Photomineralisation of 4-chlorophenol sensitised by TiO_2 thin films

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Abstract

The results of a study of the oxidative mineralisation of 4-CP by oxygen, sensitised by thin films of Degussa P25 TiO_2, are reported. The films are used under conditions in which the kinetics of photomineralisation are independent of mass transfer effects and stable towards repeated irradiation. Using a TiO_2 film, the process goes through the same mechanism as a TiO_2 dispersion, generating the same intermediates, namely: 4-chlorocatechol and hydroquinone. The kinetics of photomineralisation show clear differences between a TiO_2 film and a dispersion. With TiO_2 films the initial rate of photomineralisation is strongly dependent upon photocatalyst loading, (units; $g\,dm^{-3}$) reaching a distinct maximum, which appears to be associated with the formation of a monolayer of aggregated particles – the diameter of the aggregated particles is estimated as $0.44\,\mu m$. A simple 2D model is presented to help illustrate the features of such a system. With TiO_2 dispersions the rate usually reaches a plateau at ca. $0.5\,g\,dm^{-3}$ of TiO_2. For TiO_2 films the initial rate depends directly upon the incident light intensity, implying that the photocatalytically active particles are under low illumination conditions, partially shielded by the other particles making up each aggregated particle. In contrast, with TiO_2 dispersions R_i depends upon $I^{0.64}$, implying that the different light intensities used spanned both the high ($R_i \propto I^{1/2}$) and low ($R_i \propto I$) intensity kinetic regions. The kinetics of photomineralisation of 4-CP, sensitised by TiO_2 films obey the same Langmuir–Hinshelwood expressions as found in most semiconductor photocatalyst work conducted with TiO_2 dispersions. However, in a study of the variation R_i as a function of [4-CP] and [O_2] the values for the maximum rates were larger, and those for the apparent Langmuir adsorption coefficients were smaller, than those found for TiO_2 dispersions. © 1998 Elsevier Science S.A. All rights reserved.

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1. Introduction

The use of semiconductors as photocatalysts for a variety of processes, including the oxidative mineralisation of organic pollutants in water or in the gas phase, destruction of bacteria and reduction of trace metals, continues to be an active field of research [1]. Titanium dioxide is the current preferred semiconductor, due to its chemical and biological inertness, cheapness and reasonable photocatalytic activity, especially when used in its anatase form. Although much of the early work on semiconductor photocatalysis used the semiconductor in the form of a dispersed powder, in any practical device the semiconductor is likely to be used in the form of a film on an inert support, such as glass. As a consequence, there is an increasing interest in the photocatalytic action of semiconductor thin films, with TiO_2, once again, appearing to be the semiconductor of choice.

Thin films of TiO_2 on glass can be prepared by a number of different methods [1]. The simplest is to use as a starting material a concentrated (0.5–5% w/v) aqueous dispersion of Degussa P25 TiO_2 (effectively the bench standard TiO_2 photocatalyst for powder dispersion work) to 'wash' the glass [2,3]. The coat is then usually dried, either with a hairdryer or in an oven (e.g. at 150°C for 1 h). After each wash, poorly attached particles are washed off. With each wash, more TiO_2 sticks to the glass and, less effectively, to the emerging TiO_2 layer. Thus, using this 'wash coat' technique, a series of stable layers of TiO_2 can be built up and films of different opacity can be generated. Most other methods focus on the production of less opaque, usually less photocatalytically active, nanocrystalline thin films of TiO_2 via the alkaline hydrolysis of titanium (IV) species, such as alkoxides or chlorides [1,2,4].

One of the problems with research into semiconductor photocatalysis is the difficulty in comparing results obtained by the different research groups. This problem arises because in semiconductor photocatalysis the rate of reaction depends upon many different parameters including reactor geometry, nature and concentration of the semiconductor, nature and concentration of the electron acceptor (usually oxygen), nature and concentration of oxidisable 'test'

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substrate, light intensity, temperature, pH, and the presence of competitive interfering species. Several groups, including our own, have suggested that such comparisons would be made easier if, along with the results of a particular study, those derived from a standard test system were also reported by the investigating research group [1]. We have proposed that such a test system for photocatalytic studies conducted in an aqueous solution could be: 4-chlorophenol (10^{-3} mol dm^{-3}), TiO$_2$ (Degussa P25, 0.5 g dm^{-3}), O$_2$ (1.3×10^{-3} mol dm^{-3}, that is, 100% saturated with O$_2$) and thermostatted at 30°C [1].

The photo-oxidative mineralisation of 4-chlorophenol (4-CP) by oxygen and sensitised by TiO$_2$, can be summarised as follows:

$$ClC_6H_4OH + (13/2)O_2 \overset{hv \geq 3.2eV}{\underset{TiO_2}{\longrightarrow}} 6CO_2 + 2H_2O + HCl \quad (1)$$
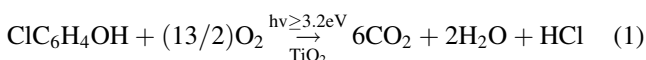
This process has been the subject of numerous, detailed, characterisation studies, the major ones which utilise Degussa P25 TiO$_2$ dispersions are summarised in Table 1 [5–14]. As a result of this work a great deal is known about this system, especially when TiO$_2$ is used in the form of a dispersed powder. With increasing emphasis in semiconductor photocatalysis on immobilised thin film semiconductor systems there is need to establish a standard, easily reproduced test system for thin film semiconductor photocatalysis.

Several studies of Eq. (1) have been conducted already using TiO$_2$ film photocatalysts [15–19]. Bideau and his co-workers [20] have recently provided a brief overview of the range of photoreactors based on immobilised TiO$_2$ films which have been reported. In many of these photoreactors the photocatalyst was used in a flow system, in which the aqueous solution containing the 4-CP was flowed over the TiO$_2$ film; the latter was usually coated over the walls of narrow glass tubing (i.d. = 4–6 mm typically). In such systems it is usually found that the overall rate of reaction depends markedly upon the flow rate of the solution. The latter finding implies that the overall rate of reaction is, at least in part, controlled by the rate of solution-to-catalyst diffusion/convection mass transfer. (In contrast, it is well established that there is normally no such dependence of rate upon diffusion/convection mass transfer for TiO$_2$ dispersions of <1 g dm^{-3}.) As a result, in such work, it is difficult to assign fundamental meaning to any observed parameters without considering the influence of both mass transfer and chemical kinetics [21].

In order to establish the fundamental chemical kinetic processes associated with TiO$_2$ films it is necessary to carry out the work under reaction conditions in which the diffusion/convection mass transfer processes are far from rate-determining. This can be achieved using very well agitated solutions. It would appear appropriate and useful, therefore, to establish the basic characteristics of Eq. (1) using a thin film of Degussa P25 TiO$_2$ on glass, deposited by the simple wash coat method, under conditions in which the rate of

disappearance of 4-CP is independent of solution-to-particle mass transfer effects. This paper reports the initial findings of such a study.

