Photocatalytic Transformation of 2,4,5-Trichlorophenol on TiO₂ under Sub-Band-Gap Illumination

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The adsorptive behavior of TiO₂ under various illumination conditions was investigated. In the dark, Degussa P25, which contains both the anatase and rutile phases of TiO₂, adsorbed significantly greater amounts of 2,4,5-trichlorophenol (TCP) than either pure anatase or pure rutile. Results in the literature and in our laboratory that appeared to indicate "photoenhanced adsorption" under ambient fluorescent lighting on P25 and anatase are in fact due to the photoreaction of TCP. On pure-phase anatase, all reactions are due to trace ultra-band-gap energy light present in the fluorescent lighting. On P25, however, reaction also occurs at sub-band-gap energies. TCP forms a charge-transfer complex with P25 that is activated by light wavelengths as long as 520 nm. The trichlorophenoxyl radicals resulting from charge-transfer couple with each other to form a suite of polyaromatic chlorinated products with detected masses as high as 1200 D. These products are not formed under UV irradiation and in fact are destroyed by conventional UV photocatalysis. No reaction occurs on pure-phase anatase or rutile as a consequence of irradiation with sub-band-gap light. Carbon mass balance was closed for all catalysts under all lighting conditions. Our results show that the wavelength of light is an important factor in determining products on P25. This knowledge can be used to avoid charge-transfer complex activation when the resulting products are undesirable. Alternatively, charge-transfer complexes on P25 may be exploitable for polymer syntheses. The differences between surface reactions on P25 and those on pure-phase TiO₂ may be explained in terms of the morphology of Degussa P25, wherein anatase–rutile interfaces give rise to active sites.

Introduction

Photocatalysis using the semiconductor titanium dioxide (TiO₂) is a rapid, robust and general method for destroying pollutants in water or in air.[1,2] The two crystalline phases of TiO₂ that are important in photocatalysis are anatase and rutile.[1] Anatase, which is generally regarded as the photoactive phase,[1] has a band gap of 3.2 eV, which corresponds to a wavelength of 385 nm, and hence the requirement of UV light. Rutile, commonly thought to have very low catalytic activity, has a band gap of 3.0 eV, corresponding to 410 nm. There exists a class of TiO₂ preparations that contain a mixture of the two phases, and many of these mixed-phase catalysts exhibit significantly higher activity than either pure phase alone. The best-known example is Degussa P25, which consists of approximately 80% anatase and 20% rutile and has set the standard for photocatalytic activity.[1] The reasons for the improved photoactivity of mixed-phase catalysts such as P25 in comparison to pure-phase catalysts are not well-understood. Recent results in our laboratory have shown that small rutile crystallites surrounded by anatase crystallites form highly active nanoclusters in which rutile harvests a wider range of radiant energy, leading to charge separation that is stabilized by electron transfer to lower-energy surface traps on anatase.[3] In this arrangement, anatase acts to prevent charge recombination in rutile, extending the light response of P25 to the band gap of rutile (410 nm), which

is just within the range of visible light. We have proposed that the close association between the anatase and rutile crystallites creates interfacial catalytic hot spots on the nanoclusters.

Degussa P25 has a markedly higher surface affinity for some organic pollutants than pure anatase.[4] Since adsorption is the first step in photocatalysis, the higher adsorbance of P25 contributes to its higher photocatalytic activity. Yet, there are indications that adsorption itself on P25 can be enhanced by illumination. Dieckmann[5] observed significant adsorption of 4-nitrophenol on P25 in ambient light despite no measurable adsorption in darkness. Differences between light and dark adsorption were apparent in the results of Cunningham and co-workers.[6,7] Dark adsorption experiments with 3-chloro-4-hydroxybenzoic acid showed that the compound does in fact adsorb on P25 in accordance with the Langmuir model. However, a Langmuir–Hinshelwood fit of their photocatalytic rate data was impossible using the same adsorption parameters derived from dark adsorption results. In particular, it is clear from their data that a good Langmuir–Hinshelwood fit would require a higher adsorption constant *K* in the photocatalytic reactor than in the dark. This implies that adsorption may be enhanced by illumination. Recently, we have observed an apparent

