

PII: S0043-1354(00)00009-9

Wat. Res. Vol. 34, No. 10, pp. 2791–2797, 2000 © 2000 Elsevier Science Ltd. All rights reserved Printed in Great Britain 0043-1354/00/\$ - see front matter

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TiO₂-MEDIATED PHOTOMINERALIZATION OF 2-CHLOROBIPHENYL: THE ROLE OF O₂

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(First received 1 March 1999; accepted in revised form 1 October 1999)

Abstract—Photocatalytic mineralization of 2-chlorobiphenyl (2-CB) in aqueous TiO₂ suspensions was conducted under four different oxygen partial pressures (Po₂) in closed reactors. The observed O₂ adsorption equilibrium constant in TiO₂ aqueous suspension was 0.88 (kPa)⁻¹ based on the Langmuir–Hinshelwood rate function. Apart from the conventional electron-scavenging function, the dissolved oxygen was critical for the degradation of the hydroxyl intermediates, i.e., 2-chlorobiphenyl-ols and biphenyl-2-ol, which are potentially toxic. Degradation of 2-CB in the irradiated H₂O₂ aqueous solutions under two different Po₂ was also studied for comparison. For UV/H₂O₂, Po₂ does not affect the removal of 2-CB, while reducing the Po₂ from 21 to 2 kPa resulted in 35% less CO₂ formation after 5 h irradiation. The similar O₂-dependent destruction of the hydroxyl intermediates was also observed in the UV/H₂O₂ system. We propose that molecular O₂ acts as a key reactant following the attack of a second ·OH radical during the ring opening in the degradation of the hydroxyl byproducts. (© 2000 Elsevier Science Ltd. All rights reserved

Key words—role of oxygen, photocatalytic degradation, 2-chlorobiphenyl (2-CB), titanium dioxide (TiO₂)

INTRODUCTION

Since it was first used to destroy aqueous phase polychlorinated biphenyls (Carey *et al.*, 1976), titanium dioxide (TiO₂-anatase polymorph) photocatalytic degradation of organic contaminants has attracted much attention as an alternative for the degradation of environmental contaminants in air and water. Various classes of organic compounds have been either partially degraded or completely mineralized in UV-irradiated aqueous TiO₂ suspensions (Pelizzetti *et al.*, 1990a; Mills *et al.*, 1993).

The primary reactions involved in TiO₂ photocatalysis have been well documented (Turchi and Ollis, 1990). Oxygen was found to be essential for semiconductor photocatalytic degradation of organic compounds (Al-Ekabi *et al.*, 1991; Okamoto *et al.*, 1985a,b; Schwarz *et al.*, 1997). Experiments have demonstrated the dependence of initial reaction rates and total mineralization of organic compounds on O₂ in the TiO₂ photocatalysis (Al-Ekabi *et al.*, 1991; Okamoto *et al.*, 1985a,b). Schwarz *et al.* (1997) gave evidence of the influence of dissolved O₂ levels on the rate of •OH radical formation on the TiO₂ surface. Oxygen is known to readily adsorb onto the TiO₂ surface (Boonstra and Mutsaers, 1975) and can be reduced by the photoinduced conduction-band electrons during which superoxides are formed (Rothenberger et al., 1985). Oxygen and its reduced species, such as O_2^- · and $\cdot O_2^{2-}$, were suggested to play important roles in TiO₂-catalyzed photomineralization (Al-Ekabi et al., 1991; Grätzel et al., 1990). In gas phase photocatalysis of trichloroethylene, instead of ·OH radicals, the gas phase O2-derived active radical species, such as HO_2 , O_2^- , were suggested to initiate the oxidation (Fan and Yates, 1996). In a study of TiO₂ photocatalytic degradation of gas phase 4chlorophenol (4-CP), Gray et al. (1993) pointed out that .OH radicals may not be exclusively responsible for the photooxidation of 4-CP and the role of oxygen is more than that of merely an electron scavenger.

