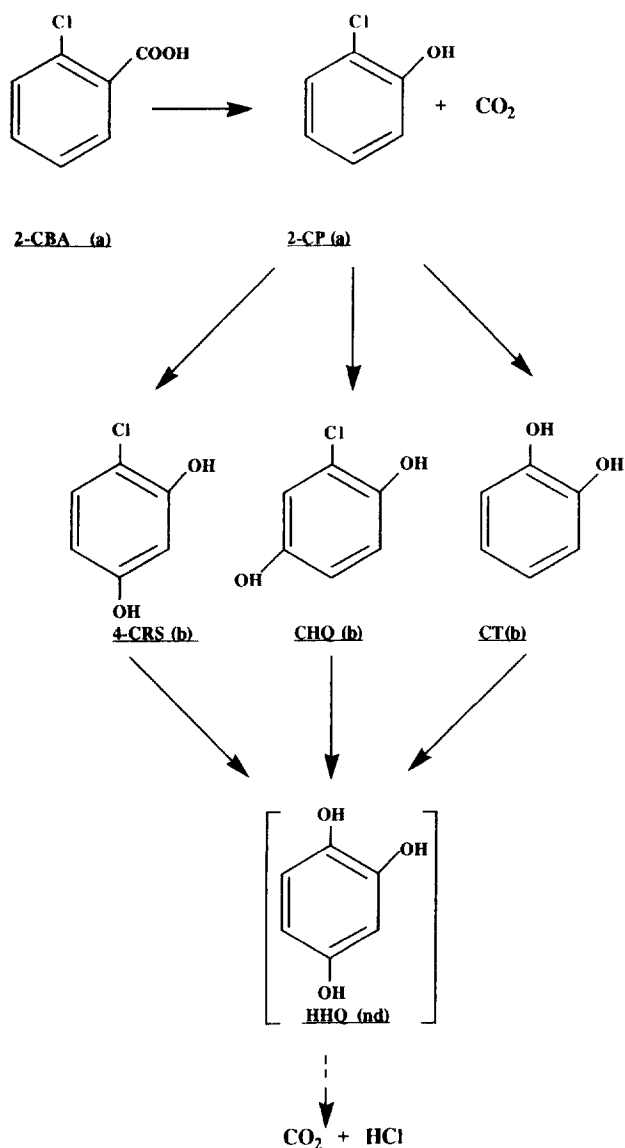


Fig. 4. Degradation pathway of 2-CBA. (a) Detected by HPLC and GC/MS; (b) detected by HPLC; (nd) not detected.

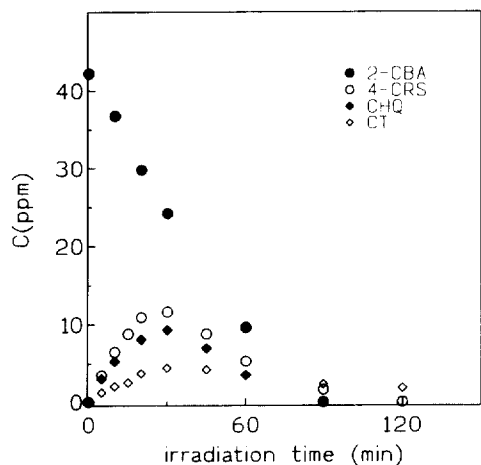


Fig. 5. Kinetics of appearance and of disappearance of intermediate products in 2-CBA degradation.

2-CBA, were found. This behavior is different from that of benzoic acid [29,30]. The presence of a chlorine substituent would contribute to favour the decarboxylation instead of the hydroxylation of the aromatic ring. This behaviour is in agreement with the easy initial decarboxylation (photo-Kolbe reaction) which readily happens in the case of aliphatic acids over UV-illuminated TiO<sub>2</sub> [17,18,20,24]. The easy decarboxylation reaction on titania was previously demonstrated by Sakata et al. [21] who studied the dehydrogenation of lactic acid (CH<sub>3</sub>-CHOH-COOH) comparatively on Pt/CdS and on Pt/TiO<sub>2</sub>: whereas Pt/CdS produced pyruvic acid (CH<sub>3</sub>-CO-COOH) plus H<sub>2</sub>, titania-deposited Pt catalysts induced a photodecarboxylation with the formation of CO<sub>2</sub>, acetaldehyde and H<sub>2</sub>.

