# Part 4.†—Effects of Surface Condition on the Photodegradation of 2,4-Dichlorophenol catalysed by $TiO_2$ Suspensions

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The photocatalysed degradation of 2,4-dichlorophenol (DCP) has been investigated in aqueous suspensions of  $TiO_2$ . A possible reaction scheme has been proposed for the degradation, in which chlorobenzoquinone (CBQ) was detected as a predominant intermediate present in the reaction solution. Kinetic details for the degradation steps have been analysed based on the experimental results. The essential role of oxygen was considered to be the capturing of the photogenerated electron to form the oxidizing species, such as  $H_2O_2$ ,  $HO_2^{-}$  and  $OH^{-}$ . In anaerobic conditions, the photodegradation rate was quite low even with the adsorbed  $Cu^{2+}$  ion on the  $TiO_2$  powder as an alternative electron scavenger. This is due to the rapid indirect recombination of the photogenerated electron trapped at the adsorbed  $Cu^{2+}$  ion to prevent it from recombining with the photogenerated hole. As a result, the hole has sufficient opportunity to participate in the oxidizing reactions. The degradation rate was dependent to some extent on the surface charge of the  $TiO_2$  particles. Positive charge always promotes the photodegradation, whereas negative change is detrimental. This was attributed to the effects of surface charge on the migration of electrons from the interior of the  $TiO_2$  particles to the surface.

During the past decades numerous studies have been conducted on the use of semiconductor particles as photocatalysts in the photodegradation of organic compounds (see recent reviews<sup>1-3</sup>). In this regard, much attention has been focused on TiO<sub>2</sub> particles since this semiconductor is stable with respect to anodic dissolution.<sup>4,5</sup> These photocatalytic reactions provide a promising method for the elimination of toxic and biologically persistent compounds from waste water.

While many studies have been made of the kinetics of photodegradation of toxic organic compounds,<sup>6-8</sup> the reaction mechanism of the degradation processes is still unclear. For example, even the origin of the hydroxyl radical (OH'), which is well known as the primary oxidizing species involved in the photomineralization of organic substrates, has not been well clarified.<sup>6,9</sup> Most researchers<sup>10-14</sup> have attributed it to the oxidation of OH<sup>-</sup> or H<sub>2</sub>O by the photogenerated hole (h<sup>+</sup>),

$$h^+ + OH^- \longrightarrow OH^-$$
 (1)

$$h^+ + H_2O \longrightarrow OH^* + H^+$$
 (2)

Whereas Okamoto *et al.*<sup>8</sup> suggested that it is formed mainly from the trapping of photogenerated electrons ( $e^-$ ) by oxygen followed by a series of redox reactions,<sup>10,15–18</sup>

$$O_2 + e^- \longrightarrow O_2^{\cdot -}$$
 (3)

$$O_2^{\cdot -} + H^+ \longrightarrow HO_2^{\cdot} \tag{4}$$

$$HO_2' + HO_2' \longrightarrow H_2O_2 + O_2$$
 (5)

$$O_2^{-} + HO_2^{-} \longrightarrow O_2 + HO_2^{-}$$
 (6)

$$\mathrm{HO}_{2}^{-} + \mathrm{H}^{+} \longrightarrow \mathrm{H}_{2}\mathrm{O}_{2} \tag{7}$$

$$H_2O_2 \xrightarrow{hv} 2OH^*$$
 (8)

$$H_2O_2 + O_2^{--} \longrightarrow OH^{-} + OH^{-} + O_2$$
(9)  
$$H_2O_2 + e^{-} \longrightarrow OH^{-} + OH^{-}$$
(10)

‡ Deceased.

The transfer of the photogenerated charge carriers, either electrons or holes, at the semiconductor/liquid interface is believed to be influenced to some extent by the surface properties of the semiconductor.<sup>19-23</sup> Therefore, the photocatalytic mineralization of organic substrates is expected to be influenced in the same way, with one of the above two routes for the formation of OH<sup>•</sup> ultimately predominating. In the previous papers of this series<sup>24</sup> it has been shown that the transfer of the photogenerated charge carriers from ultrafine ZnS particles to the adsorbates is strongly dependent on the surface charge and composition of the ZnS particle. In the present work, the effects of pH and the addition of cations or anions on the photodegradation of DCP catalysed by a TiO<sub>2</sub> suspension have been studied in order to investigate the dependence of the photoinduced interfacial charge transfer on the surface properties of  $TiO_2$ .