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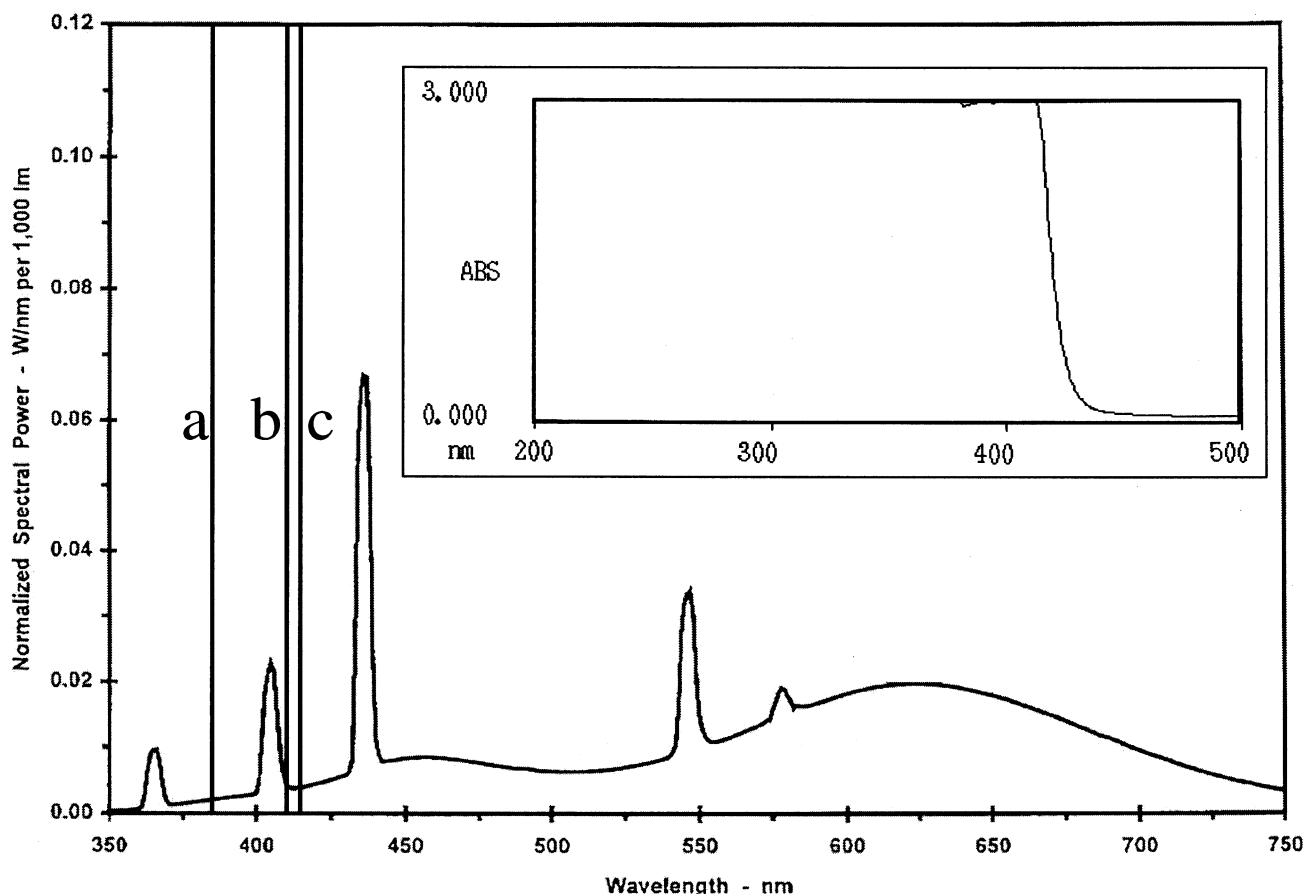
Figure 1. Manufacturer's emission spectrum of fluorescent lighting. Lines indicate (a) anatase band gap, (b) rutile band gap, and (c) cutoff of Kodak Wratten 2E filter. Inset: absorption spectrum of Kodak Wratten 2E filter.

increase in adsorption due to visible light in aqueous P25 slurries containing 2,4,5-trichlorophenol (TCP). This is a surprising result since P25 is expected to be active only under ultraviolet light, and TCP does not absorb visible light. Furthermore, it is intriguing that this phenomenon does not occur on pure-phase anatase or rutile.

The goals of this research are to investigate the phenomenon of "photoenhanced adsorption" and to determine the extent to which it explains the enhanced photoactivity of P25 compared to pure-phase TiO$_2$. To that end we have systematically examined the adsorption of TCP on three types of TiO$_2$ (pure-phase anatase and rutile, and mixed-phase Degussa P25) exposed to three different lighting conditions: ambient fluorescent light, fluorescent light filtered to render it free of UV, and darkness. Adsorption was determined by the difference in the aqueous TCP concentration before and after 18 h contact with TiO$_2$ under the appropriate lighting condition. Adsorbed carbon was extracted and identified by HPLC and GC/MS to close mass balance and to probe the nature of surface reactions. The findings of this research explain how light influences the surface chemistry occurring on these three materials.