2. Experimental

2.1. Materials

The TiO$_2$ used throughout this work was Degussa P25. The 4-CP (99%), along with all other chemicals, were obtained from Aldrich and were used as received. The water used to make up solutions was deionised and doubly distilled. All gases used were obtained from BOC.

2.2. Methods

Details of the photochemical reactor have been reported elsewhere [7,8]. In brief, the photoreactor comprised two half cylinders, each containing six 8W Black Light UVA lamps set against a half-cylinder aluminium reflector. Each of the lamps (Coast Air$^®$) emitted a broad range of UVA light, typically 320–390 nm with λ_{max} at 355 nm; the number of UVA photons emitted per lamp into the 100 cm^3 reaction solution was found to be 6.4×10^{16} photons s^{-1} per lamp by ferrioxalate actinometry. Light intensity measurements inside the photoreactor with a TiO$_2$ dispersion or coat were made with a calibrated power meter (Lidam Scientific).

The photochemical reaction vessel was placed in the centre of the photochemical reactor. The vessel comprised a 125 cm^3 borosilicate glass Dreschel bottle (i.d. 4 cm) fitted with a rubber septum to allow samples from either the headspace or the reaction solution to be withdrawn. The vessel had an outer water jacket that was always thermostatted at 30°C. The vessel was coated with TiO$_2$ using a wash coat procedure. The TiO$_2$ slurry used to coat the inside of the glass reaction vessel was 5% (w/v). After leaving the photoreactor in contact with the stirrer coating slurry for 30 min, the slurry was drained off, dried in a stream of air and then dried in an oven at 100°C for 1 h. The coat was then washed with excess water to remove any poorly attached TiO$_2$ and dried again in a stream of dry air. The process was repeated as required to produce up to six coats of TiO$_2$.

The amount of TiO$_2$ attached to the glass for 1–6 coats was determined spectrophotometrically, using a simple procedure involving washing the coating off the glass with a strong alkaline solution and measuring the 'absorbance' of the resulting alkaline TiO$_2$ dispersion at 380 nm, described in detail elsewhere [21]. The results of this work are illustrated in Fig. 1, a plot of the amount of TiO$_2$ adsorbed onto glass using the wash coat procedure (units: mg cm^{-2}) versus the number of wash coats laid down. The results show that the amount of TiO$_2$ deposited by the wash coat method increases with an increasing number of wash coats. From the results illustrated in Fig. 1 it also appears that as more and more TiO$_2$ is deposited the amount of TiO$_2$ that stays to form

Table 1
Major studies on the photomineralisation of 4-CP sensitised by Degussa P25 TiO2 dispersions

$[TiO_2]/(g\ dm^{-3})$	$K_{4\text{-}CP}/$ $(10^3\ dm^3\ mol^{-1})$	$K_{O_2}/$ $(kPa)^{-1}$	θ (as in I^θ)	$I/(10^{15}$ photons s$^{-1})$	FQE (or δ)	pH	$E_a/(kJ\ mol^{-1})$	Comments	Ref.
2	–	–	–	–	–	4.5–12	–	One of the first reported photomineralisation of 4-CP by TiO2 studies	[5]
0–4; typically 2	16.6	–	0.5	3–90; typically 90 note: per cm^{-2}	0.009–0.013	–	5.5	Also shows that the process obeys the reaction stoichiometry of Eq. (1), the photocatalyst exhibits little evidence of photochemical aging and that the major intermediates are HQ, BQ and 4-CC with HQ>>BQ>>4-CC	[6]
0.5	5	0.044	0.74	550	0.011	2	16	Also identifies the major intermediates as: 4-CC and HQ, where 4-CC>HQ>>BQ and $K_{4\text{-}CP}$(dark) 130 dm^3 mol^{-1}	[7,8]
2	0 at high I	–	–	17–2100	0.024 at high I and 0.2 at low I	5–6	–	Langmuir–Hinshelwood kinetics only observed at low light intensites; at high intensity rate independent of [4-CP]. Suggested that the latter effect was due to O2 becoming the rds.	[9]
0.05–1	–	–	–	1100	–	6	–	Both 4-CP and HQ produced (typically 4-CC>>HQ), but [4-CP]/[HQ] decreases, and R_i decreases markedly with increasing [TiO2]. Reactor configuration and catalyst loading are identified as having a significant effect on product distribution. Suggested that the overall process involves a combination of hydroxyl radical oxidation, direct electron transfer and surface chemical reactions. A mechanistically based model is presented.	[10–12]
5	24^a	–	–	1500	0.007^a	3	–	Both Degussa P25 and Hombikat TiO2 were used in this study and most kinetic data reported were for the latter (data denoted by ^{a}). However, the paper reports the results of an extensive study of the intermediates generated as a function of pH using Degussa P25. At pH 3 HQ, BQ and 4-CC are generated, between pH 5–11, HHQ, HQ, BQ, HBQ and THB are the major intermediates, increasing in level with increasing pH (especially THB). The HQ/BQ system appears to act as a short-circuit electron relay. A comprehensive degradation mechanism is proposed.	[13]
0.025–1, typically 1	1	–	0.8	1100^b	0.012 at 360 nm	–	–	^{b}Although the lamp output is quoted as 1.85 μergs s^{-1} this is almost certainly meant to be 1.85 μE s^{-1}, as in previous work from this group. $K_{4\text{-}CC}$ (dark) was found to be 130×10^3 dm^3 mol^{-1}. Rate of disappearance of 4-CP largely independent of [TiO2]	[14]

FQE: formal quantum efficiency=rate of reaction/(incident light intensity) [1].
Intermediates abbreviations: hydroquinone (HQ), benzoquinone (BQ), 4-chlorocatechol (4-CC), hydroxy hydroquinone (HHQ), Hydroxybenzoquinone (HBQ), trihydroxybiphenyl (TBP).
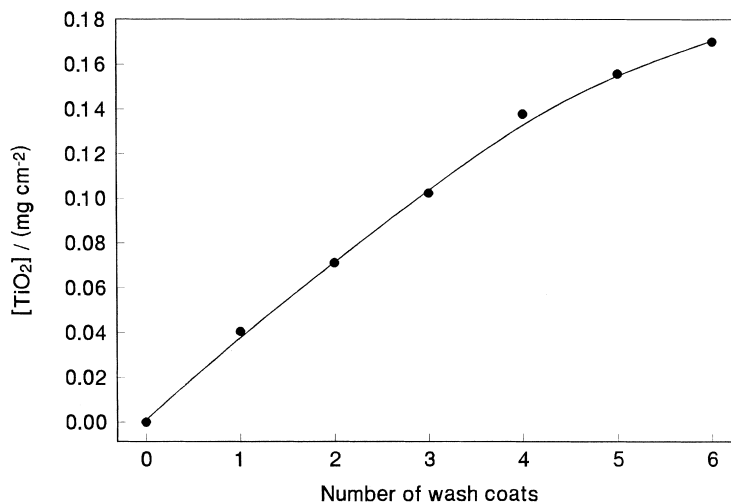
Fig. 1. Amount of TiO_2 deposited cm^{-2} of glass, determined spectrophotometrically [22], versus the number of wash coats.

a stable layer decreases. The geometric surface area of the TiO_2 film exposed to the reaction solution was 120.5 cm^2.