# Experimental

#### Materials

2,4-Dichlorophenol (DCP), chlorohydroquinone (CHQ), (CBQ), chlorobenzoquinone  $Cu(NO_3)_2$ ,  $Zn(NO_3)_2$ ,  $Na_2HPO_4$ , NaOH and HClO<sub>4</sub> were of laboratory reagent grade and were used without further purification. Doubly distilled water was used throughout this study. The commercial TiO<sub>2</sub> powder (Beijing Chemical Co.) consisted mainly of anatase as characterized by the peak at  $2\theta = 25.2^{\circ}$  (3.52 Å) in the X-ray diffraction (XRD) spectra recorded on the D/max-RB diffractometer (Rigaku Co.). The specific surface area, measured by the BET method, was ca. 10.9 m<sup>2</sup> g<sup>-1</sup> (Micrometrics ASAP 2400). Transmission electron microscopy (TEM) measurements indicated that the mean particle size was about 150 nm (Philips EM-400). The TiO<sub>2</sub> suspension was prepared by adding an appropriate amount of the powder to 160 ml of water and sonicating it for 20 min.

# **Photoreactors**

The photocatalytic reactions were performed in a jacketed Pyrex reactor. Running water was circulated through the jacket to cool the reaction mixture and to remove the IR fraction of the light. The reaction temperature during the illumination was kept constant at  $26 \pm 1$  °C. Magnetic stirring was used to prevent the precipitation of the TiO<sub>2</sub> particles and to keep all of the reactants steadily irradiated. Most of the reactions were carried out in aerobic conditions. In these cases, the mouth of the reactor was opened to air to keep the suspension air-equilibrated. When anaerobic conditions were necessary, the reactor was 'sealed' with a Teflon-rubber septum equipped with four glass tubes for N<sub>2</sub> bubbling. A hole in the centre of the septum enabled sampling, N<sub>2</sub> removal and measurement of pH. Irradiation was provided by a 500 W Xe arc lamp.

# Procedure

In typical experiments, 160 ml of a 3 g  $l^{-1}$  TiO<sub>2</sub> suspension containing 2.5 × 10<sup>-4</sup> mol  $l^{-1}$  DCP and other additives (if necessary), such as Cu<sup>2+</sup>, Zn<sup>2+</sup> and HPO<sub>4</sub><sup>2-</sup>, was used. Before illumination, the solution was magnetically stirred for 30 min (or 60 min if with additives) to ensure that the adsorption process goes to completion on the TiO<sub>2</sub> surface. During a run, the pH of the solution was measured and *ca*. 3.5 ml samples were taken at given time intervals. The samples were then centrifuged and the centrifugates were analysed. For the reactions in different pH media, the initial pH of the suspension was adjusted by adding HClO<sub>4</sub> or NaOH solution.

Prior to studying the effects of oxygen on the photodegradation, the solutions were de-aerated for at least 150 min by bubbling N<sub>2</sub> through them at a rate of *ca.* 500 ml min<sup>-1</sup>. After 200 min of reaction, illumination and N<sub>2</sub> bubbling were stopped and the suspensions were re-equilibrated with air for about 30 min. The illumination was then restarted.

#### Analysis

The degradation of DCP was followed by measuring the absorption spectra of the reaction solution using Hitachi 330 or Hewlett-Packard 8451A spectrophotometers. Since the pH of the reaction solution varies during the course of degradation, the pH of all the centrifugates was adjusted to about 3.0 prior to absorption measurements, because the absorption spectra of the phenols are pH dependent. The pHs of the reaction solutions were determined with a digital pHmeter.

Owing to difficulties in taking IR measurements with aqueous solutions, a pretreatment of the centrifugate was necessary. An appropriate amount of KBr was added to ca. 1 ml of the centrifugate. This supersaturated solution was then evaporated at ca. 40 °C under a nitrogen gas stream. The dry crystals thus obtained were subjected to IR analysis, which was performed on a Perkin-Elmer 983G IR spectrophotometer. In order to confirm that the compounds in the centrifugate are not destroyed during pretreatment, the pretreatment procedure was repeated with pure samples of DCP, CHQ and CBQ and their IR spectra were analysed as described above. Comparison of these IR spectra with those measured without pretreatment showed no obvious difference between the two.