The difficulties in understanding the complex roles of oxygen in photocatalysis are mainly due to the lack of proper reaction intermediates. The 2-CB used in this study is an ideal compound for this purpose because it has two aromatic rings with different electron densities. The advantage of using 2-CB has been demonstrated by the formation of stable aromatic intermediates at various stages in

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the process of TiO_2 photocatalysis (Hong *et al.*, 1998).

The main objectives of this study were to investigate the effect of O_2 on the degradation of the aromatic intermediates and to provide mechanistic insight into the role of dissolved oxygen in TiO₂ photocatalysis. The effect of O_2 on the evolution of intermediates and CO₂ in the UV/H₂O₂ system was also studied as a comparison to discern the function of molecular oxygen and that of the superoxide species.

EXPERIMENTAL

Materials

The nonporous P-25 TiO₂ powder (80% anatase, average diameter 0.02 μ m and surface area ~50 m²/g) was a gift from Degussa Corporation (Dublin, OH). 2-CB was purchased from AccuStandard (New Haven, CT) and was used without further purification. Hydrogen peroxide (30%, reagent grade) and Na₂CO₃·H₂O (reagent grade) were obtained from Baker Analyzed. All the organic solvents used were nanograde from Mallinckrodt, Inc. (St Louis, MO). Ultrapure compressed O₂ and N₂ used in this study were provided by Praxair (Albany, NY). The water used in all experiments was produced by a Milli-Q water purification system (Millipore).

Photocatalytic degradation

Aqueous 2-CB solutions were produced by the generator column technique (Hong and Qiao, 1995). Photocatalytic degradation of 2-CB was carried out in 100-ml borosilicate glass bottles. 2-CB aqueous solutions with TiO₂ suspensions were stirred for 1 h in the dark to establish a 2-CB adsorption-desorption equilibrium. Then, 50 ml of this solution was transferred into the bottle. The bottles were sealed with Teflon-lined septa and aluminum crimp tops. The light intensity through borosilicate glass was measured to be 1400 $\mu W/cm^2$ using a radiometer (Model DIX-365, Spectronic Corporation). A laboratoryconstructed 'solarbox' equipped with eight UVA-340 light tubes (Q-Panel Company) provided the UV irradiation source. This UV source has a maximum emission at 340 nm. The reaction bottles were placed up-side down on a special rack on a multi-magnetic stirrer (Lab-line instruments, Inc.) in the solarbox. A fixed distance (5 cm) from the light source to the solution surface was kept for all the experiments. To better monitor the degradation process, a relatively low TiO₂ loading of 25 mg/l for all the experiments was used. The 2-CB solutions were used at natural pH (6.8 \pm 0.1). Hydrogen peroxide concentration for the UV/H2O2 experiments was 0.01 M. H2O2 was added to the reaction solutions prior to irradiation.

Oxygen partial pressure

The reactor headspace was purged with pure N_2 or O_2 to control the oxygen partial pressure (Po₂). Throughout the purging, direct blowing on the solution was carefully avoided. The headspace Po_2 was then determined by an HP 5890 GC equipped with a packed HP carbosphere column and a thermal conductivity detector. The detector was operated at 150°C. The column temperature was kept constant at 30°C. Ambient air was used as the reference.

Analytical determination

 CO_2 was quantitated by headspace gas chromatographic analysis with a GC (HP 5890)/FTIR (HP 6968B) equipped with a 25 m HP-Ultra 2 column. The detailed method was described previously (Hong *et al.*, 1998).

Following CO₂ measurement, the suspensions were subjected to hexane extraction three times. The extracts were dehydrated and followed by GC/ECD (HP 5890) analysis. Details about 2-CB determination can be found elsewhere (Hong et al., 1998). The hexane-extracted suspensions were then acidified to pH \sim 1 with H₂SO₄ and extracted three times with dichloromethane for more polar intermediates. The hexane and dichloromethane extracts were concentrated individually to around 1.0 ml with a Kuderna-Danish (K-D) apparatus and further concentrated down to 0.1 ml with gentle nitrogen blowing. Five microliters of each concentrated sample was injected into GC/FTIR/MS (HP 5890/HP 6968B/HP 5970). The identification and quantitation of the intermediates were described in our previous papers (Hong et al., 1998; Wang et al., 1998).