Experimental Methods

Adsorption Experiments. The extent of adsorption on TiO$_2$ was determined by experiments conducted in 25-mL borosilicate centrifuge tubes (Corex II). To each tube was added either 0.500 ± 0.005 g of anatase (Aldrich) or P25 (courtesy of Degussa), both of which had surface areas of 50 m²/g, or 1.000 ± 0.010 g of rutile (Alfa Aesar) with a surface area of 3.3–6.1 m²/g. With indirect light exposure limited to a single 60 W incandescent bulb at a distance of 4.7 m, each tube received 25.0 mL water or 2,4,5-trichlorophenol (TCP) solution added from a 50-mL glass buret,

and was then capped and shaken. Dark samples were immediately wrapped in aluminum foil. The TCP solutions were prepared at approximately 10, 50, 100, 200, 300, and 400 μM. A sample of each TCP solution was filtered and analyzed as described below to determine the exact TCP concentration. Tubes were placed on a Barnstead/Thermodyne Labquake rocking tray (for mixing and to keep the catalyst suspended) 25 cm from a fluorescent light fixture containing two 24-in. bulbs (Sylvania GRO/WS). An emission spectrum of the lamps provided by the manufacturer is shown in Figure 1. For ambient light experiments, no material stood between the fluorescent bulbs and the centrifuge tubes, which are transparent to light wavelengths above 340 nm. For filtered light experiments, the light fixture was covered with a Kodak Wratten 2E filter that removed light of $\lambda < 415$ nm with an absorbance greater than 3.0. A spectrum (taken with a Hitachi U-2000 double-beam spectrophotometer) of the filter is shown in the inset of Figure 1. After all tubes were prepared, the light was switched on, beginning the experiment. Ambient temperature was 21 ± 1°C. After 18 h, the light was switched off, and samples were kept in near-total darkness thereafter. All tubes were centrifuged (Sorvall RC 5B Plus with an SA-600 rotor) for 60 min at 6000 rpm. The TiO$_2$ formed a paste at the bottom of the tube, but some cloudiness remained in the supernatant. A sample of the aqueous phase (11 mL) was withdrawn with a nominally 10-mL plastic syringe (B-D). The first 2 mL was pushed through a 0.45 μm PTFE filter (Gelman) and discarded; the remaining filtrate was collected in an 8-mL borosilicate glass vial (with no remaining headspace) for later HPLC analysis. Adsorption was calculated from the difference in TCP concentration between the supernatant after 18 h adsorption and the initial TCP sample according to

$$q = \frac{C_i - C_f}{m/V}$$

where q is the extent of TCP adsorption in μmol TCP per g TiO$_2$, C_i and C_f are the initial and final TCP concentrations in solution,

respectively, in μM, m is the mass of TiO_2 in g, and V is the volume of liquid in L.

Extraction. Procedures for extraction of TiO_2 were carried out in near-darkness. Following an adsorption experiment, remaining supernatant was poured off, leaving a TiO_2 paste in the bottom of the centrifuge tube. To recover polar transformation products, triple extractions were conducted by adding 15 mL methanol (HPLC grade) to the tube followed by vigorous shaking. The tube was placed on a rocking tray overnight, centrifuged, and filtered in the same manner as described above. The remaining methanol was decanted before the next methanol aliquot was added. The second and third aliquots were shaken for 1 h instead of overnight. For nonpolar extractions designed to recover coupling products, 2 g of anhydrous sodium sulfate (Fisher) were added followed by 20 mL of acetone/hexane (1:1 v/v). The tube was capped and shaken vigorously and was placed on the rocking tray overnight. After centrifugation (as above), all of the supernatant was removed by a glass syringe and filtered (as above) into a 24-mL glass vial. The vial was blown to dryness with N_2, leaving a solid residue, which was then redissolved in 1 mL of acetone/hexane. The concentrated extract was analyzed by gas chromatography–mass spectroscopy (GC-MS).