The primary intermediates of photocatalytic degradation of 2-CBA were detected by HPLC and/or by GC/MS. They correspond to successive hydroxylations of the aromatic ring, either at C-H or at C-Cl bond levels, and they are respectively

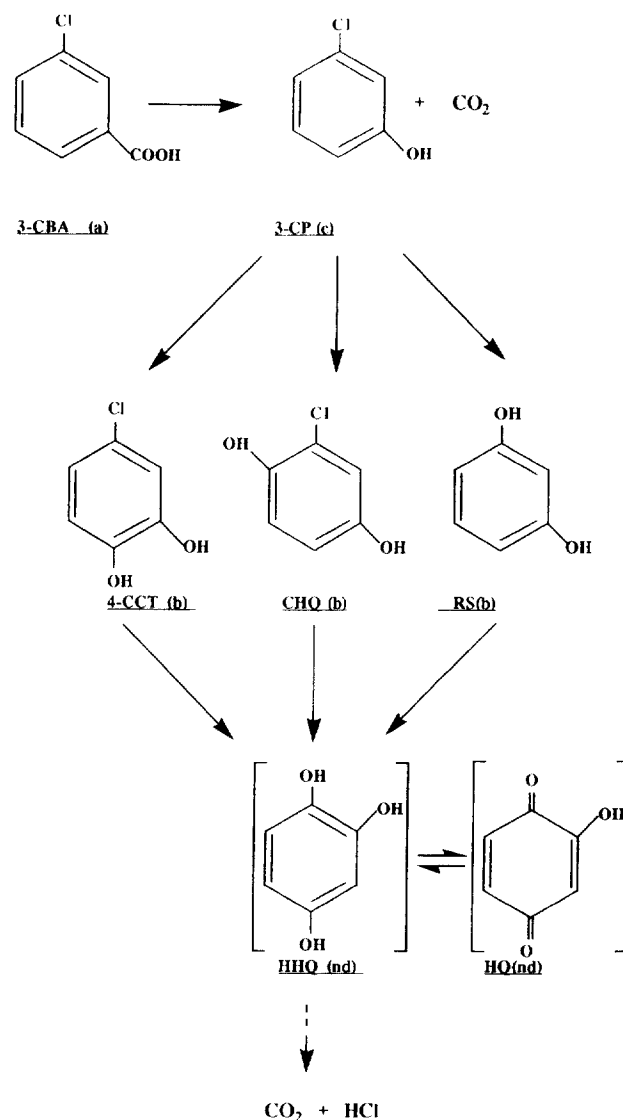


Fig. 6. Degradation pathway of 3-CBA. (a) Detected by HPLC and GC/MS; (b) detected by HPLC; (nd) not detected.

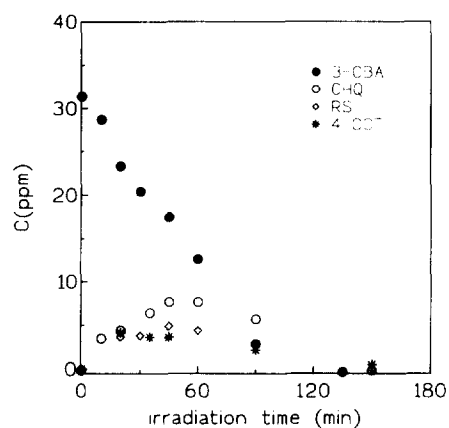


Fig. 7. Kinetics of appearance and of disappearance of intermediate products in 3-CBA degradation.