#### **Results and Discussion**

# **Identification of Intermediates**

Photodegradation of DCP occurred when it was irradiated with light ( $\lambda > 300$  nm) in the presence of oxygen. This process could be followed by measuring the absorption spectra of DCP solution as shown in Fig. 1. The absorption

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**Fig. 1** Absorption spectra of DCP solution recorded at different time intervals following photodegradation catalysed by TiO<sub>2</sub> particles: (a) 0, (b) 20, (c) 60, (d) 100, (e) 150, (f) 210 min. Initial conditions: [DCP] =  $2.5 \times 10^{-4}$  mol  $1^{-1}$ , 3 g  $1^{-1}$  TiO<sub>2</sub>, pH 6.4. The inset shows the standard absorption spectra of 0.1 g  $1^{-1}$  DCP (a), CHQ (b) and CBQ (c) measured on a Hewlett-Packard 8451A spectrophotometer.

peaks corresponding to DCP disappeared completely as a result of the photo-oxidation, indicating thereby complete degradation of DCP. As observed by previous workers,<sup>14</sup> the absorbance in the wavelength region above 240 nm increased at short irradiation times. This indicates the formation of some intermediates in the degradation process. In the standard absorption spectrum of CHQ (inset in Fig. 1), which is believed to be the dominant intermediate in the degradation of DCP,<sup>19a</sup> it can be seen that there is little absorbance at 250 nm and no absorbance at wavelengths longer than 320 nm. Obviously, the increase in absorbance was not caused by CHQ. It is plausible to regard CBQ as the main reaction intermediate, since this compound has an absorption band at 250 nm and a long tail at longer wavelengths (inset in Fig. 1). Further confirmation is shown in Fig. 2, in which changes in absorbance at 310 and 330 nm are plotted as a function of illumination time. If CHQ was the main intermediate as proposed by previous workers, the two curves would be different shapes as CHQ has an absorbance at 310 nm with an absorption coefficient of ca.  $1.8 \times 10^3$  and no absorbance at 330 nm. The good agreement between the two curves implies



Fig. 2 Changes in the absorbance (normalised at 80 min) of the DCP solution at (+) 310 and  $(\bigcirc)$  330 nm as a function of illumination time

that little CHQ was present in the reaction solution. In fact, it is also evident from the blue shift of the 285 nm band ( $\lambda_{max}$ of DCP) in Fig. 1, that CHQ is not the main intermediate, since otherwise a red shift would be expected because the absorption maximum of CHQ is at longer wavelengths, 297 nm.

To detect CBQ in the reaction solution, an IR method was developed. Fig. 3 shows the IR spectrum of DCP solution measured after irradiation for 60 min. Owing to disturbance due to water, the peaks at higher wavenumbers were not shown. The IR pattern indicated the coexistence of DCP and CBQ, as shown in Table 1. Note that UV absorption spectra resembling those in Fig. 1 and IR absorption spectra similar to those in Fig. 3 can also be obtained under other experimental conditions, for example, with the addition of  $Cu^{2+}$  ions to the reaction suspension.

In previous papers, such as ref. 19(a), the dominant intermediate in the photodegradation of DCP was found to be CHQ, not CBQ as detected in our study. This disagreement can be attributed to different experimental conditions, such as the intensity and spectral range of the irradiation used. In ref. 19(a), a high-pressure mercury lamp with a low power of 125 W was used as the irradiation source, which yields very sharp mercury-line spectra. Since a 340 nm cut-off filter was employed only the light at 365 nm was available to cause band-gap excitation of TiO<sub>2</sub>. In our experiments, however, irradiation was supplied by a 500 W Xe arc lamp which provides a continuous light output from 270 to 700 nm. Since no filter was used, all the radiation from 300 to 385 nm (bandgap of TiO<sub>2</sub>) can be used in the photodegradation process. In



Fig. 3 IR spectrum of DCP solution measured after irradiation for 60 min. Initial conditions:  $[DCP] = 4 \times 10^{-4} \text{ mol } l^{-1}$ , 5 g  $l^{-1}$  TiO<sub>2</sub>, pH 6.3.