RESULTS AND DISCUSSION

The conventional concept of oxygen function

Near UV irradiation of anatase-TiO₂ generates conduction-band electron (e_{CB}^-) and valence-band hole (h_{VB}^+) pairs, some of which are trapped on the particle surface at some defect sites where redox chemistry can take place (Turchi and Ollis, 1990). Without a surface-bound reducible adsorbate, the surface-trapped e_{CB}^- and h_{VB}^+ recombine rapidly (Bahnemann et al., 1997). Dissolved oxygen readily adsorbs on the TiO2 surface and can be reduced by e_{CB}^{-} to form superoxide ion radicals O_2^{-} and/or O_2^{2-} (Bahnemann *et al.*, 1997). The surviving surface-trapped h_{VB}^+ then oxidizes TiO₂ surface-sorbed H₂O or OH⁻ to produce ·OH radicals (Matthews, 1984). Hitherto, conduction-band electron scavenging, which is essential for ·OH radical formation, was considered the major function of the dissolved O_2 in semiconductor photocatalysis.

According to Henry's Law, the dissolved oxygen concentration is proportional to the gas phase Po_2 . To explore the effect of dissolved O_2 , TiO₂ photoca-



Fig. 1. Effect of oxygen partial pressure on 2-CB disappearance and CO₂ formation in the UV/TiO₂ system.
[TiO₂]=25 mg/l. Illumination intensity was 1400 μW/cm².
(■ □) 186 kPa, (● ○) 21 kPa, (▼ ▽) 4 kPa, (♦ ◊) 0.5 kPa. The solid symbols are for 2-CB and the hollow symbols for CO₂.

talytic degradation of 2-CB was conducted under four different Po₂s in the closed reaction vessels. Figure 1 shows the effect of Po₂ on 2-CB disappearance and total mineralization. A higher Po₂ was accompanied with a quicker 2-CB disappearance and a faster CO₂ formation. The molar ratio of CO₂ produced to 2-CB removed after 80 min of irradiation for Po₂s of 0.5, 4, 21, and 186 kPa were 1.3, 2.7, 6.3, and 5.4, respectively, which are far lower than the stoichiometric ratio of 12 at complete mineralization. At the low Po₂ of 0.5 kPa, only 16% of the 2-CB was mineralized to CO₂, compared with mineralization of 53%, 84% and 94%, respectively, under increasing Po₂s, after 5 h illumination.

The initial reaction rate (r_o) of 2-CB degradation first increased rapidly and then progressively leveled off with increasing Po₂ (Fig. 2 curve a). Recently, Schwarz *et al.* (1997) reported a similar relationship between Po₂ and the observed ·OH radical formation rate on the TiO₂ surface. The initial rate of 2-CB removal was directly related to the concentration of the TiO₂ surface-adsorbed ·OH radical. The result demonstrates the function of O₂ in preventing electron and hole recombination.

The Langmuir–Hinshelwood reaction kinetics model is often used (Okamoto *et al.*, 1985a,b; Augugliaro *et al.*, 1988) to describe the relation of r_{o} and Po₂:

$$\mathbf{r}_o = \mathbf{k} K \mathbf{o}_2 \mathbf{P} \mathbf{o}_2 / (1 + K \mathbf{o}_2 \mathbf{P} \mathbf{o}_2)$$

where Ko_2 is the adsorption equilibrium constant of O_2 on the TiO₂ surface under aqueous colloid conditions and k is the reaction rate constant. A directly transformed form of the above equation is:

$$1/r_o = 1/(kKo_2Po_2) + 1/k$$

which predicts a linear relationship between $1/r_o$



and $1/Po_2$ as shown in Fig. 2 curve b. From the values of the intercept 1/k and the slope $1/(kKo_2)$, $Ko_2 = 0.88 (kPa)^{-1}$ was derived. This is comparable with those of 0.11 (kPa)^{-1} (Okamoto *et al.*, 1985a) and 1.1 (kPa)^{-1} (Augugliaro *et al.*, 1988) reported in the studies of the TiO₂ photocatalytic degradation of phenol.