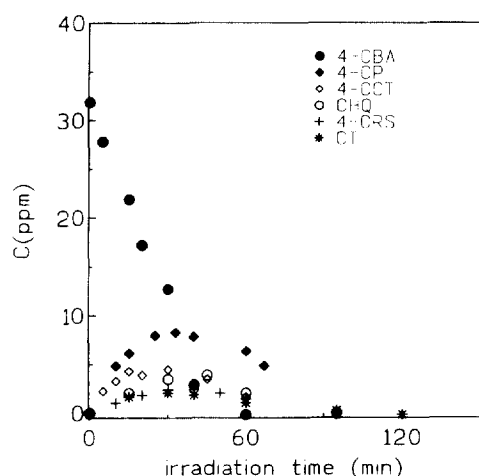


Fig. 8. Kinetics of appearance and of disappearance of intermediate products in 4-CBA degradation.

2-chlorophenol (2-CP), 4-chlororesorcinol (4-CPS), chlorohydroquinone (CHQ) and catechol (CT). From these intermediates, a degradation pathway of 2-CBA is presented in Fig. 4, whereas the kinetics of their appearance and disappearance in the aqueous phase is given in Fig. 5.

For 3-CBA, the first intermediate identified by HPLC and GC/MS was 3-chlorophenol (3-CP) which corresponds to a decarboxylation and a subsequent hydroxylation at the same site of the molecule. 3-CP produced 4-chlorocatechol (4-CCT) and chlorohydroquinone (CHQ) in agreement with previous results obtained in the laboratory [8]. However, hydroxyhydroquinone (HHQ) and hydroxyquinone (HQ) could not be presently detected, probably because of too low concentrations released in the aqueous phase. However, they constitute logical subsequent intermediates. The reaction pathway of 3-CBA degradation is given in Fig. 6, whereas the kinetics of (RS), (CHQ) and (4-CCT) evolution are presented in Fig. 7.

4-CBA degradation produced mainly 4-chlorophenol (4-CP), 4-chlorocatechol (4-CCT) and 4-chlororesorcinol (4-CRS), whose kinetics of evolution are given in Fig. 8. The first intermediate seems to be (4-CP) resulting from an