Table 1	Assignments of	bands in the IR	spectrum of Fig. 3 <sup>a</sup>
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wavenumber/cm <sup>-1</sup>	assignment	
1321	DCP, CBQ	
1283	DCP, CBQ	
1177	DCP	
1068	DCP	
1008	CBQ	
885	CBQ	
850	DCP, CBQ	

addition, the area of the optical window of the photoreactor in our experiments was about 60 cm<sup>2</sup>, much larger than that of the photoreactor used in ref. 19(a) (only  $11 \text{ cm}^2$ ). The much higher irradiation intensity in our experiments could lead to a rapid conversion of CHQ to CBQ (Scheme 1, see later). This is understandable considering the strong reducibility of CHQ.<sup>26</sup> As a result, CHQ cannot be detected in the reaction solution by the steady-absorption technique. Note also that the irradiation (300-385 nm) used in the present experiments was able to photolyse DCP and its aromatic intermediates directly. Consequently, products could be formed by photolysis as well as by photocatalysis, particularly for CHQ, which has quite a large absorption above 300 nm and can therefore be directly photolysed by the irradiation used. The involvement of direct photolysis could enhance the rapid photocatalysed conversion of CHQ to CBQ. This is in contrast to the illumination conditions used in ref. 19(a), where a 340 nm cut-off filter was employed; which meant that no direct photolysis could be expected.

#### **Mechanism of Mineralization**

If we accept that CBQ is the main intermediate of the photodegradation of DCP, the extent of degradation can be quantitatively monitored from the decrease in absorbance at 230 nm with illumination time, because of the low absorption coefficient of CBQ at 230 nm (Fig. 1), and the small amount of it produced in the degradation process (Fig. 4). Simultaneously, the change in concentration of CBQ due to the degradation process can be followed by measuring the absorbance at 250 nm. The absorbance of DCP at this wavelength is negligible (inset in Fig. 1). Fig. 4 illustrates the photodegradation of DCP together with the formation of H<sup>+</sup> and CBO as a function of irradiation time. As reported by Al-Ekabi et al.,<sup>9a</sup> an approximately linear relationship between DCP concentration and irradiation time was obtained in the early stages of the degradation. Within this period, the reaction follows apparent zero-order kinetics with a rate constant of 98  $\mu$ mol  $1^{-1}$  h<sup>-1</sup>. Complete mineralization was achieved after about 4 h of irradiation. The decrease in reaction rate in the later stage must be caused by some reaction intermediates and/or mineralization products. Different reasons for this effect have been given in previous work.9a,27 Ollis<sup>27</sup> attributed it to the consumption of OH' by reaction with Cl- produced in the mineralization process, whereas Al-Ekabi et al.<sup>9a</sup> suggested that protonation of the TiO<sub>2</sub> surface at low pH was responsible for the inhibition of degradation. However, our experimental results do not support these



Fig. 4 Degradation of DCP (+) and formation of  $H^+$  ( $\Box$ ) and CBQ (·) as a function of illumination time. Initial conditions as in Fig. 1.

hypotheses. The degradation rate of DCP was little affected by the addition of  $2 \times 10^{-4}$  mol  $1^{-1}$  NaCl to the reaction solution (DCP  $2.5 \times 10^{-4}$  mol  $1^{-1}$  and 3 g  $1^{-1}$  TiO<sub>2</sub> at pH 6.4, the same conditions as in Fig. 4). The effect of pH on reaction rate has also been studied (see Fig. 11, later). The optimum pH for the degradation of DCP over TiO<sub>2</sub> was found to be  $\leq 6.4$ .<sup>28</sup> In such conditions, the surface of TiO<sub>2</sub> must be protonated. It can therefore be concluded that the inhibition was not due to the protonation of the TiO<sub>2</sub> surface, as can also be seen from Fig. 4. The photodegradation rate of DCP in the early stages of illumination is little affected by the increase in concentration of H<sup>+</sup> as a result of the mineralization according to

$$Cl_2C_6H_3OH + 6O_2 \rightarrow 6CO_2 + 2HCl + H_2O$$
 (11)

It is reasonable to assign the decrease in degradation rate at the later stages of illumination (Fig. 4) to some acidic intermediates (possibly in the form of RCOOH) produced in the degradation process. These acidic compounds can be adsorbed onto the TiO<sub>2</sub> surface through the carboxylic acid group.<sup>29</sup> The adsorbed carboxylate anions can inhibit the migration of the photogenerated electrons from the interior of the TiO<sub>2</sub> particles to the surface and thus prevent their participation in the photodecomposition reactions (as will be discussed below). This was confirmed by experiments in which addition of either CH<sub>3</sub>CO<sub>2</sub>H or CH<sub>3</sub>CH<sub>2</sub>CO<sub>2</sub>H ( $2 \times 10^{-4}$  mol  $1^{-1}$ ) to a reaction solution containing  $2.5 \times 10^{-4}$  mol  $1^{-1}$  DCP and 3 g  $1^{-1}$  TiO<sub>2</sub> did result in a pronounced decrease in the reaction rate, as in the case of the addition of the HPO<sub>4</sub><sup>2-</sup> ion (see Fig. 10, later).