A typical reaction solution placed in the photochemical reaction vessel comprised 10^{-3} mol dm^{-3} 4-CP dissolved in 100 cm^3 of 0.01 mol dm^{-3} $HClO_4$. The reaction solution was continually purged with oxygen and magnetically stirred (600 rpm) at least 15 min before, as well as throughout, any irradiation. When required, a variation in the dissolved oxygen concentration was achieved using a gas blender (Signal Instruments, model: Series 850) to provide purging N_2/O_2 gas streams of different levels of O_2, ranging from 5% to 100% O_2.

In the initial part of the work HPLC was used to monitor the temporal variations in [4-CP] and the major reaction intermediates. However, for most of the work described here HPLC was used to monitor primarily the temporal variations in [4-CP] with irradiation time. In any kinetic run, the initial rate of loss of 4-CP, that is, R_i, was calculated from the measured decay of [4-CP] with irradiation time over the first 20% of reaction. Samples were taken from the reaction solution using a hypodermic syringe fitted with a 0.2 μm in-line filter to remove the TiO_2 particles. Details of the HPLC apparatus are described elsewhere. In experiments where CO_2 evolved during an irradiation was measured, the system was sealed and the gas phase (41 cm^3) sampled, using a gas-tight syringe, and analysed by GC, details of which are described elsewhere [7,8].

3. Results and discussion

3.1. Initial experiments: Relative photocatalytic activity, stirrer speed dependence and stability,

Unless stated otherwise, in all experiments the 100 cm^3 reaction solution was oxygen-saturated, stirred at 600 rpm, set at pH 2 using $HClO_4$ and contained 10^{-3} mol dm^{-3} 4-CP.

Table 1 lists some of the characteristics of the mineralisation of 4-CP, via reaction (1), photosensitised by dispersions of Degussa P25 TiO_2. In such work, the initial rate, R_i, of loss of 4-CP generally increases with increasing [TiO_2], reaching a broad maximum at ca. 0.5 g dm^{-3}. Above this level, many find that the rate is independent of [TiO_2]. At [TiO_2] levels ≥ 0.5 g dm^{-3} the dispersion is strongly absorbing to UV photons; for a TiO_2 dispersion of 0.5 g dm^{-3} the measured transmittance is ca. 0.5 in the centre of our photoreaction vessel and similar values have been noted by others [14]. It is usually assumed that at and above the broad maximum level of TiO_2 the amount of UV photons absorbed by the dispersion is at a maximum and thus the value of R_i is at a maximum.

A three-coat TiO_2 film coat, is a film generated by exposing the glass to the coating slurry three times; this level of coating was found to be optimum (vide infra) and used throughout, unless stated otherwise. It might be thought initially that TiO_2 films are likely to be much less photoactive than their dispersion counterparts, since such films will lose a sizeable fraction of the incident light through scattering and losses at the glass/TiO_2 film interface. In addition, the films will usually use significantly less TiO_2 than an optimum dispersion, thus the total available surface area and UV-photon absorbing potential will be less. However, it does not appear to be the case that TiO_2 films are much less photocatalytically active than their dispersion counterparts. Thus, we find the optimum-coated TiO_2 film (e.g. three coats; [TiO_2]=0.102 mg cm^{-2}) of Degussa P25 is about twice as photocatalytically active than a 0.5 g dm^{-3} dispersion of the same photocatalyst, as indicated by the [4-CP] versus time profiles in Fig. 2. In the latter system the total amount of TiO_2 in the film is four times less than that in a 0.5 g dm^{-3} dispersion. However, the percentage transmittance in the centre of the photoreactor is 16%, that is, ca. three times less than the dispersion. Although a lot of the light absorbed by a TiO_2 film will be reflected and scattered,
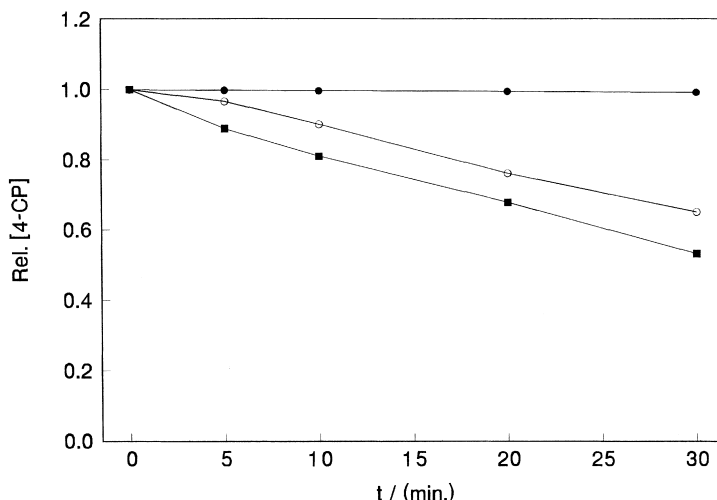
Fig. 2. Observed variation in [4-CP] as a function of time under standard conditions (i.e., 10^{-3} mol dm^{-3} 4-CP, 30°C, 600 rpm stirrer speed) with the following conditions with respect to TiO$_2$: none (●), 0.5 g dm^{-3} dispersion (○) and a 3-coat layer (■).

overall it appears that sufficient quantity of light is absorbed in a three-coat TiO$_2$ film to render it more photocatalytically efficient at mediating Eq. (1) than four times more TiO$_2$ used in dispersion form.

Initial experiments showed that the initial rate of Eq. (1) was independent of stirrer speed over the range 400–800 rpm, for both TiO$_2$ films and dispersions. Previous experiments carried out by our group [7,8] and others [6] established that TiO$_2$ dispersions show little evidence of photochemical wear with repeated use; similar results were obtained for TiO$_2$ films. For example, a three-coat TiO$_2$ film showed no evidence of loss of photocatalytic activity in mediating Eq. (1) (initial [4-CP]=10^{-3} mol dm^{-3} for each irradiation) when used six times in succession.