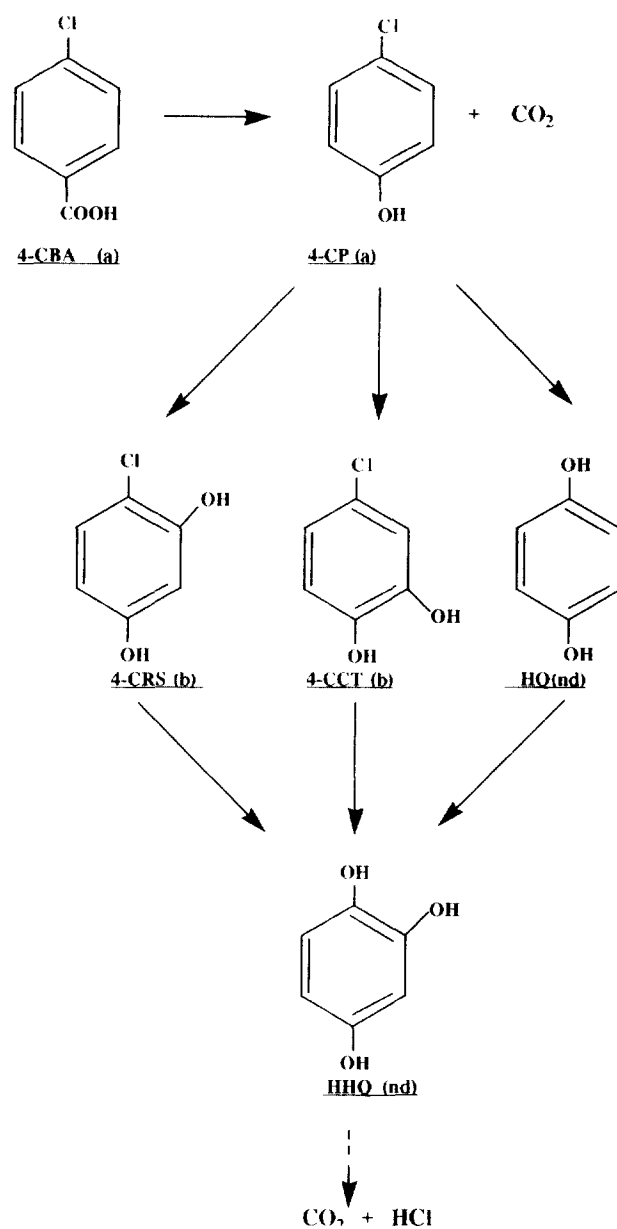


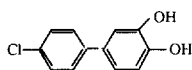
Fig. 9. Degradation pathway of 4-CBA. (a) Detected by HPLC and GC/MS; (b) detected by HPLC; (nd) not detected.

initial decarboxylation of 4-CBA. The other two products, 4-CCT and 4-CRS, result from the degradation of 4-CP in agreement with previous results [9]. However no hydroquinone was detected. A possible reaction pathway is presented in Fig. 9.

### 3.3.1. Identification of a condensation product

Because of the presence of substituted aromatic compounds, condensation products may be produced. Such condensation products have been tentatively detected and identified by GC/MS in the case of 3- and 4-CBA photocatalytic degradation. After centrifugation of the suspension, the solution was acidified by HCl and extracted in  $\text{CH}_2\text{Cl}_2$  for 10 min. The organic phase was then concentrated in a

rotavapor before injection in the GC/MS. According to the mass spectra at  $m/z = 220.5$ , the only condensation product seen by chromatography could correspond either to a chlorophenoxyphenol or to a chlorodi-hydroxybiphenyl isomer. By comparison of the various fragment peaks of various commercial authentic products, the presence of a substituted biphenyl ether could be rejected as well as the 2'-chloro,2,5-dihydroxy-(1,1')biphenyl isomer. By comparison with spectra in the library, the most probable condensation product was estimated to be the 4'-chloro,3,4-dihydroxy-(1,1') biphenyl



### 3.4. Influence of various factors on the photocatalytic activity

#### 3.4.1. Influence of the modification of titania

Pure titania, (mainly anatase), was structurally modified by two ways: either by ion doping or by metal deposition. In the first case, 0.86 at %  $\text{Cr}^{3+}$  ions were dissolved into the lattice of titania during the preparation in a flame reactor. In the second case, 1 wt% platinum was deposited on  $\text{TiO}_2$  using the method indicated in Ref. [39] (incipient wetness impregnation, followed by drying and reduction by hydrogen at  $400^\circ\text{C}$ ). The results are presented in Table 2.

The deposit of 1% Pt decreases the activity by a factor of 2.5. This decrease in activity is in agreement with an electron transfer from the support to the metal which is detrimental to oxygen ionsorption  $\text{O}_2^-$  species of titania. Since metal particles are negatively charged, they attract photoinduced positive holes and act as recombination centers [40].

Similarly, chromium doping decreases titania's activity but by a higher factor  $R$  of ca. 42, which is close to other inhibition factors found for gas-phase propene oxidation ( $R = 50$ ) (Ref. [41]), liquid-phase 2-propanol oxidation ( $R = 25$ ) (Ref. [42]) or cyclohexane ( $R = 21$ ) (Ref. [40]) and aqueous-phase oxalic acid oxidation ( $R = 85$ ) (Ref. [43]). In that case, trivalent substitutional  $\text{Cr}^{3+}$  ions behave as acceptor centers, evidenced by photoconductivity measurements [42] and which, once filled, attract positive holes and produce electron-hole recombination. As a consequence, the best cat-

alyst remains pure titania without any additives, as observed for 4-chlorophenol degradation [9].