The formation of acidic intermediates during the degradation was inferred from the fact that the increase in concentration of H<sup>+</sup> in the later period of the degradation was more than the amount expected from reaction (11), as indicated in Fig. 5. These acidic compounds, which may be formed from the photo-oxidative cleavage of the aromatic ring by attack of OH<sup>+</sup>, were subsequently converted to other intermediates or to the final products, CO<sub>2</sub> and H<sub>2</sub>O. As a result, the concentration of H<sup>+</sup> decreased steadily to ca.  $5 \times 10^{-4}$  mol 1<sup>-1</sup>, the stoichiometric quantity for the complete mineralization of DCP. Based on the above discussion and the results obtained by other researchers,<sup>6,9a,19a</sup> we propose that the main routes for photomineralization of DCP are as described in Scheme 1.



Fig. 5 Changes in the concentration of H<sup>+</sup> in the reaction solution as a function of illumination time. The concentrations of  $Cu^{2+}$  ions (mol 1<sup>-1</sup>) added as cocatalyst are: ( $\bigoplus$ ) 0, (+) 5.0 × 10<sup>-6</sup>, ( $\triangle$ ) 2.5 × 10<sup>-5</sup>, ( $\square$ ) 1.0 × 10<sup>-4</sup>, ( $\Rightarrow$ ) 5.0 × 10<sup>-4</sup>. The dotted line indicates the stoichiometric quantity of H<sup>+</sup> formed from the complete degradation of DCP. Initial conditions: [DCP] = 2.5 × 10<sup>-4</sup> mol 1<sup>-1</sup>, 3 g 1<sup>-1</sup> TiO<sub>2</sub>.



Scheme 1 The main routes of photo-oxidative mineralization of DCP. Some other possible intermediates, such as 4-chlorocatechol and 2,4-dichlorocatechol, are omitted because they form only minor amounts in the degradation reactions.<sup>19a</sup> The multi-step reactions, (4) and (5), are represented as single conversion processes, the details of which require further study.

The linear increase in the concentration of  $H^+$  up to the stoichiometric amount as predicted from reaction (11) suggests that the elimination of the chlorine radical from DCP is not faster than that from CBQ,  $k_1 \leq k_3$ . The chlorine radical (Cl') eliminated can be removed immediately by  $H_2O$  to produce OH',  $H^+$  and Cl<sup>-</sup>. In view of the fact that CHQ was hard to detect in the reaction solution, the conversion of CHQ to CBQ should be very fast,  $k_2 > k_1$ . The presence of CBQ in the reaction solution implies that  $k_3 < k_2$ . The photo-oxidative cleavage of hydroxybenzoquinone ( $k_4$ ) must be faster than the final mineralization of RCOOH ( $k_5$ ) to produce CO<sub>2</sub> and H<sub>2</sub>O, otherwise RCOOH could not be accumulated in the reaction solution. Thus, the sequence of the reaction rates of the five steps can be given as  $k_1 \leq k_3 < k_2$ ,  $k_2, k_4 > k_5$ .

# Effects of O2 and adsorbed Cu2+

Fig. 6 shows the photodegradation of DCP in TiO<sub>2</sub> suspensions with the addition of  $Cu^{2+}$  ions. In the absence of air, the reaction rate was very low, only about 15% of the DCP present was mineralized during 200 min of irradiation. During the same period, trace amounts of CBQ and H<sup>+</sup> were formed in the reaction solution. Once the system was saturated with air, the concentration of DCP decreased very rapidly, accompanied by a sharp increase in the concentration of H<sup>+</sup>. The mineralization rate increased by nearly 30



**Fig. 6** Effects of oxygen on the photodegradation of DCP in the TiO<sub>2</sub> suspension with addition of  $Cu^{2+}$  ions. Initial conditions: [DCP] =  $2.5 \times 10^{-4}$  mol  $1^{-1}$ , 3 g  $1^{-1}$  TiO<sub>2</sub>, [Cu<sup>2+</sup>] =  $2.5 \times 10^{-5}$  mol  $1^{-1}$ , pH 6.1. See text for details. (•) DCP, ( $\Delta$ ) CBQ, ( $\Box$ ) H<sup>+</sup>.