3.2. Reaction intermediates

HPLC can be used to probe not only the loss of 4-CP, but also the generation of any major intermediate. In addition the CO$_2$ generated via Eq. (1) can be monitored using GC. In a previous work using TiO$_2$ dispersions we found 4-chlorocatechol (4-CC), hydroquinone (HQ) and benzoquinone (BQ) to be the major intermediates under the reaction conditions (i.e. pH 2, [TiO$_2$] = 0.5 g dm^{-3}), with [4-CC]>[HQ]>>[BQ]. In a detailed study of Eq. (1) Bahnemann and his co-workers [13] established that the intermediate product distribution arising from Eq. (1) is very pH-dependent. Under alkaline conditions, 4-CC is not usually found in significant amounts and more hydroxylated species, such as hydroxyhydroquinone (HHQ), hydroxybenzoquinone (HBQ) and trihydroxybiphenyl (TBP) are found in significant amounts, in addition to HQ and BQ. Such species are more stable, and less strongly absorbed, the greater the alkalinity of the reaction solution. Under the very acidic conditions employed in this study, 4-CC appears to be the most stable of the reaction intermediates.

The generation of the observed reaction intermediates can be readily explained though reaction schemes which involve OH· radical attack of 4-CP, initially to give the 4-chlorodihydroxycyclodienyl radical, leading on to the generation of 4-CC, HQ and BQ as intermediates to the eventual mineralisation of 4-CP. The primary oxidant appears to be surface-absorbed OH· radicals generated through the reaction between a photogenerated valence-band hole and a surface-bound OH$^-$ or H$_2$O group. Other sources of oxidant, which may also make a significant contribution, include OH· radicals derived from the oxygen reduction side of the photomineralisation process and direct attack of the substrate by the photogenerated hole [1,23]. Fig. 3 illustrates a typical degradation reaction scheme for Degussa P25 TiO$_2$ power dispersions in acidic solution. Fig. 4 illustrates the temporal variations in: [4-CP], [4-CC], [HQ], [CO$_2$] and [total carbon content] observed using a three-coat TiO$_2$ film under standard reaction conditions. These results show that for such a TiO$_2$ film: (i) Eq. (1) is stoichiometric and (ii) the major reaction intermediates generated are the same as a TiO$_2$ dispersion. From the results in Fig. 4 it appears likely that the reaction scheme illustrated in Fig. 3 is also applicable to TiO$_2$ films of Degussa P25, that is, there is no major difference in the overall degradation reaction mechanism for films or dispersions of the same TiO$_2$ source material (Degussa P25 in this case).

3.3. Rate versus [TiO$_2$] and I

As noted above, the variation of R_i with [TiO$_2$] (units: g dm^{-3}) for TiO$_2$ dispersions usually has the form of a Langmuir–Hinshelwood kinetic expression, that is, $R_i = kK[\text{TiO}_2]/(1+K[\text{TiO}_2])$, with R_i appearing largely invariant at high [TiO$_2$]. There appears little in the literature about the variation in R_i with [TiO$_2$] (units: g cm^{-2}) for TiO$_2$ films. Fig. 5 illustrates the observed variation in R_i with
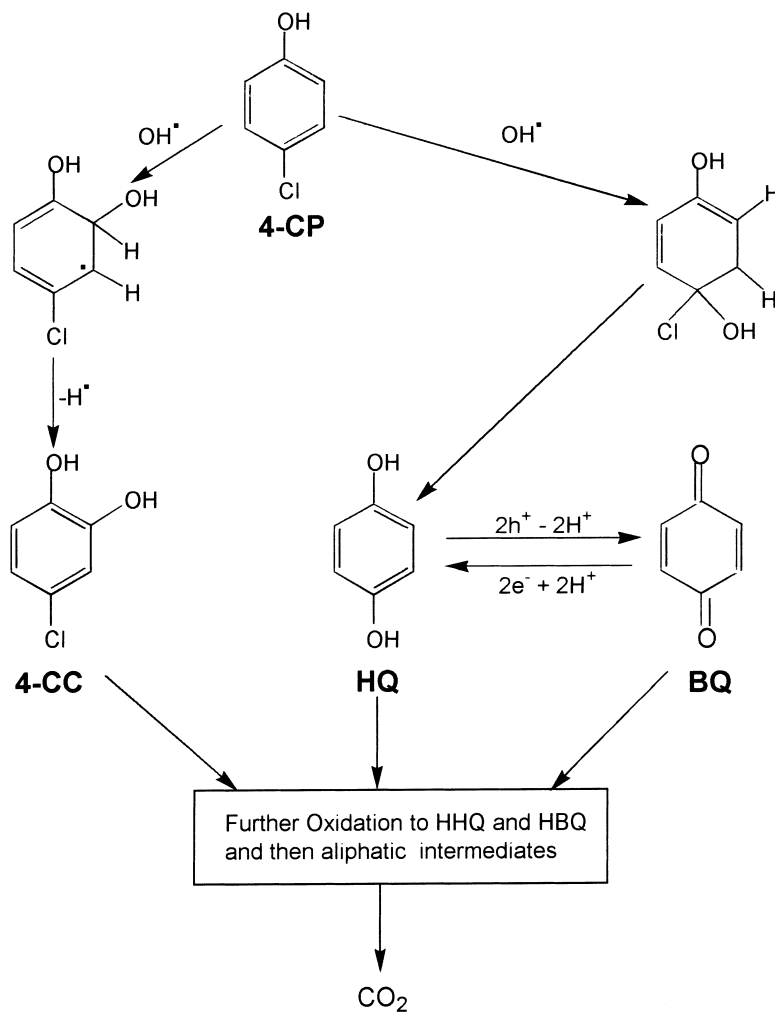
Fig. 3. Reaction scheme illustrating the likely mechanistic pathways to the formation of the major intermediates, 4-chlorocatechol (4-CC), hydroquinone (HQ) and benzoquinone (BQ), generated during the photomineralisation of 4-CP, sensitised by Degussa P25 TiO_2 under acidic conditions.
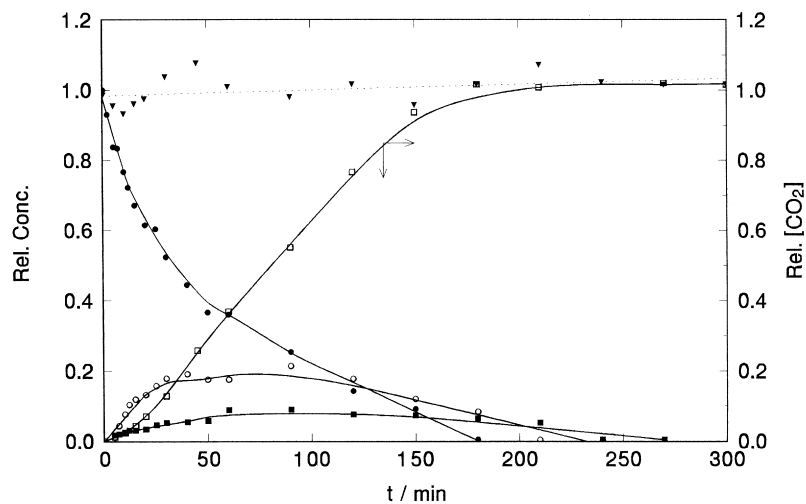
Fig. 4. Observed temporal variations in the relative concentrations of 4-CP ($\bullet$), CO_2 ($\square$), 4-CC ($\bigcirc$), HQ ($\blacksquare$) and total carbon concentration ($\blacktriangledown$) during the illumination of a standard 4-CP system, using a three-coat film of TiO_2 as the photocatalyst.
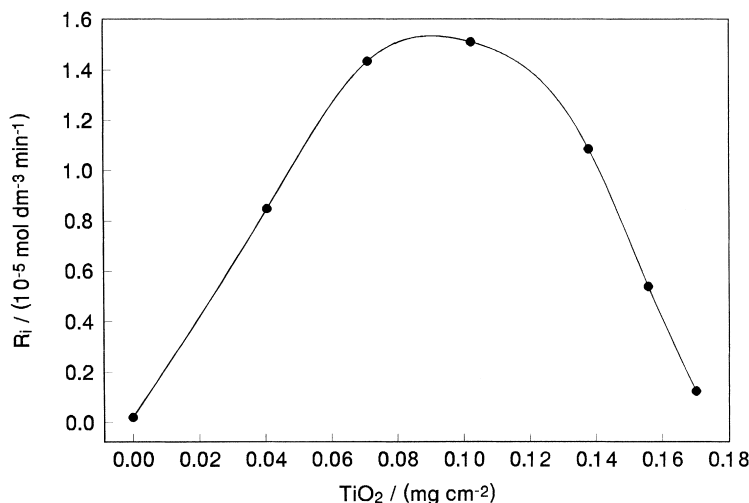
Fig. 5. Observed variation in the initial rate of disappearance of 4-CP, R_i, as a function of the amount of TiO_2 adsorbed on to 1 cm^2 of the glass inner face of the photoreactor. From left to right, the data correspond to 0–6 TiO_2 coats laid on by the wash coat procedure, respectively.