#### 3.4.2. Influence of the light flux. Quantum efficiency

The light flux  $\Phi_0$ , equal to  $43 \text{ mW cm}^{-2}$  was attenuated with calibrated grids whose transmittance is independent of the wavelength. It was observed that below a relative flux value  $\Phi/\Phi_0$  equal to ca. 0.5, the rate of 2-CBA disappearance varied proportionally to the radiant flux, whereas above this value, the reaction rate varied as the square root of the radiant flux. According to Ref. [44], the first linear part indicates that most of incident photons are efficiently converted into active species, whereas the square root region signifies that electron-hole recombination becomes predominant. This behavior, already observed for other oxidation reactions [9,40], indicates that for a certain photocatalytic system the reaction rate cannot be linearly increased above an optimum value of the radiant flux.

To determine the quantum efficiency, defined as the ratio of the number of converted molecules per unit of time to the number of efficient incident photons reaching the surface during the same time unit, several parameters were taken into account: the spectral distribution and the nominal power of the lamp as provided by the manufacturer, the transmission of the optical filter (Corning 0.52), the total incident radiant flux measured with a radiometer detector, the response of this detector and the absorption of  $\text{TiO}_2$  at each wavelength of the mercury lines of the lamp. The amount of semiconductor was such that the absorption of the radiant flux was maximal. Two values of the initial quantum yield of 2-CBA disappearance were obtained, in the low range of radiant flux ( $\leq 20 \text{ mW cm}^{-2}$ ) and in the high one. They were respectively equal to 0.013 and 0.006. Simultaneously, the initial quantum yield obtained for  $\text{CO}_2$  production was equal to ca. 0.01. All these values are in agreement with those obtained for the different isomers of chlorophenol [8,9]. It has to be noted that the high initial quantum yield of  $\text{CO}_2$  which is close to that of 2-CBA disappearance, is in agreement with an initial decarboxylation of the molecule (photo-Kolbe reaction).

### 3.5. Reaction mechanism

According to the various results concerning (i) the kinetics of the reaction, (ii) the influence of the various parameters and (iii) the identification of various intermediates, the following reaction mechanism can be proposed.

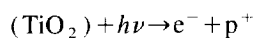
(1) Adsorption of CBA isomers with a saturation of the adsorption sites in agreement with a high density of adsorbed molecules and an initial zero kinetic order. The carboxylic group is in ionic interaction with the OH groups of titania as indicated by the influence of the pH. This interaction would induce a preferential orientation of the molecule with the plane of the aromatic ring perpendicular to the surface as proposed by Ogawa [38].

(2) Absorption of efficient photons ( $\lambda < 400 \text{ nm}$ ) and creation of electrons and holes:

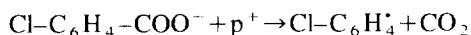
Table 2  
Comparison of the photocatalytic activities of neat and modified  $\text{TiO}_2^a$

Catalyst	Initial rate of formation of $\text{CO}_2$ (mol/h)
$\text{TiO}_2$ Degussa P.25	8.5
1 wt.% Pt/ $\text{TiO}_2$	3.4
0.86 at.% $\text{Cr}^{3+}$ - $\text{TiO}_2$	0.2

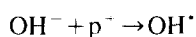
<sup>a</sup>Modification with a deposit of 1 wt.% Pt or with chromium doping.



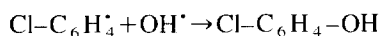
(3) Reaction of the photoholes with the carboxylate ions:



(4) Simultaneous reaction of the photoholes with the surface hydroxyl groups of titania:



(5) Radical recombination with the formation of the corresponding chlorophenol:



(6) Subsequent hydroxylation of chlorophenols by the  $\text{OH}^\cdot$  radicals. The hydroxylated intermediates are given in Figs. 4, 6 and 9. They correspond to those previously observed [8,9]. The  $\text{OH}^-$  groups of titania are spontaneously renewed by dissociatively chemisorbed water.