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times. Therefore, it can be seen that oxygen is essential for the photodegradation of DCP. Many researchers consider the role of oxygen only to involve electron scavenging.<sup>6,9a,14,30</sup> This is obviously not supported by the experimental results shown in Fig. 6. Oxygen is also involved in the formation of the hydroxyl radicals via reaction with e<sup>-</sup> and H<sup>+</sup> [eqn. (3)-(10)]. This is in agreement with the results obtained by Soria et al.,<sup>31</sup> who investigated the radicals formed during the photo-oxidation of phenol on TiO<sub>2</sub> particles by electron paramagnectic resonance methods and found that most of the HO<sub>2</sub> species are generated by oxygen trapping of the conduction-band electrons [eqn. (3) and (4)]. Any factor favourable for the migration of the photogenerated electrons from the bulk of the TiO<sub>2</sub> particle to the oxygen at the interface should increase the rate of photodegradation of the organic substrates.

It was found in our experiments that the  $Cu^{2+}$  ion can be strongly adsorbed on the surface of the  $TiO_2$  particle.<sup>32</sup> The  $Cu^{2+}$  ion adsorbed on the  $TiO_2$  particle ( $\equiv Ti-O-Cu^+$ ) can trap an electron to form  $\equiv Ti-O-Cu$ ,

$$\equiv Ti - O - Cu^{+} + e^{-} \rightarrow \equiv Ti - O - Cu$$
(12)

This is understandable considering the high redox potential of  $E^{0}(\text{Cu}^{2+}/\text{Cu}^{+}) = 0.17 \text{ V} (vs. \text{ NHE})^{33}$  compared with the conduction-band potential of TiO<sub>2</sub>,  $E_{\text{CB}} = E_{\text{CB}}^{0} - 0.059 \text{pH V}$  (vs. NHE),<sup>34</sup> where  $E_{\text{CB}}^{0}$ , the conduction-band potential at pH 0, is in the region of -0.1 V (vs. NHE).  $\equiv \text{Ti}-\text{O}-\text{Cu}$  is unstable and can then be reoxidized by oxygen at the interface,

$$\equiv Ti - O - Cu + O_2 \rightarrow \equiv Ti - O - Cu^+ + O_2^{-1}$$
(13)

The high redox potential,  $E^{0}(O_{2}/OH^{-}) = 0.41 \text{ V} (vs. \text{ NHE})$ ,<sup>33</sup> makes it possible for this reaction to proceed. It seems possible that  $\equiv$ Ti-O-Cu could accept another electron to produce metallic copper on the TiO<sub>2</sub> particle surface because of the favourable redox potential of  $E^{0}(Cu^{+}/Cu) = 0.52 \text{ V} (vs. \text{ NHE})^{33}$  with respect to the conduction-band potential of TiO<sub>2</sub>. However, some controlled experiments have indicated that the Cu<sup>2+</sup> ion is very hard to reduce to copper metal. Similar results have been obtained by Herrmann *et al.*,<sup>35</sup> who found that copper could not be photodeposited onto TiO<sub>2</sub> from Cu<sup>2+</sup> ions. This may be due to the reoxidation of the deposited copper by the valence-band hole, the oxidizing potential of which is very positive, *ca.* 2.4 V *vs.* SCE.<sup>36a</sup>

From the above discussion, an induction period in the photodegradation process should be expected in the presence of  $Cu^{2+}$  ions. The higher the concentration of  $Cu^{2+}$  ions added, the longer the induction period (see Fig. 7). During the induction period the photodegradation rate is quite low and tends to zero with the addition of Cu<sup>2+</sup> at higher concentrations. In such cases, it is no longer reasonable to use the initial reaction rate to study the effects of the Cu<sup>2+</sup> ion on the photodegradation kinetics of DCP. For the overall mineralization reaction, the half-life (i.e. the time necessary to reduce half of the initial reactant) of the reaction can be used for this purpose. Fig. 8 shows the dependence of the half-life  $(t_{1/2})$  on the concentration of Cu<sup>2+</sup> ions; an optimum concentration of ca.  $2.5 \times 10^{-5}$  mol l<sup>-1</sup> was obtained. In fact, if one focuses on the degradation rate at  $t_{1/2}$ , one can see that increases in Cu<sup>2+</sup> concentration always increase the reaction rate, as shown in Fig. 8. This can be explained by the more efficient trapping of the photogenerated electron owing to the higher adsorption coverage of Cu<sup>2+</sup> and the resulting more efficient transfer of the electron from the TiO<sub>2</sub> particles to the oxygen molecule.