Photocatalytic Treatment. Following adsorption in the light, a 25-mL slurry of water, TCP, and P25 was diluted to 1 L. This resulted in a TiO_2 concentration of 0.5 g/L, which is in line with catalyst loadings typically used in photocatalysis.[2] The mixture was sparged with O_2 for 1 h resulting in a dissolved oxygen concentration of 39.7 mg O_2/L, measured with an Orion 835 meter and dissolved oxygen probe. The slurry was then transferred to a 1 L annular reactor (Ace Glass) equipped with a 450 W medium-pressure Hg vapor lamp at the axis, separated from the slurry by a jacketed quartz finger through which pure water was circulated for cooling. The headspace was displaced with O_2. The reactor was then sealed under a slight positive pressure of O_2. The slurry was well-mixed with a magnetic stirbar. The lamp was warmed up for 3 min outside the reactor, then inserted. 60 min later the lamp was turned off. The slurry was transferred to four 250-mL Nalgene bottles and centrifuged for 15 min at 5000 rpm. The cloudy supernatant was filtered through six Gelman Supor filters (47-mm diameter, 0.45 μm pores). The filters and residual TiO_2 in the centrifuge bottles were transferred to a clean 25-mL glass centrifuge tube. An acetone/hexane extraction was performed in this tube as above. For the control experiment, all procedures were the same except that the reactor was dark.

Analysis. A method for TCP analysis was adapted from the literature.[8] Aqueous and methanol samples were analyzed for TCP by HPLC (Hitach L-6200A pump with L-4500 diode array detector) using a Supelcosil LC-18 column (Supelco, 25 cm × 4.6 mm, 5 μm particles) at ambient temperature and a mobile phase of 70:30:0.2 methanol:water:acetic acid flowing at 1 mL/min. Methanol and acetic acid were HPLC grade and water was high purity (>18 MΩ). TCP eluted around 13 min with a peak absorbance at 296 nm. Concentrations were measured against a standard curve of six gravimetrically prepared solutions. Pure methanol samples were diluted with water to yield a phase composition similar to that of the HPLC mobile phase. Aqueous samples were probed for organic acids by HPLC with a Supelcogel C-610H column (Supelco, 30 cm × 7.8 mm, 9 μm particles) with 0.5% phosphoric acid as the eluent at 1 mL/min and detection at 195 nm.

Chloride was analyzed by capillary electrophoresis with a Waters Capillary Ion Analyzer using a chromate/TTAB electrolyte and a voltage of 15 kV. Chloride results have been corrected for the amount of chloride released by TiO_2 itself. Total organic carbon was analyzed with a Tekmar-Dohrmann Apollo 9000 unit using catalyzed combustion at 680 °C. TiO_2 surface organic carbon was analyzed using a Dohrmann 183 boatsampler unit operating at 800 °C following adsorption, centrifugation, and overnight drying of the TiO_2 at 60 °C.

GC-MS analyses employed a Hewlett-Packard 6890 chromatograph with an HP-5 column interfaced to an HP 5972

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quadropole mass selective detector. The injection volume was 5 μL, and the column temperature began at 50 °C for 2 min, ramped to 150 °C at 10 °C/min, ramped to 300 °C at 15 °C/min, then held for 8 min. Direct MS analyses were performed with a VG 70–250SE using atmospheric pressure chemical ionization in negative ion mode (APCI-).

Diffuse reflectance UV–vis spectra were taken using a Cary 1E double-beam spectrophotometer with a diffuse reflectance attachment. TiO_2 samples were prepared as in dark adsorption experiments, but the entire supernatant was discarded following centrifugation. A portion of the remaining TiO_2 paste was coated on a 1 cm × 0.5 cm area of a black card, which was mounted vertically in the spectrophotometer and scanned with a resolution of 1 nm and a scan rate of 300 nm/min. Samples received minimal exposure (about 1 min) to ambient light prior to scanning. Alumina samples were prepared in the same way, but alumina yielded a gel rather than a thick paste following centrifugation. Mounting the alumina on a card for spectroscopy required allowing the gel to air-dry for 24 h which was carried out in the dark. Alumina spectra exhibited more variations than TiO_2 in baseline offset and/or slope, which we attributed to varying gel thickness. Therefore, four alumina-coated cards were prepared and scanned for each sample (TCP and water blank). The results were averaged to give a single spectrum for each type of sample.

Results

Adsorption Experiments. To study the effects of illumination on adsorption, adsorption isotherms for TCP on TiO_2 were measured for the three different catalysts (P25, pure anatase, pure rutile) and three different light conditions: ambient light, filtered light, and dark. Ambient light experiments were conducted to determine the response of a TiO_2/TCP/H_2O system to ordinary fluorescent lighting. To separate out any effects of trace amounts of ultra-band-gap energy wavelengths in the fluorescent light emission, additional experiments employed an optical filter that removed light of λ < 415 nm, thereby blocking any band-gap excitation (Figure 1). These results were compared to dark adsorption data. The results for P25 and anatase are shown with equal scales for ease of comparison (Figure 2), with $[TCP]_f$ denoting the final (equilibrium) concentration of TCP in solution. In interpreting the results, it is important to keep in mind that adsorption was not directly measured. Rather, as indicated in the Experimental Methods section, depletion of aqueous-phase TCP was measured, and from this adsorption was calculated. Therefore, any nonadsorptive processes that reduce $[TCP]_f$, including transformation of TCP, would appear to increase adsorption. To verify true adsorption requires accounting for the TCP lost from solution in order to rule out loss due to reaction rather than adsorption.