The reactivity pattern in the initial photo-Kolbe reaction has to be ascribed to the effect of Cl-substitution. Using Ingold's approach, induction and mesomeric effects are important in substituted benzoic acids. The last consideration is due to Cl p-orbitals interacting with  $\pi$ -orbitals of the ring. They introduce a second electronic charge redistribution in the ring independent of the withdrawing effect on the ring electrons due to the high electronegativity of the Cl atom. Mesomeric structures are favorable to a higher electronic distribution in ortho- and para-positions. This is in agreement with a higher reactivity of the negatively charged carboxylic groups with positive holes  $p^+$ . The Hammett constants ( $\sigma=0.373$  for 3-CBA and 0.227 for 4-CBA) indicate that 4-CBA is more acidic than 3-CBA and will react more easily with a positive hole, in agreement with the reactivity pattern observed.

#### 4. Conclusions

The three isomers of chlorobenzoic acid were easily destroyed. Total mineralization could be achieved for all of them, but with different reaction times depending of their nature. The aromatic intermediate products detected progressively disappeared during illumination, indicating that this method does not generate stable byproducts that could be more toxic than the initial pollutant. This study confirms the potentialities of heterogeneous photocatalysis to decontaminate waste waters containing aromatic pollutants, particularly chlorinated ones, which are often toxic for bacteria in biological treatments.

#### Acknowledgements

The authors thank Dr. P. Pichat for valuable discussions.

#### References

- [1] M. Schiavello (Ed.), Photocatalysis and Environment. Trends and Applications, Kluwer Acad. Publ., Dordrecht, 1988.
- [2] N. Serpone, E. Pelizzetti (Eds.), Photocatalysis. Fundamentals and Applications, Wiley Interscience, New York, 1989.
- [3] H.A. Al-Ekabi, D. Ollis (Eds.), Photocatalytic Purification and Treatment of Water and Air, Elsevier, Amsterdam, 1993.
- [4] O. Legrini, E. Oliveros, A. Braun, Chem. Rev. 93 (1993) 671.
- [5] D.W. Bahnemann, J. Cunningham, M.A. Fox, E. Pelizzetti, P. Pichat, N. Serpone, in: R.G. Zepp, G.R. Helz, D.G. Crosby (Eds.), Aquatic Surface Photochemistry, F.L. Lewis Publishers, Boca Raton, 1994, p. 261.
- [6] C. Guillard, J.M. Herrmann, P. Pichat, Catal. Today 17 (1993) 7.
- [7] D.M. Blake, Bibliography of Work on Photocatalytic Removal of Hazardous Compounds from Water and Air, NREL/TP-430-22197, National Renewable Energy Laboratory, Golden, 1997.
- [8] J.C. D'Oliveira, G.H. Al-Sayyed, P. Pichat, Environ. Sci. Technol. 24 (1990) 990.
- [9] G.H. Al-Sayyed, J.C. D'Oliveira, P. Pichat, J. Photochem. Photobiol. A: Chem. 58 (1991) 99.
- [10] J.C. D'Oliveira, C. Minero, E. Pelizzetti, P. Pichat, J. Photochem. Photobiol. A: Chem. 72 (1992) 261.
- [11] J.C. D'Oliveira, C. Maillard, C. Guillard, G.H. Al-Sayyed, P. Pichat, Innovation, Industrial Progress and Environment, Proc. Int. Cong. MCI, Paris, 1991, p. 421.
- [12] C. Maillard, C. Guillard, P. Pichat, M.A. Fox, New J. Chem. 16 (1992) 821.
- [13] J.C. D'Oliveira, C. Guillard, C. Maillard, P. Pichat, J. Environ. Sci. Health A 28 (1993) 941.
- [14] L. Amalric, C. Guillard, N. Serpone, P. Pichat, J. Environ. Sci. Health A 28 (1993) 1393.
- [15] M. Kerzhentsev, C. Guillard, J.M. Herrmann, P. Pichat, in: D.F. Ollis, H. Al-Ekabi (Eds.),  $\text{TiO}_2$  Photocatalytic Purification and Treatment of Water and Air, Elsevier, 1993, p. 601.
- [16] M. Kerzhentsev, C. Guillard, J.M. Herrmann, P. Pichat, Catal. Today 27 (1996) 215.
- [17] M. Bideau, B. Claudel, B. Otterbein, M. Otterbein, J. Photochem. 14 (1980) 291.
- [18] M. Bideau, B. Claudel, L. Faure, M. Rachimoallah, Chem. Eng. Comm. 93 (1993) 167.
- [19] B. Krautler, A.J. Bard, J. Am. Chem. Soc. 100 (1978) 2239.
- [20] M. Bideau, B. Claudel, L. Faure, H. Kazouan, J. Photochem. Photobiol. A: Chem. 61 (1991) 269.
- [21] T. Sakata, T. Kawai, K. Hashimoto, J. Phys. Chem. 88 (1984) 2844.
- [22] H. Miyoshi, H. Mori, H. Yoneyama, Langmuir 7 (1991) 503.
- [23] D.F. Ollis, C.Y. Hsiao, L. Budiman, C.L. Lee, J. Catal. 88 (1984) 89.
- [24] A. Chemseddine, H.P. Boehm, J. Mol. Catal. 60 (1990) 29.
- [25] M. Lindner, J. Theurich, D.W. Bahnemann, Water Sci. Technol. 35 (1997) 79.
- [26] J.M. Herrmann, M.N. Mozzanega, P. Pichat, J. Photochem. 22 (1983) 333.
- [27] R.W. Matthews, J. Catal. 111 (1988) 264.
- [28] J. Cunningham, G.H. Al-Sayyed, J. Chem. Soc., Faraday Trans. 86 (1990) 3935.
- [29] V. Brezova, M. Ceppan, E. Brandsteterova, M. Breza, L. Lapcik, J. Photochem. Photobiol. A: Chem. 59 (1991) 385.
- [30] R.W. Matthew, J. Chem. Soc., Faraday Trans. 1 80 (1984) 457.
- [31] M. Abdullah, G.K.C. Low, R.W. Matthews, J. Phys. Chem. 94 (1990) 6820.
- [32] S. Tunesi, M.A. Anderson, J. Phys. Chem. 95 (1991) 3399.
- [33] J.E. Pacheco, C.E. Tyner, Proc. ASME Int. Solar Energy Conf., Miami, 1990.
- [34] J. Sabate, M.A. Anderson, H. Hikkawa, Q. Xu, S. Cervera-March, C.G. Hill, J. Catal. 134 (1992) 36.