Since the photogenerated electrons can be effectively scavenged by the adsorbed  $Cu^{2+}$  ions, the photogenerated holes left in the valence band would therefore have more



Fig. 7 Photodegradation of DCP as a function of illumination time in TiO<sub>2</sub> suspensions containing  $2.5 \times 10^{-4}$  mol  $1^{-1}$  DCP and 3 g  $1^{-1}$ TiO<sub>2</sub>. The concentrations of Cu<sup>2+</sup> ions (mol  $1^{-1}$ ) added as cocatalyst are: ( $\bullet$ ) 0, (+)  $5.0 \times 10^{-6}$ , ( $\pm$ )  $2.5 \times 10^{-5}$ , ( $\Box$ )  $1.0 \times 10^{-4}$ , ( $\triangle$ )  $5.0 \times 10^{-4}$ .

opportunity to participate in the oxidizing reactions. Unfortunately, however, in anaerobic conditions the DCP mineralization rate was quite low, as shown in Fig. 6. This indicates that the formation of hydroxyl radicals via reactions (1) and (2) under such conditions is almost impossible. A plausible explanation for this could be the reoxidation of  $\equiv$ Ti-O-Cu formed in eqn. (12) by the photogenerated hole, which is believed to be trapped at the surface of the TiO<sub>2</sub> particles.<sup>37</sup>

$$\equiv Ti - O - Cu + h^+ \rightarrow \equiv Ti - O - Cu^+$$
(14)

Eqn. (12) and (14) form a short circuit reaction for  $Cu^{2+}$ ,<sup>36b.c</sup> thus enhancing the recombination of photogenerated electrons and holes, and retarding the photodegradation of DCP [Fig. 9(*a*)]. In aerobic conditions, however, oxygen captures an electron from  $\equiv$ Ti-O-Cu to prevent it from recombining with the surface-trapped hole [Fig. 9(*b*)]. The superoxide ion (O<sub>2</sub><sup>•-</sup>) thus formed can then react with H<sup>+</sup> to produce HO<sub>2</sub><sup>•</sup> and other oxidizing species [eqn. (3)–(10)]. The Cu<sup>2+</sup> ion in the form of  $\equiv$ Ti-O-Cu<sup>+</sup> involved in such a process can be regarded as an electron-transfer relay which facilitates



**Fig. 8** Dependence of reaction half-life  $(t_{1/2})$  and the degradation rate at  $t_{1/2} (r_{1/2})$  on the concentration of Cu<sup>2+</sup> ions added





Fig. 9 Schematic diagram illustrating the effects of adsorbed  $Cu^{2+}$  ions on the charge transfer at the interface of TiO<sub>2</sub> particles under anaerobic (a) and aerobic (b) conditions

the migration of the electron from the  $TiO_2$  particle to the  $O_2$  molecule. In one of our previous papers,<sup>24c</sup> a similar electrontransfer relay was found in methyl viologen,  $MV^{2+}$ , which successfully mediated the electron transfer from the ZnS colloid to the adsorbed methyl orange molecule. It can be seen that the presence of oxygen increases the opportunity for the photogenerated charge carriers (holes and electrons) to participate in the interfacial redox reactions. A hole that has avoided recombination can therefore oxidize surface-bound hydroxy groups or water molecules to produce hydroxyl radicals [eqn. (1) and (2)].

### Effects of Surface Charge on Photodegradation Rate

The surface charge is an essential factor affecting the rate of transfer of the photogenerated electron and hole from the bulk of the TiO<sub>2</sub> particle to the redox species at the interface.<sup>24</sup> When anions are adsorbed onto the TiO<sub>2</sub> surface, the transfer of an electron will be inhibited by the electrostatic repulsion of the negative electric field around the TiO<sub>2</sub> particle and the hole transfer will be enhanced. Fig. 10 shows a comparison between the photodegradation of DCP without any added ions and that with the addition of  $10^{-4}$  mol  $1^{-1}$  $HPO_4^{2-}$ , which is known to be strongly bound to the surface of TiO<sub>2</sub>.<sup>38</sup> The reaction rate was strongly decreased by the addition of  $HPO_4^{2-}$ , especially in the initial period. However, when the TiO<sub>2</sub> surface is positively charged by the addition of cations, a positive electric field will be formed around the TiO<sub>2</sub> particle. This aids the migration of the photogenerated electron to the surface of the TiO<sub>2</sub> particles and is detrimental to the migration of the hole. Fig. 10 also shows the effects of addition of  $Zn^{2+}$  ions, which cannot act as an electron-transfer relay in the same way as the  $Cu^{2+}$  ion owing to the much more negative redox potential of  $E^{0}(Zn^{2+}/Zn) = -0.76 \text{ V}$  (vs. NHE).<sup>33</sup> As in the case of Cu<sup>2+</sup> ions, there was also an induction period for  $Zn^{2+}$  ions. This indicates that in the initial period of irradiation, most of the electrons escaping from the recombination are first trapped at the surface of the TiO<sub>2</sub> particles as a result of the Coulombic attraction of the positive electric field. After the induction period, the reaction rate tends to be higher than that in the case without added ions. On the bases of these results and the above discussion, one can see that the surface charge of TiO<sub>2</sub>