On P25, there was significant adsorption in the dark, as shown in Figure 2. These data for dark adsorption did not exhibit Langmuir behavior but were fitted with a line of slope 4.16×10^{-3} μmol g^{-1} μM^{-1}. No byproducts were observed in solution, and no chloride was released. Under fluorescent lighting, the apparent extent of adsorption at $[TCP]_f = 300$ μM was higher than in the dark by a factor of 2.9. Apparent adsorption under light was fit by a Langmuir isotherm with $q_m = 16.4$ μmol g^{-1} and $K = 1.6 \times 10^{-3}$ μM^{-1}. The absence of byproducts in HPLC chromatograms of the aqueous phase suggested photo-enhanced adsorption as the reason for the illumination effect. In addition, the total organic carbon (TOC) content of the water decreased during the experiment by an amount corresponding to the decrease in [TCP]. This is consistent with adsorptive transport of the organic carbon from the aqueous phase to the catalyst surface, although it does not reveal whether the adsorbed organic carbon
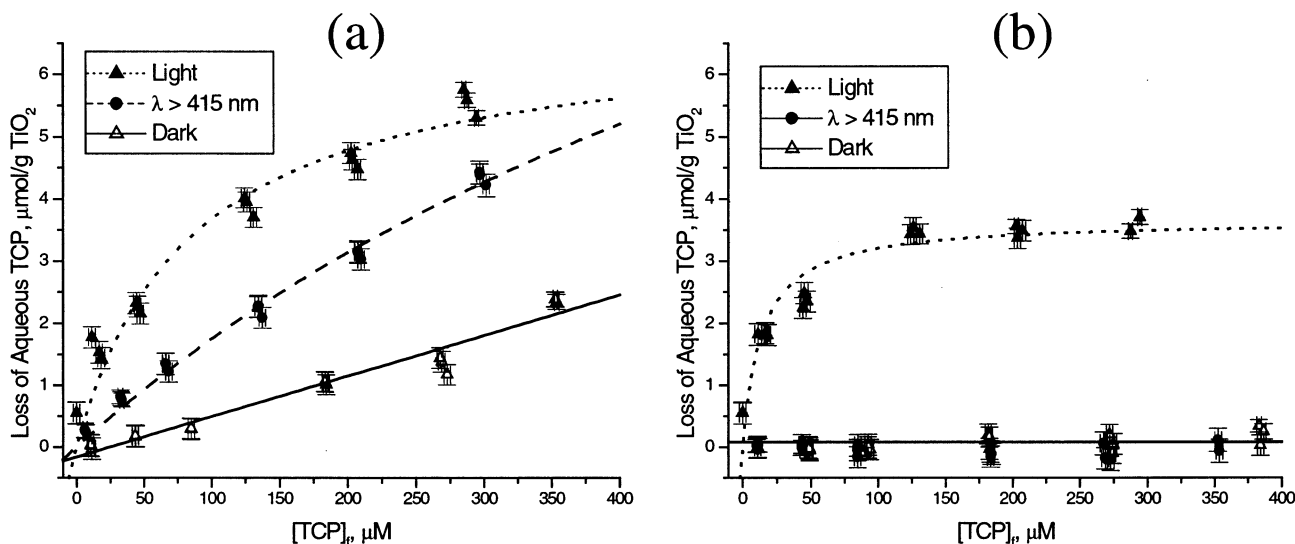
Figure 2. Adsorption isotherms of TCP on (a) P25 and (b) anatase.

was TCP or reaction byproducts. However, the release of $3.3\,\mu mol\,Cl^-/g\,TiO_2$ indicates that some reaction occurred.

To ensure that the photoeffect on P25 was not the result of band-gap excitation due to trace UV in the fluorescent light, the adsorption measurement was repeated with the optical filter in place. Eliminating band-gap excitation diminished but clearly did not eliminate the illumination effect (see Figure 2). At $[TCP]_f = 300\,\mu M$, the apparent adsorption in filtered light was 2.4 times that in the dark, or approximately 20% below that in ambient light. Adsorption in filtered light fit a Langmuir isotherm with $q_m = 7.5\,\mu mol\,g^{-1}$ and $K = 2.5 \times 10^{-3}\,\mu M^{-1}$. Under filtered light, no significant amount of chloride was found, and as in unfiltered light, no byproducts were observed in HPLC analysis.