Effect of O_2 on intermediate degradation

Evolution of the aromatic intermediates was investigated using single ion monitoring mass spectrometry. The distribution profiles of some intermediates as a function of reaction time are shown in Figs 3 and 4. There was a general trend towards more accumulation of hydroxyl by-products at a lower Po2. Meanwhile, the maximum accumulation shifted to longer reaction times (Fig. 3). Noting that a slower rate of 2-CB disappearance was accompanied with a lower Po2 (Fig. 1) and the primary intermediates are directly formed from the loss of H or Cl from 2-CB by ·OH radical attack (Hong et al., 1998), the higher accumulations of the hydroxyl byproducts under lower O2 levels is obviously the result of their slower degradation rates. It is also noted that the one-ring aromatic intermediates at the Po2 of 0.5 kPa were hardly detectable compared to that in the higher Po₂ conditions (Fig. 4), which implies that the photocatalytic activity responsible for the transformation of the primary by-products was nearly cut off under this low O2 condition. The observed higher accumulations of the primary intermediates under lower Po2s suggest that O2 was needed for the degradation of the hydroxyl by-products, i.e., the clea-



Irradiation time (min)

Fig. 2. (a) Effect of oxygen partial pressure on reaction rate; (b) $1/r_o$ vs $1/Po_2$.

Fig. 3. Effect of oxygen partial pressure on the evolution of two primary intermediates in the UV/TiO₂ system. Experimental conditions are as in Fig. 1. (\bullet) 21 kPa, (\blacklozenge) 0.5 kPa.

vage of one of the aromatic rings of 2-CB. The marginal formation of the secondary and tertiary by-products observed at the Po_2 of 0.5 kPa is obviously due to the residual oxygen, because there was no effort made to completely remove the oxygen from the system. Once the oxygen is consumed, the degradation of the primary intermediates may cease.

For the secondary intermediate, i.e., the aromatic aldehyde, carboxylation of the branch chains to form 2-chlorobenzoic acid may be the major pathway of their oxidation, while direct ring cleavage should be a much slower route (Augugliaro *et al.*, 1988). For the aromatic acid, i.e., 2-chlorobenzoic acid, a slower build-up process and a smaller accumulation peak (Fig. 4) accompanied a lower Po₂, because the formation was slower under a lower Po₂.

The involvement of molecular oxygen in ring cleavage

 H_2O_2 -photosensitized degradation of organic compounds has been well-documented as an ·OHinitiated destruction process (Izumi *et al.*, 1981; Stefan *et al.*, 1996). Besides the homogeneous property, a unique characteristic of the UV/H₂O₂ system is that there is no molecular O₂ reduction by electrons as in the UV/TiO₂ system (Howe and Grätzel, 1987; Izumi *et al.*, 1981; Liao and Gurol, 1995; Stefan *et al.*, 1996). Therefore, by comparing the influence of Po₂ on the intermediate degradation in these two systems, we can discern whether the molecular O₂ itself or the superoxide species formed from the reduction of O₂ on the TiO₂ surface, or both, are responsible for the observed O₂-dependent



Fig. 5. Effect of oxygen partial pressure on 2-CB disappearance and mineralization in the irradiated H_2O_2 solutions. $[H_2O_2] = 0.01$ M. ($\bigcirc \bigcirc$) 21 kPa, ($\blacksquare \square$) 2 kPa. The solid symbols are for 2-CB and the hollow symbols for CO₂.

destruction of the primary aromatic intermediates in the process.

Figure 5 shows the disappearance of 2-CB and the resulting formation of CO₂ in the irradiated H_2O_2 solutions with Po₂s of 21 and 2 kPa. The disappearance of 2-CB was similar in the two cases, because ·OH radicals were directly generated through photolysis of H_2O_2 . However, reducing the Po₂ from the ambient level of 21 kPa to 2 kPa significantly lowered the CO₂ formation. When Po₂ was 21 kPa, 2-CB was completely mineralized to CO₂ after 5 h irradiation, in contrast to only 65% mineralization under the lower O₂ level. The accumulation of some aromatic intermediates as a



Irradiation time (min)



Fig. 4. Effect of oxygen partial pressure on the evolution of one secondary and one tertiary intermediates in the UV/TiO₂ system. Experimental conditions are as in Fig. 1. (\bigcirc) 21 kPa, (\diamondsuit) 0.5 kPa.