**Fig. 10** Effects of the addition of ( $\bigcirc$ )  $Zn^{2+}$  or (+)  $HPO_4^{2-}$  ions ( $10^{-4}$  mol  $1^{-1}$ ) on the photodegradation of DCP in TiO<sub>2</sub> suspensions containing 2.5 ×  $10^{-4}$  mol  $1^{-1}$  DCP and 3 g  $1^{-1}$  TiO<sub>2</sub>; ( $\triangle$ ) no added ion

mainly affects the photodegradation rate through the migration of the photogenerated electron from the  $\text{TiO}_2$  particle to the oxygen molecule, and the behaviour of the photogenerated hole involved in the formation of OH' [eqn. (1) and (2)] is little affected. This is in agreement with the results obtained by Micic *et al.*,<sup>37</sup> who found that the photoinduced holes were located as deep traps on the surface of the aqueous TiO<sub>2</sub> colloid and did not convert into other radicals, such as OH'.

It should be emphasized here that in the case of the addition of  $Cu^{2+}$  ions, the DCP photodegradation rate can also be enhanced by the positive surface charge of the adsorbed  $Cu^{2+}$  ions, in addition to their specific role as an electrontransfer relay.

The effects of the surface charge on the mineralization rate can be further confirmed by the results obtained at different initial pHs of the reaction solution. The surface groups of  $TiO_2$  are amphoteric and the surface acid-base equilibria can be written as,<sup>28</sup>

$$\equiv$$
Ti $-OH_2^+ \rightleftharpoons \equiv$ Ti $-OH + H^+; pK_{a(1)} = 4.95$  (15)

$$\equiv Ti - OH \rightleftharpoons \equiv Ti - O^- + H^+; \quad pK_{a(2)} = 7.8 \quad (16)$$

The zero point of charge  $(pH_{ZPC})$  for the surface of TiO<sub>2</sub> can be calculated as:

$$pH_{ZPC} = [pK_{a(1)} + pK_{a(2)}]/2 = 6.4$$

At  $pH > pH_{ZPC}$ , the particle surface will be negatively charged. The negative electric field thus formed around the TiO<sub>2</sub> particle is detrimental to the electron transfer, as in the case of adsorbed  $HPO_4^{2^-}$ . The mineralization under these conditions will be hindered as shown in Fig. 11. A decrease in the pH will cause a positive charge to form on the TiO<sub>2</sub> surface, which will favour an increase in the reaction rate as discussed for  $Zn^{2^+}$  (Fig. 11).

There remains the possibility that the effects of surface charge on the photodegradation rate are caused by an electrostatic interaction between DCP and the surface of TiO<sub>2</sub>, which causes DCP to be adsorbed. This explanation, however, was shown to be unreasonable by experiments in which the adsorption of DCP  $(2 \times 10^{-4} \text{ mol } 1^{-1})$  on TiO<sub>2</sub> (3 g l<sup>-1</sup>) was attempted under different conditions, such as at various pH (4–10) and with the addition of DCP was not observed under any conditions.<sup>29</sup> Similar results have also been



Fig. 11 Dependence of  $t_{1/2}$  on the pH of the reaction suspension containing  $2.5 \times 10^{-4}$  mol  $l^{-1}$  DCP and 3 g  $l^{-1}$  TiO<sub>2</sub>

obtained by Okamoto et al.,8 who found that phenol was hardly adsorbed at all on TiO<sub>2</sub> powder. This can be explained by considering the polarity of phenols. Huang and co-workers<sup>39</sup> investigated the adsorption of some chlorinated phenols onto hydrous CdS and ZnS. They found that the non-specific hydrophobic interaction is the determining driving force for the adsorption. For the TiO<sub>2</sub> powder, the hydrophilic surface (bound with hydroxy groups) makes it difficult for DCP to be adsorbed, i.e. DCP favours hydrophobic adsorption.

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