In ambient light experiments, excitation of the anatase phase in P25 is expected due to the peak in the lamp output spectrum (Figure 1) at about 370 nm. The peak near 405 nm is also important, since it can trigger reactions via activation of the rutile phase. Conventional wisdom holds that anatase is the active phase of TiO₂, and therefore light wavelengths below 385 nm are required to activate mixed-phase TiO₂. Rapid charge recombination in rutile is thought to explain its very low photoactivity.[9] Rutile has been thought to serve as an electron sink, helping to physically separate electrons from holes and thereby slowing recombination and increasing pollutant degradation rates.[1,10] However, recent EPR experiments refute this view and showed that direct excitation of rutile followed by electron transfer to anatase trap sites is an important process below the band gap of rutile.[3] Nevertheless, band-gap excitation remains impossible at wavelengths longer than 415 nm. Therefore, photoenhanced depletion of aqueous TCP on P25 under filtered light is the result of a sub-band-gap process.

Pure-phase TiO₂ behaved differently than P25. On an anatase preparation having the same surface area as Degussa P25 (50 m²/g), no adsorption was detected under dark conditions. Illumination with filtered light produced the same "no adsorption" result (see Figure 2b). Under ambient fluorescent light, however, aqueous [TCP] decreased from 374 ± 2 to 315 ± 2 μM, which is a reduction of 3.0 ± 0.1 μmol TCP per g TiO₂. However, in contrast

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Table 1. Adsorption, Extraction, and Chloride Release Data for P25 and Anatase Samples Contacted with Approximately 400 μM TCP[a]

	P25			anatase	
	ambient light	filtered light	dark	ambient light	dark
adorbed TCP	5.4± 0.1	4.2± 0.2	1.8± 0.1	3.0± 0.1	<0.2
recovered TCP	1.3± 0.2	1.5± 0.2	1.7± 0.2	<0.2	<0.2
% recovery	24± 3	35± 5	96± 12	N/A	N/A
Cl⁻ released	3.3± 0.5	<0.5	<0.5	1.3± 0.5	<0.5

[a] All units (except percentages) are $\mu mol/g\,TiO_2$.

to the P25 results, solution-phase TCP loss was not concomitant with a corresponding decline in TOC. Rather, TOC in solution did not significantly change from its initial value of 27.2 ± 0.2 ppm C, which corresponds to 378 ± 3 μM TCP. While this observation closes mass balance on organic carbon, it also indicates that TCP underwent transformation under ambient light, and that within experimental error the products did not adsorb to the surface but remained in solution. The release of 1.3 μmol Cl⁻/g TiO₂ (Table 1) confirms that transformation took place. Since products were not detected by HPLC conditions appropriate for analysis of aromatics (see Experimental Methods), they are therefore probably aliphatic. Also, no carboxylic acids were detected by an appropriate HPLC method. Clearly, then, the only effect that light had on the anatase/TCP system is traditional band-gap activation and photocatalysis induced by the UV portion of the fluorescent light. Indeed, the manufacturer's emission spectrum of the bulb (Figure 1) includes a small peak around 370 nm, which is capable of directly activating anatase.

Pure-phase rutile was totally inactive: in slurries containing only the rutile phase of TiO₂, there was no loss of aqueous TCP under any conditions. The surface area of rutile given by the manufacturer was 3.3−6.1 m²/g, which was less than that of P25 or anatase, but this was partially compensated for by doubling the amount of rutile used in experiments relative to the amounts of P25 or anatase. Although the resulting amount of surface area in rutile experiments was still 5-fold less than that in the anatase and P25 experiments, the absence of observed adsorption on rutile was not a surface area effect: had rutile adsorbed comparably to P25 on a per-surface area basis, it would have been detected. Our dark adsorption results are similar to those of Gray and Stafford,[4] whose
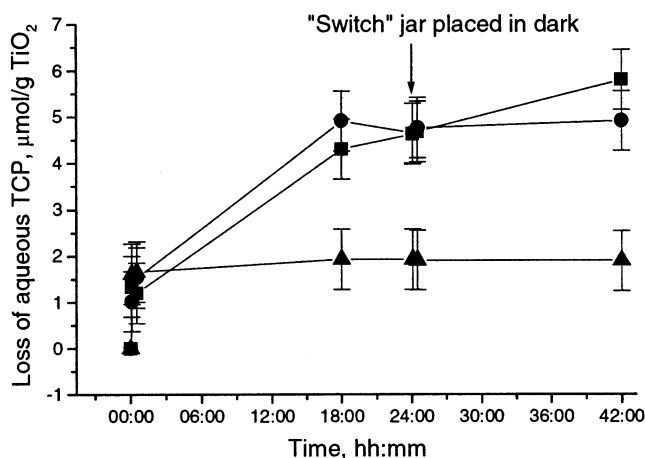
Figure 3. Adsorption reversibility experiment: samples "Dark" (triangles), "Light" (squares), and "Switch" (circles). See text for details.