$[TiO_2]$ for TiO_2 films. Most striking about these results is the marked maximum in photocatalytic activity with increasing $[TiO_2]$. It is quite simple to generate profiles of a similar nature using a very simple two-dimensional kinetic model, which represents a rough approximation to the likely real system.

In our simple 2D kinetic model the following approximations are made: (i) the TiO_2 particles are squares, with a reactivity which depends upon the amount of light absorbed by the particle and the number of 'free' sides (i.e. not bound to glass or another particle); (ii) the particles stick at random onto a flat glass surface (300 sites) or to attached TiO_2 'particles'; (iii) the amount of light absorbed by a particle is a fixed fraction of the incident light intensity, progressively reduced with each particle it traverses and (iv) the incident light intensity is perpendicular to the flat glass surface. Fig. 6 illustrates the typical trend in the variation in R_i with $[TiO_2]$ predicted by this model; a trend which is similar to that observed for real TiO_2 films (compared with the data in Fig. 5). Fig. 6 also shows a set of five representative 'snapshots' of part of the surface as the number of TiO_2 'particles' is increased. From the results in Fig. 6, it appears that as the number of TiO_2 'particles' on the surface increases so does the rate increase, until typically a monolayer coverage is approached. Around the point of a monolayer coverage, the rate begins to decrease with increasing TiO_2 as the 'particles' next to the glass surface begin to screen the second and third layer of 'particles'. Of course, the shape of the model predicted R_i versus $[TiO_2]$ plot will depend very much on the fraction of incident light absorbed by each 'particle.' In Fig. 6 this fraction was set at 0.6; Fig. 7 illustrates the predicted profiles using this fraction set at: 0.9, 0.6, 0.4 and 0.05. From the results illustrated in the latter plot it can be seen that the higher the fraction: (i) the greater the rate in the early stages of monolayer coverage and (ii) the greater

the maximum rate and the nearer it is to a monolayer coverage.

Comparing these results, with those illustrated in Fig. 5 for the real system, it appears that the TiO_2 particles are strongly absorbing and that the near optimum rate after three coats ($[TiO_2] = 0.102$ mg cm^{-2}) is, most probably, associated with the formation of a monolayer of these strongly absorbing (and scattering) particles. This suggestion is not unreasonable, although the oft-quoted fundamental particle size of TiO_2 in Degussa P25 is 30 nm (diameter, d) – a size which provides a rationale for its incredible specific surface area of 50 m^2 g^{-1} ($=6/(d.\rho)$; ρ=3.8 g cm^{-3}). In practice these fundamental particles do not operate in isolation but rather as an irreducible complex of primary aggregates, typically 0.1 μm in diameter [1]. If the observed maximum rate of reaction (1) with $[TiO_2]$, illustrated in Fig. 5, is due to an approximate monolayer coverage of aggregate TiO_2 particles, that is, $[TiO_2] = [TiO_2]_{mono}$, then we can estimate the approximate size of these aggregate particles, by assuming that they are spherical in shape and closely packed, like hexagons (of area$=2 \cdot \sqrt{3} \cdot r^2$), on the assumed smooth glass surface. It can be shown that the diameter, d', of such aggregates is given by the expression:

$$d' (\text{in cm}) = 3 \cdot \sqrt{3} \frac{[TiO_2]_{mono}}{(\pi \cdot \rho)} \qquad (2)$$