- [35] P. Pichat, J.C. D'Oliveira, J.F. Maffre, D. Mas, in: D.F. Ollis, H. Al-Ekabi (Eds.), *TiO<sub>2</sub> Photocatalytic Purification and Treatment of Water and Air*, Elsevier, Amsterdam, 1993, p. 683.
- [36] M. Barbeni, M. Morello, V. Pramauro, E. Pelizzetti, M. Vincenti, E. Borgarello, N. Serpone, *Chemosphere* 16 (1987) 1165.
- [37] J.C. D'Oliveira, W.D.W. Jayatilake, K. Tennakone, J.M. Herrmann, P. Pichat, in: L. Guzzi et al. (Eds.), *New Frontiers in Catalysis*, Elsevier, Amsterdam, Vol. C, 1993, p. 2167.
- [38] H. Ogawa, *J. Phys. Org. Chem.* 4 (1991) 346.
- [39] P. Pichat, M.N. Mozzanega, J. Disdier, J.M. Herrmann, *Nouv. J. Chim.* 6 (1982) 559.
- [40] W. Mu, J.M. Herrmann, P. Pichat, *Catal. Lett.* 3 (1989) 73.
- [41] P. Pichat, J.M. Herrmann, J. Disdier, M.N. Mozzanega, *J. Phys. Chem.* 83 (1989) 3122.
- [42] J.M. Herrmann, J. Disdier, P. Pichat, *Chem. Phys. Lett.* 108 (1984) 618.
- [43] J.M. Herrmann, M.N. Mozzanega, P. Pichat, *J. Photochem.* 22 (1983) 33.
- [44] T.A. Egerton, C.J. King, *J. Oil Col. Chem. Assoc.* 62 (1979) 386.