Figure 4. Results of adsorption measurements on and methanol extractions from P25 following adsorption in ambient light, filtered light, and darkness.

gas−solid gravimetric adsorption experiments showed that P25 adsorbs far more 4-chlorophenol (27 ± 2 mg/g) than anatase (8 ± 2 mg/g) or rutile (5 ± 2 mg/g).

Despite the fact that anatase constitutes 80% of Degussa P25, there were significant differences in the behavior of P25 and pure-phase anatase toward TCP as a function of the lighting conditions. Important differences were evident in dark adsorption and in reactivity under filtered or ambient illumination. In the dark, P25 exhibited much greater surface affinity for TCP than did anatase. Under dark conditions, P25 adsorbed 1.8 ± 0.1 μmol TCP/g TiO$_2$, whereas no dark adsorption could be measured on pure anatase. In filtered light, adsorption of TCP onto P25 appeared to be increased by a factor of 2.3 over dark conditions; no adsorption was detected under filtered light on anatase. In ambient light, the decrease in aqueous TOC in a P25 slurry was concomitant with the decrease in TCP. In an anatase slurry, however, the TOC did not change. The combination of declining [TCP] and steady [TOC] in anatase slurries indicates that the TCP in anatase slurries subjected to ambient light was converted to products that themselves did not adsorb. On P25, the TOC decrease suggests either photoenhanced adsorption of TCP or transformation of TCP to strongly adsorbed byproducts.

Adsorption or Reaction? To resolve whether the depletion of aqueous TCP in the P25 adsorption experiments was in fact due to adsorption, the reversibility of TCP adsorption to P25 with respect to light was tested. The results are shown in Figure 3. To allow the withdrawal of multiple aliquots over time, the experiments were conducted in 250 mL borosilicate bottles containing 150 mL of slurry loaded with 8 g/L P25 and having an initial TCP concentration of 388 μM. A sample kept in darkness reached an equilibrium adsorption condition of 1.9 ± 0.6 μmol TCP/g TiO$_2$ within 18 h and did not change over the following 24 h. Samples "Light" and "Switch" began in the light, where the measured adsorption continued to increase for the first 24 h to the statistically equivalent values of 4.3 ± 0.6 and 4.9 ± 0.6 μmol TCP/g TiO$_2$, respectively. At that point, the Switch bottle was returned to darkness. If the apparent photoinduced adsorption were completely reversible, desorption would have occurred, and aqueous TCP would have equaled that observed under dark conditions. Instead, no change occurred in the Switch sample after illumination was stopped. Although a completely irreversible photoenhanced adsorption effect is possible, it is more likely that these results indicate photocatalytic reaction of TCP driven by the ambient light.
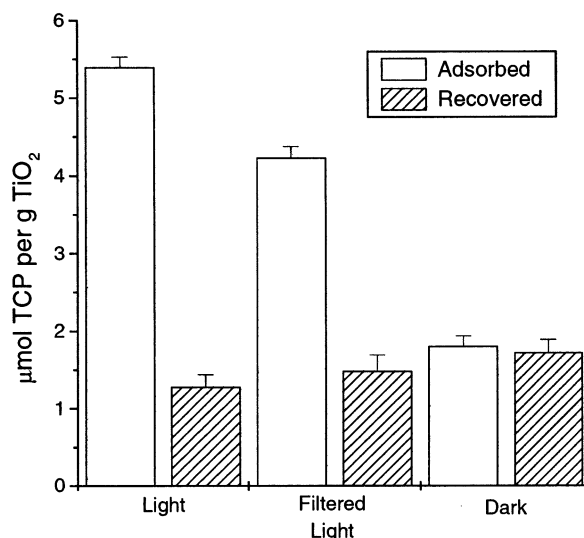
Any transformation of TCP must result in byproducts. However, no typical photocatalytic aromatic intermediates—e.g., dichloro-dihydroxy species or other chlorophenolic compounds—were observed in the bulk water of illuminated TCP/TiO$_2$ systems, although standards of such compounds in solution are easily observed by HPLC. Nor were any organic acids detected in the aqueous phase by an appropriate HPLC method. The low amount of chloride released in anatase systems (0.4 mol Cl$^-$ per mol TCP lost from solution) indicates that the aqueous products remained chlorinated. The amount of Cl$^-$ released in a P25/TCP system under filtered light was not statistically different from the amount of Cl$^-$ released from P25 alone. On P25 under ambient light, about one chloride ion was released per unaccounted for TCP molecule (see Table 1). This rules out mineralization as an explanation for the missing TCP, since conversion to CO$_2$ would require the release of 3 Cl$^-$ ions per TCP. Therefore, the organic carbon removed from the aqueous phase must be chlorinated and bound to the catalyst in some form.