Assuming, $[TiO_2]_{mono} = 0.102 \times 10^{-3}$ g cm^{-2}, then, from Eq. (2), $d' = 0.44$ μm, which does not appear unlikely, given that the basic aggregate particle size is ca. 0.1 μm. The approximate transmittance of such a monolayer can be easily estimated, since it should act as an absorbing solid film of TiO_2 of thickness β (units: cm), where $\beta = [TiO_2]_{mono}/\rho$, and in a semiconductor the extinction of light follows the exponential law, $I = I_o.\exp(\alpha \cdot \beta)$, where α is the reciprocal absorption length; $\alpha = 1.6 \cdot 10^4$ cm^{-1} for
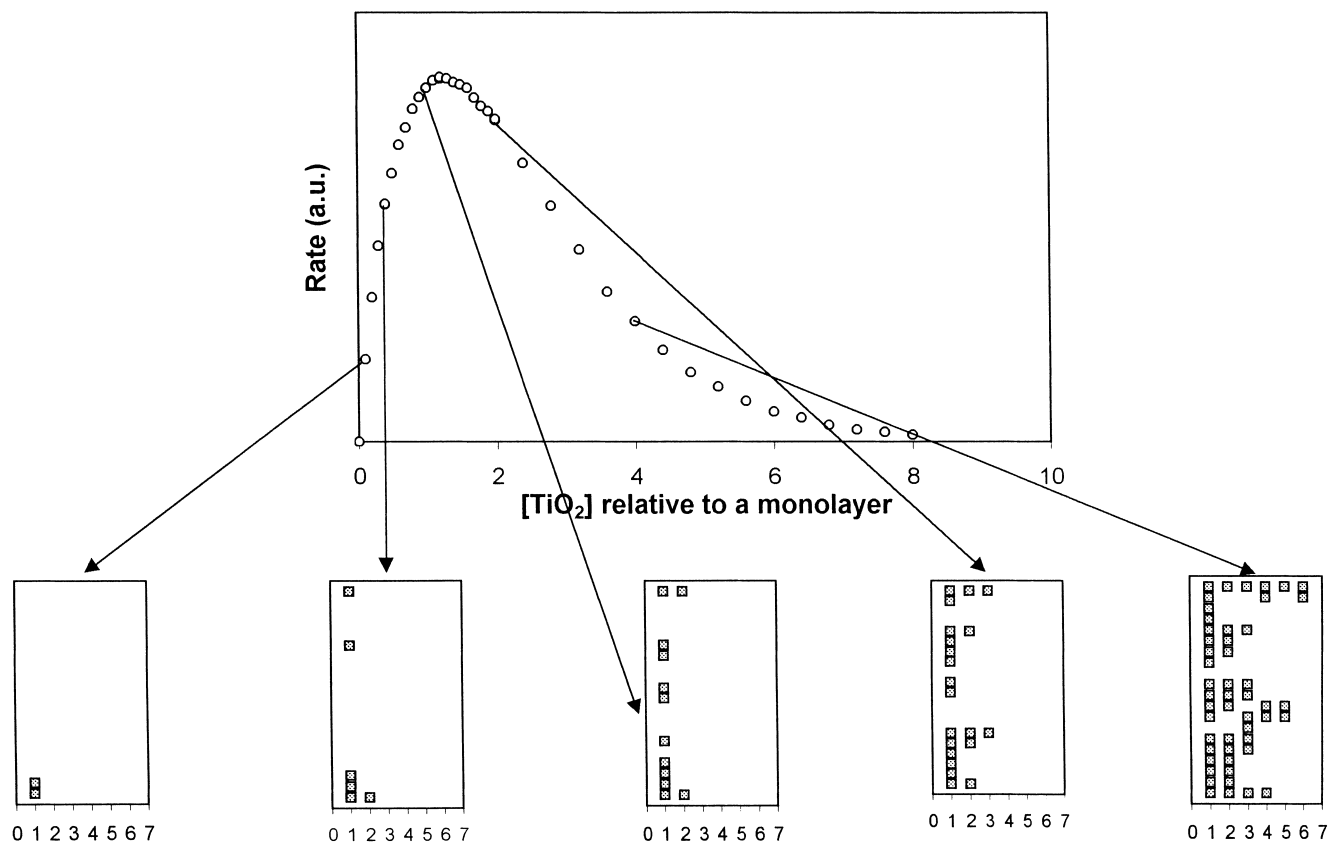
Fig. 6. Rate of photocatalysis versus number of TiO_2 monolayers predicted by a simple, rough 2D kinetic model. In this model the semiconductor particles are envisaged as squares with a reactivity which depends upon the number of free (unbound) faces and the fraction of incident light, perpendicular to the TiO_2 film, absorbed by each particle. In the example shown the fraction is set at 0.60. The five smaller diagrams illustrate the typical distribution of 'particles' at different monolayer coverage. The x-axis gives the monolayer number and the glass face of the photoreactor is represented by the y-axis at the 'zero-th' (x=0) layer. The five diagrams represent (from left to right): 0.2, 0.4, 1, 2 and 4 TiO_2 monolayer coverages, respectively. Each of these coverages are associated with a specific value for the overall predicted rate and these are identified by the arrows.
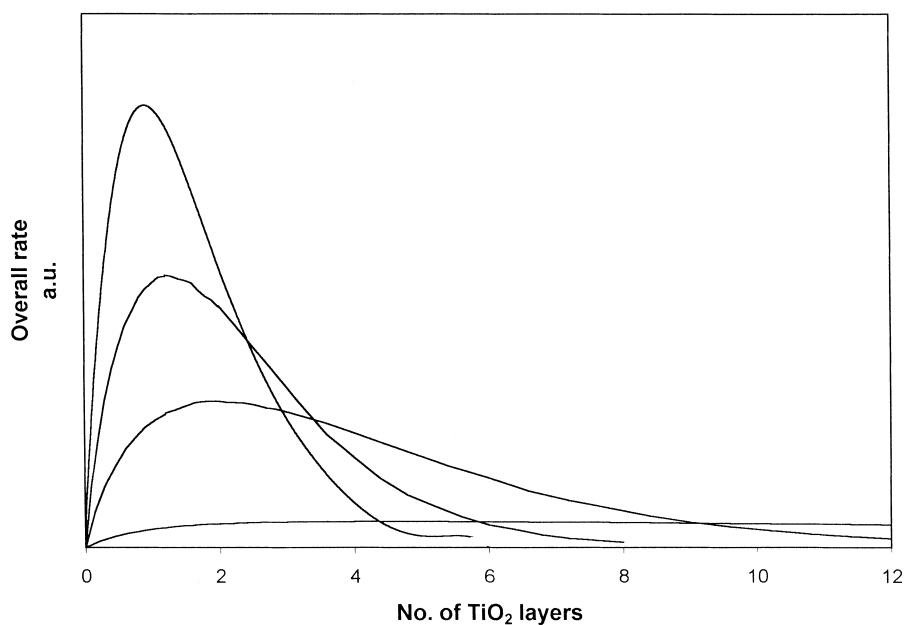

Fig. 7. Rate of photocatalysis versus number of TiO_2 monolayers predicted by a simple, rough 2D kinetic model. In the examples given, the fraction of light absorbed by each particle was set at (from left to right): 0.9, 0.6, 0.3 and 0.05, respectively.

TiO_2 at 365 nm [24]. From these expressions it would appear that the monolayer coverage of aggregated TiO_2 particles of 0.44 μm diameter would be expected to absorb 19% of the incident UV light. However, as noted earlier, a three-coat film of TiO_2 appears to absorb 84% of the incident light (i.e. transmittance in the centre of the photoreactor is 16%). Thus, comparing the two figures highlights the extensive loss (65%) of incident light by TiO_2 films via scattering and reflection. A high degree of reflection and scattering by TiO_2 (13–71%) is a general feature of particulate systems and has been noted by others for dispersions [25,26].