Fig. 6. Effect of oxygen partial pressure on the evolution of two primary intermediates in the irradiated H_2O_2 solutions. $[H_2O_2]=0.01$ M. (\odot) 21 kPa, (\bigcirc) 2 kPa.

function of reaction time is depicted in Figs 6 and 7. As found in the TiO_2 photocatalysis, the reduction of Po_2 significantly increased the accumulation of the hydroxyl byproducts. The times for the highest accumulation for the hydroxyl intermediates were shifted about 30 min later under the lower O_2 level. Considering the formation rates for the primary products were the same, as indicated by the same rate of 2-CB disappearance (Fig. 5), the degradation of the hydroxyl byproducts was slower at the reduced Po_2 . Therefore, the aromatic ring-opening process for the hydroxyl intermediates showed an O_2 -dependent behavior in both UV/ H_2O_2 and UV/TiO₂ systems.

The secondary intermediate, i.e., the aromatic aldehyde, in the UV/H_2O_2 system was found to accumulate at similar levels under two different Po_2 , which is much lower than that in UV/TiO_2 system with similar O_2 conditions. This may be due to the relatively fast branch-chain carboxylation process in this homogeneous system.

In contrast to that in the TiO_2 photocatalysis system, the aromatic acid in the UV/H₂O₂ system had significantly higher accumulations at the lower Po₂. The degradation of the primary intermediates became slower under the reduced Po₂, which indicates a slower formation process for the aromatic acid. Therefore, the degradation of 2-chlorobenzoic acid was slower under the lower Po₂. This suggests that the ring cleavage for the aromatic acid may also require O₂.

The O_2 -dependent aromatic ring cleavage observed in the UV/H₂O₂ system, in which there is no superoxide oxygen species, provides direct evidence that molecular O_2 plays a key role in the ring-opening process.

Nucleophilic OH substitution remarkably increases the electron density of the benzene ring, which normally makes the double bonds more vulnerable to an attack from a peroxo group. Grätzal et al. (1990) has proposed that O_2^{2-} formed in the UV/TiO₂ system directly attacks an aromatic double bond. Recently, Bahnemann et al. (1997) reported that most of the trapped charge carriers $(e_{CB}^{-} and h_{VB}^{+})$ recombine within 200 ns, only a minority survives and is available for the reduction of surface-sorbed molecular O2. This indicates that molecular O_2 is the dominant oxygen species on the TiO₂ surface. Therefore, instead of a reduced oxygen species, molecular oxygen seems to be directly involved in the ring-opening reactions for 2-CB in both UV/TiO₂ and UV/H₂O₂ systems.

Possible mechanism for O_2 -dependent ring opening

In the TiO₂ photocatalytic degradation of other aromatics, dimers or diol was often reported as the minor byproducts (Okamoto *et al.*, 1985a; Pelizzetti *et al.*, 1990a,b; Pichat *et al.*, 1993). In this study, the failure to detect chlorobiphenol dimers or chlorobiphenyl-diol could be due to the analytical limitations, however, oxidative ring cleavage should be the major route for the further oxidation of the hydroxyl intermediates (Okamoto *et al.*, 1985a; Pelizzetti *et al.*, 1990a,b; Pichat *et al.*, 1993).

The intermediate profile indicates that the singlering aromatic intermediates were all derived from



Fig. 7. Effect of oxygen partial pressure on the evolution of one secondary and one tertiary intermediates in the irradiated H_2O_2 solutions. $[H_2O_2]=0.01$ M. (\odot) 21 kPa, (\bigcirc) 2 kPa.



