HETEROGENEOUS PHOTOCATALYSIS AS A METHOD OF WATER DECONTAMINATION: DEGRADATION OF 2-, 3- AND 4-CHLOROBENZOIC ACIDS OVER ILLUMINATED TiO2 AT ROOM TEMPERATURE

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Abstract

Chlorobenzoic acids(CBA) are completely mineralized into CO_2 and Cl^- over UV-illuminated TiO_2 in water according to the following reactivity order : 4-CBA>2-CBA>3-CBA. The identification of various intermediates of 2-CBA shows the decarboxylation and the progressive hydroxylation of the aromatic ring.This study confirms the potentialities of photocatalysis for water detoxification.

1 - INTRODUCTION

Heterogeneous photocatalysis appears as an efficient method to destroy and totally mineralize organic pollutants in water (1,2). For example, chlorophenols are totally converted into CO_2 and Cl^- over illuminated titania (3,4) whereas benzamide and nitrobenzene are converted into CO_2 and NO_3^- (5). The degradation of various carboxylic acids has been reported, either aliphatic (6,7), or aromatic, such as benzoic acid (8), salicylic acid (9, 10), and chlorinated phenoxyacetic acids(13,14) which are herbicides. This paper describes the total mineralization by heterogeneous photocatalysis of the three chlorobenzoic acid isomers chosen as model compounds, in particular to study the influence of the relative positions of the substituents on the aromatic ring.

2 - EXPERIMENTAL

The organics were obtained from Aldrich . The photocatalyst was Degussa P - 25 TiO_2 (50 m^2 g^{-1}, non porous).The degradations were carried out in a static batch photoreactor containing 50 mg of TiO_2 in $20cm^3$ of solution illuminated at 340 nm with a radiant flux of 50 mW cm^{-2}. TiO_2 was stirred in the dark for 40 minutes to reach the adsorption equilibrium .Organics were analyzed by HPLC using a UV and a photodiode array detector. The eluent was 40 % methanol/60 % water buffered by acetic acid. Some of the intermediates were also identified by GC-MS. Cl^- and CO_2 were analyzed by HPLC (conductivity detector) or GC,respectively.

3 - RESULTS AND DISCUSSION

3.1 Photocatalytic degradation of 2-CBA

The concentration C of 2-CBA decreases linearly with illumination time from C_0 = 0.5 mM,i.e.80ppm (mg l^{-1}) with an apparent zero order and disappears within about 2 h (Fig.1). The kinetic order can be explained by a strong adsorption with saturation of the adsorption sites

$$v = - d(2\text{-CBA})/dt = k\ KC/1+KC \simeq k \qquad (1)$$
$$\text{or} \qquad C = C_0 - kt \qquad (2)$$

where k is the true rate constant of 2-CBA disappearance and K is the adsorption constant of 2-CBA. This is in line with the important fraction of adsorbed molecules in the dark prior to illumination : decrease in C from 80 ppm (nominal concentration) to 60 ppm . This behavior is different from that of other compounds whose extent of adsorption is lower (1-5)

Cl^- are progressively released in the solution (Fig.1) The final amount is reached within 2h and is equal to 90 % of the expected value if no chlorinated organic compound remained ,which can be explained by Cl^- adsorption on TiO_2 .

The final level of carbon dioxide formation (Eq.3)is reached within 5h (Fig. 1).

$$Cl - C_6 H_4 - COO H + 7\ O_2 \quad \rightarrow \quad 7\ CO_2 + HCl + 2H_2O \qquad (3)$$

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 the regulations.
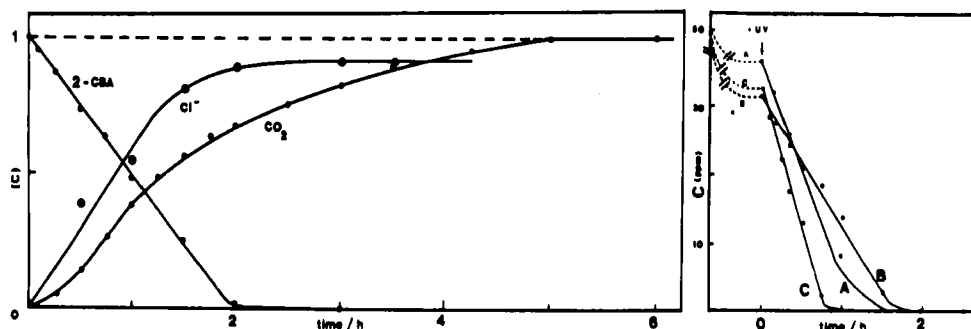
Fig.1. Kinetics of 2-CBA disappearance and of CO_2 and Cl^- formation ; (C) = normalized concentrations

Fig. 2. Photocatalytic disappearance of the three chlorobenzoic acids (A,B,C for 2-, 3- and 4-CBA, respectively).

Chlorobenzene and 2-chlorophenol were identified as intermediates , the former being present only as traces because of its very poor solubility in water and its high reactivity with OH· radicals to yield 2- and 4- chlorophenol by attack at ortho- and para- sites (15). Chlorohydroquinone was also detected. All these intermediates disappear within about 2h. No hydroxybenzoic acids such as salicylic acid were found contrary to the case of benzoic acid (8), probably because of the presence of a chlorine substituent, which contributes to deactivate the aromatic ring. This is in agreement with the initial easy decarboxylation (cf.the case of aliphatic acids (6,11)).Taking into account the nature of these identified intermediates and the degradation pathways of chlorophenols (3,4), the following degradation scheme is proposed :
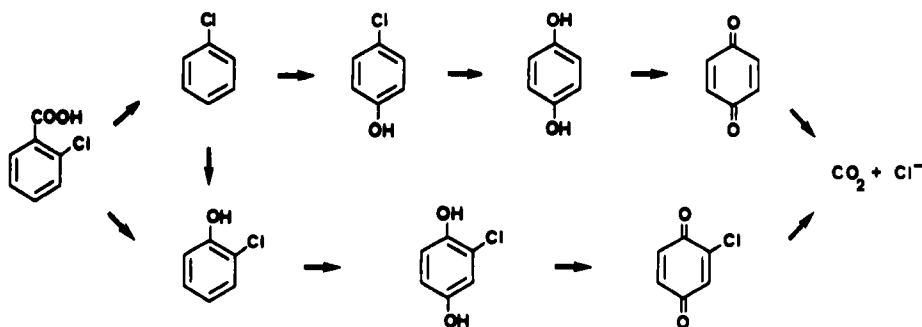
3.2 Comparison of the degradation of the three isomers.

2-, 3- and 4- CBA were tested separately under identical contitions (50 ppm because of the very poor solubility of 4-CBA). The disappearance of the three pollutants (Fig.2) exhibits an apparent zero-order kinetics with rate constants equal to 4.1 ,2.4 and 5.3 μmol h^{-1} for o. ,m. and p. CBA,respectively.The same order of reactivity is also observed for the total mineralization .The para-position induces a higher reactivity than the ortho- and the meta-one. This is in agreement with what has been found for monochlorophenols (3,4).

4 - CONCLUSION

This study confirms the potentialities of heterogeneous photocatalysis to decontaminate waste waters. In particular, the high efficiency for dechlorination enables one to suggest this method as a complementary process for biological treatment of water, since chlorinated products are often toxic for bacteria.Additionally, photocatalysis appears, up to now, as the only example of heterogeneous catalytic treatment of used waters working at room temperature.

5 - REFERENCES

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