Several studies have been made of the dependence of R_i with incident light intensity, I, for Degussa P25 dispersions, and some of the results are summarised in Table 1. In theory, R_i is expected to depend upon I^θ, where $\theta = 1$ for low intensity irradiation (where electron–hole pair recombination is not the dominant process) and where $\theta = 1/2$ for high-intensity work (electron–hole pair recombination is the dominant process) [27,28]. According to the work of others, the transition of θ from a value of 1 to 1/2 occurs around an intensity of $6 \cdot 10^{14}$ ultra-band gap photons $cm^{-2} s^{-1}$ [29] for rutile TiO_2. In our work, typically the maximum irradiation intensity was 6.4×10^{15} photons $cm^{-2} s^{-1}$. In a preliminary set of experiments the variation in R_i for Eq. (1), photo-sensitised by a 0.5 g dm^{-3} dispersion of TiO_2, was determined as a function of irradiation intensity, over the range $(6.4–0.5) \times 10^{15}$ photons $cm^{-2} s^{-1}$. The variation in light intensity was achieved by placing very fine metal mesh screens between the light source and the photoreactor vessel. From the results of this work it appeared that R_i depends upon $I^{0.64}$; in a previous study using slightly lower (ca. 10% less) light intensities, R_i was found to depend upon $I^{0.74}$ [8]. Others, have found $\theta = 0.8$ [14] for Eq. (1) and Pichat et al. [6] have reported a value for 0.5 for θ [14,6] using the very high intensity range of $3–90 \times 10^{15}$ ultra-band gap photons $cm^{-2} s^{-1}$.

The above work is consistent with notion that the transition region for Degussa P25 TiO_2 is around $(2–3) \times 10^{15}$ ultra-band gap photons $cm^{-2} s^{-1}$ and that in our work, using 8W black light bulbs, the observed direct dependence of R_i upon $I^{0.64}$ arises because the intensity range used spanned both the high- and low-intensity kinetic regions.

In contrast to the TiO_2 dispersion work, a study of the variation in R_i for Eq. (1), photosensitised by a three-coat layer of TiO_2 as a function of irradiation intensity, over the same intensity range, revealed a direct dependence of R_i upon I, that is, $\theta = 1$. The latter finding implies that the photocatalytically active particles in an optimum coating of Degussa P25 on glass are subject to lower light intensities than their dispersion counterparts. We have already suggested that the optimum film coat comprises a layer of aggregated particles. Thus, it would appear that only those smaller particles, making up an aggregate particle, which are in contact with the solution, but partially screened from the incident irradiation by the other particles making up the aggregate, are photocatalytically active. The screening

action would provide a rationale for the direct dependence of R_i upon I for TiO_2 coats.

Some support for the above suggestion arises from the results of a study conducted on a one-coat film (in which the $[TiO_2]$ is 2.5 times less than a three-coat film). Such a film should comprise ca. 40% of a monolayer of aggregated particles. However, the screening action of the photocatalytically active TiO_2 particles, by those others which go to make up the aggregated particles should still take place, even though there is less than a monolayer coverage of aggregate particles. Thus, from this model it is expected that even for a one-coat TiO_2 film R_i will still depend directly upon I, and this was confirmed experimentally.

3.4. Rate versus [4-CP] and [O_2]

In most work with aqueous dispersions of TiO_2 the initial rate related to the concentrations of 4-CP and O_2 via a Langmuir–Hinshelwood-type expression, that is,

$$R_i = f(O_2)k.I^\theta.K_{4-CP}[4 - CP]/(1 + K_{4-CP}[4 - CP]) \quad (3)$$

where

$$f(O_2) = K_{O_2}[O_2]/(1 + K_{O_2}[O_2]) \quad (4)$$

It is usually suggested that the value of K_{O_2} is that associated with the dark Langmuir adsorption of O_2 onto TiO_2 at Ti(III); a process which is independent of [4-CP], since the latter adsorbs non-competitively at other sites. However, the same cannot be said about K_{4-CP}, the value of which, $(5–24) \times 10^3$ $dm^3 mol^{-1}$ (see Table 1), is recognised as being much larger than the dark Langmuir adsorption constant, $K_{4-CP}(dark)$, the value of which we have previously estimated to be 130 $dm^3 mol^{-1}$ [8]. The observation that the value for $K_{substrate}$ is $\neq K_{substrate}(dark)$ is not specific to 4-CP, but is a general one and several kinetic models have been proposed to help explain it and are described elsewhere [29].

In one set of experiments R_i for Eq. (1), sensitised by a three-coat film of TiO_2, was determined as a function of [4-CP] over the range $(0.05–1) \times 10^{-3}$ mol dm^{-3}, under otherwise standard conditions, and the results of this work are illustrated in Fig. 8. A double reciprocal plot of the data produced a good straight, (see insert diagram in Fig. 8) as predicted by Eq. (3). The latter plot also revealed values for $k \cdot f(O_2)$. I^θ and K_{4-CP} and these are listed in Table 2, along with those determined for a 0.5 g dm^{-3} dispersion of TiO_2. From the results of this work it appears that although the maximum rate of photocatalysis for a three-coat TiO_2 film, that is, $k \times f(O_2) \times I^\theta$, is larger than that for a 0.5 g dm^{-3} dispersion (a feature which is responsible for the results in Fig. 2), the value for K_{4-CP} for a film is less than that for a dispersion. It is not clear how much, if at all, this difference in K_{4-CP} value is due to a difference in $K_{4-CP}(dark)$ for TiO_2 dispersions and films and further work is required in this area.

In another set of experiments R_i for Eq. (1), sensitised by a three-coat film of TiO_2, was determined as a function of
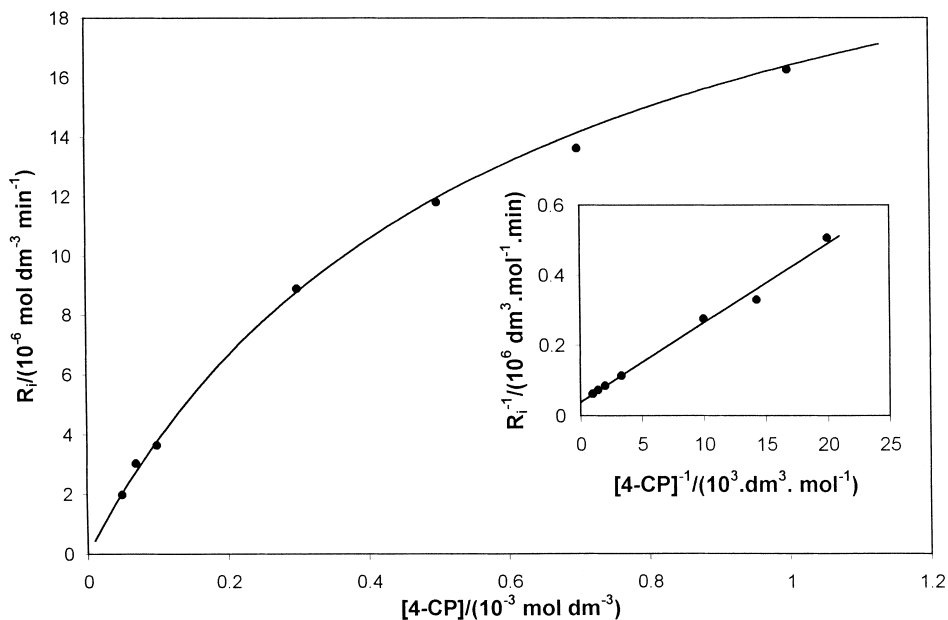
Fig. 8. Observed variation in R_i versus [4-CP] for Eq. (1), using a standard irradiation system, with a three-coat TiO$_2$ film. The insert diagram shows the double reciprocal plot of the data in the main diagram. A least squares analysis of the data in the insert diagram revealed the following values for the gradient and intercept, respectively: 0.0226×10^3 min and 0.0384×10^6 dm^3 mol^{-1} min.