Fig. 8. Proposed mechanism for the O₂-dependent ringopening process of 2-chlorobiphenyl-ol.

the opening of the ring with a hydroxyl group (Hong *et al.*, 1998). It becomes clear that the opening of the aromatic ring with hydroxyl group consists of the attack of a second \cdot OH radical followed by an involvement of molecular O₂.

Figure 8 gives a proposed mechanism for the observed O2-dependent ring-opening process. Radicals resulting from OH radical addition are frequently detected in TiO₂ photocatalysis of aromatic compounds (Harbour and Hair, 1979; Schwarz et al., 1997; Sehested et al., 1977). Before the hydroxyl molecules escape from the TiO2 surface, a diol radical (A) is expected to form from the attack of a second ·OH radical. This diol radical was also proposed in an OH-initiated ring cleavage for o-cresol in atmospheric chemical processes (Chien et al., 1998) although there was no demonstration. The TiO₂ surface-sorbed molecular O₂ is then readily trapped by radical A to form B (Cermenati et al., 1997; Okamoto et al., 1985a; Takagi et al., 1985). The highly reactive 'on-site' peroxo radical then attacks an ortho hydroxyl group. This results in the formation of a less reactive radical (HO₂) and an epoxide intermediate (C) (Chien et al., 1998; Grätzel et al., 1990), which is subjected to immediate hydrolysis, rearrangement, the opening of the ring, and formation of a bifunctional species (D). D is then quickly degraded and proceeds to the formation of the relatively stable aldehyde or ketone intermediates. Generation of aldehyde or ketone may depend on the position of ring opening. The superoxide radicals, h_{VB}^+ , e_{CB}^- , $\cdot OH$ radicals, and O_2 as well may all be involved in the oxidative degradation of D. In UV/H₂O₂ system, HO₂ and ·OH radicals may similarly be involved in this degradation process.

The O₂-dependent aromatic ring-cleavage of the hydroxyl intermediates is obviously one of the major rate-limiting steps in the process of TiO_2 photocatalytic mineralization of 2-CB. This may also be true in UV/H₂O₂ system.

Hydroxyl aromatic products were often found to be the initial oxidation products for the degradation of aromatic compounds in semiconductor photocatalysis (Cermenati et al., 1997; Theurich et al., 1996) and other OH-based oxidation processes (Chien et al., 1998; Moza et al., 1988). The identification of the seven 2-chlorobiphenyl-ols and biphenyl-2-ol as the primary byproducts in TiO2 photocatalysis of 2-CB (Hong et al., 1998; Wang et al., 1998) indicates that hydroxyl PCBs might be the major preliminary products in TiO₂ photocatalysis of PCBs. Polychlorinated biphenyl-ol and polychlorinated biphenyl-diol were also found in TiO₂ photocatalytic degradation of dichlorophenol as the condensation products (Minero et al., 1995). These hydroxyl intermediates are similar to those PCB metabolites in biological systems, which are potentially toxic or more toxic than the parent PCB congeners (Gierthy et al., 1997; Safe, 1994). The results from this study suggest that dissolved oxygen may play a critical role in the degradation of the hydroxyl aromatic products, which are potentially toxic, in TiO_2 photocatalysis of PCBs and other halogenated aromatics.

CONCLUSIONS

- 1. A higher Po_2 resulted in faster initial rate of 2-CB transformation and CO_2 formation. The effect of oxygen partial pressure on 2-CB mineralization is more significant than that on 2-CB transformation. At Po_2 of 0.5 kPa, 75% of 2-CB were transformed but only 16% of 2-CB were mineralized to CO_2 after 5 h illumination.
- The distribution profiles of aromatic intermediates indicate that molecular oxygen was needed for the degradation of the hydroxyl by-products, which implies the involvement of molecular oxygen in the cleavage of aromatic ring.
- 3. The similar O_2 -dependent destruction of the hydroxyl intermediates was also observed in the UV/H_2O_2 system.

Acknowledgements—This research was supported by NIEHS Superfund Basic Program under Grant No. ESO 4913-07. The authors wish to thank Dr Rajinder Narang for his assistance with oxygen analysis.

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