[O$_2$] over the range $(0.065–1.3) \times 10^{-3}$ mol dm^{-3}, under otherwise standard conditions, and the results of this work are illustrated in Fig. 9. A double reciprocal plot of the data produced a good straight, see insert diagram in Fig. 9 as predicted by Eq. (4). The latter plot also revealed values for $k \times f(4\text{-CP}) \times I^\theta$ (where, $f(4\text{-CP}) = K_{4\text{-CP}}[4\text{-CP}]/(1+K_{4\text{-CP}}[4\text{-CP}])$) and K_{O_2} and these are listed in Table 2, along with those determined for a 0.5 g dm^{-3} dispersion of TiO$_2$. From

the results of this work it appears that, as with the previous study, the maximum rate of photocatalysis for a three-coat TiO$_2$ film, that is, $k \times f(4\text{-CP}) \times I^\theta$, is larger than that for a 0.5 g dm^{-3} dispersion, but K_{O_2} for a film is less than that for a dispersion. This latter finding implies that O$_2$ adsorbs less readily on the TiO$_2$ aggregated particles that form a film than it does on those that form dispersions. Further work is required to examine these differences in more detail.
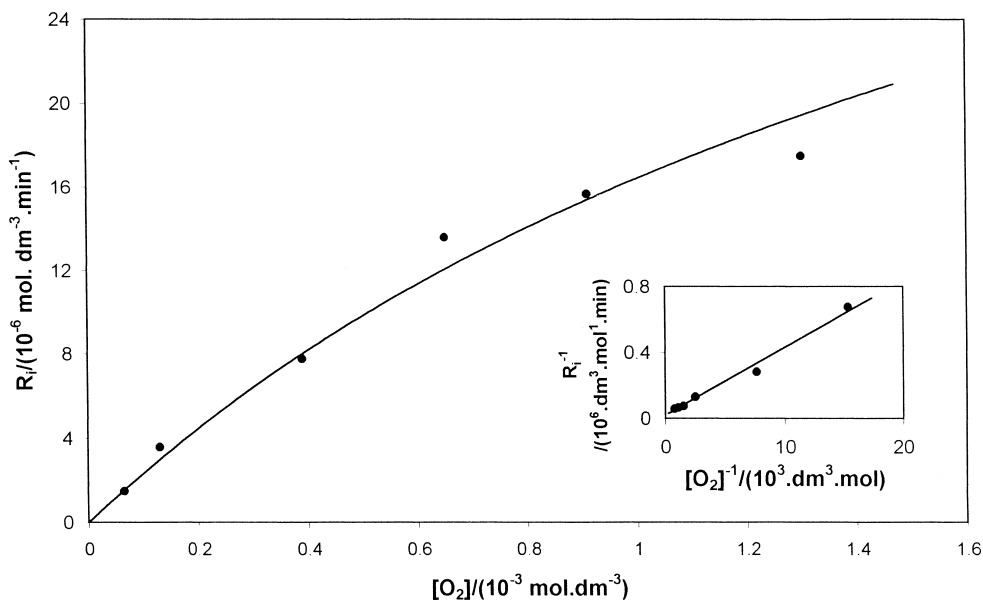

Fig. 9. Observed variation in R_i versus [O$_2$] for reaction (1), using a standard irradiation system, with a three-coat TiO$_2$ film. The insert diagram shows the double reciprocal plot of the data in the main diagram. A least squares analysis of the data in the insert diagram revealed the following values for the gradient and intercept, respectively: $0.0409 \cdot 10^3$ min and $0.02 \cdot 10^6$ dm^3 mol^{-1} min.

Table 2
$k \times f(O_2) \times I^0$, K4-CP, $k \times f$(4-CP)$\times I^0$ and K_{O2} data for TiO_2 films (three-coat) and dispersions (0.5 g dm^{-3})

	$k \times f$(4-CP)$\cdot I^0$ (mol dm^{-3} min^{-1})	K_{4-CP} (dm^3 mol^{-1})	$k \times f(O_2) \times I^0$ (mol dm^{-3} min^{-1})	K_{O_2} (dm^3 mol^{-1})
TiO_2 film	26.10^{-6}	1700	50.10^{-6}	489
TiO_2 dispersion	14.10^{-6}	4000	33.10^{-6}	1170

4. Conclusions

The oxidative mineralisation of 4-CP by oxygen, sensitised by a thin film of Degussa P25 TiO_2, has been studied. The films were used under conditions in which the kinetics of photomineralisation appeared independent of the mass transfer effects and stable towards repeated irradiation. The process appears to go through the same mechanism, generating the same intermediates, as when a dispersion of TiO_2 is used. A closer inspection of the kinetics of the photomineralisation process shows clear differences between a TiO_2 film and a dispersion of the same material. With TiO_2 films the initial rate of photomineralisation is strongly dependent upon photocatalyst loading, reaching a distinct maximum, which appears to be associated with the formation of a monolayer of aggregated particles – the diameter of the aggregated particles was estimated as 0.44 μm. Using TiO_2 dispersions, the rate usually reaches a plateau at ca. 0.5 g dm^{-3} of TiO_2. For TiO_2 films the initial rate depends directly upon the incident light intensity, implying that the photocatalytically active component particles of an aggregated particle are under low illumination conditions and, therefore, are shielded to some extent by the other particles that go to make the aggregated particle. In contrast, using TiO_2 dispersions R_i depends upon $I^{0.64}$, implying that the different light intensities used in this part of the study spanned both the high ($R_i \propto I^{1/2}$) and low ($R_i \propto I$) intensity kinetic regions. The kinetics of photomineralisation of 4-CP, sensitised by TiO_2 films appeared to obey the same Langmuir–Hinshelwood expressions as found in most semiconductor photocatalyst work conducted with TiO_2 powder dispersions. However, in a study of the variation R_i as a function of [4-CP] and [O_2] the values for the maximum rates were higher and those for the apparent Langmuir adsorption coefficients were smaller than those found for a TiO_2 dispersion.

Acknowledgements

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