Recovery of Products. Two different extractions were performed with the goal of recovery, identification, and quantification of the organic carbon adsorbed to the surface of P25 following adsorption under illumination. Polar extractions were designed to recover expected photocatalytic byproducts of TCP, such as monochloro and dichloro phenols and benzenediols. Samples of P25 exposed to TCP under dark, light, or filtered light conditions were extracted with methanol, for which TCP and other chlorophenolic compounds have a high affinity. The results are presented numerically in Table 1 and graphically in Figure 4. After dark adsorption, all TCP lost from solution was recovered intact from the catalyst surface; thus in the dark, depletion of aqueous TCP did in fact correspond to adsorption, and there was no degradation of TCP. However, in the light, ambient or filtered, only 24% or 35% of TCP lost from the water could be recovered from the catalyst, respectively. In no case was the amount of TCP extracted higher than in the dark condition. The extraction results, therefore, do not support photoenhanced adsorption. On the other hand, no significant byproduct peaks were observed in HPLC or GC-MS analysis of the polar extract.

Nonpolar extractions using acetone/hexane (1:1 v/v) followed by concentration and GC-MS analysis were conducted with the purpose of recovering coupling prod-

ucts. Extracts of P25 samples exposed to TCP in ambient or filtered light contained polychlorinated, multiring comopunds, including small amounts of dibenzo-*p*-dioxins and dibenzofurans containing between four and six chlorines. We estimate that the dioxins and dibenzofurans accounted for no more than 1% of surface-bound organic carbon. Some larger molecules were observed but could not be identified; the largest molecule commonly observed by GC-MS had a mass of 448 amu, and an isotopic distribution pattern indicating six chlorines. All of these byproducts typically elute at a column temperature of around 300 °C, which is the upper limit for the column, suggesting that larger products might be present in the extract but fail to elute. Indeed, a direct MS injection of an unseparated extract revealed many polychlorinated compounds with a range of masses extending to about 1250 D. The same byproducts were found in filtered or unfiltered light-exposed samples. Production of the products required TCP, P25, and light. No coupling products were observed on anatase, or under dark conditions, or in illuminated solutions of TCP without P25.

Mass balance on carbon was closed under all lighting conditions for all catalysts. In the dark, methanol extraction alone closed mass balance by recovering 96% ± 12% of TCP lost from solution. For P25 in the light, closing mass balance requires measuring C present in unidentified products on the P25 surface. This was achieved by solid total organic carbon analysis. Obtaining reproducible results with this technique required drying each TiO_2 sample overnight at 60 °C, which led to the evaporation of some of the TCP and therefore some loss of surface carbon. To account for this loss, it is necessary to determine the amount of TCP lost. This could be determined by measuring surface TOC on a dried dark-adsorbed sample, where all surface-bound carbon is TCP and the initial amount prior to drying is known from methanol extraction. It was found that 35% of adsorbed TCP evaporated under our drying conditions. For illuminated samples, it was assumed that the heavy coupling products do not significantly evaporate at 60 °C, and that all loss of carbon is in the form of TCP. It was further assumed that all TCP is extracted by methanol (i.e., the amount of surface-bound TCP is known from methanol extraction experiments) and that the proportion of surface TCP lost through evaporation is the same in illuminated samples as in the dark samples. We calculated the total amount of adsorbed carbon by measuring the TOC on dried samples and correcting for the 35% loss of adsorbed TCP. By this method we accounted for 101% ± 11% of the carbon lost from solution in ambient light and 93% ± 12% in filtered light. On anatase under ambient light, we accounted for all carbon using liquid TOC measurements, which showed that all transformed TCP products remained in the aqueous phase. No depletion of aqueous TCP was detected in anatase slurries under filtered light or in the dark. On rutile, there was no significant loss of TCP under any conditions.

Mechanisms of Sub-Band-Gap Photoreaction. These results indicate that the higher levels of TCP loss from solution in the illuminated P25 systems, then, are due to reactions driven by different light energies and producing different products than those observed with anatase. Some compounds are known to form charge-transfer complexes with TiO_2, typically producing starkly colored systems.[11,12] TCP adsorption, however, did not

result in such coloration, instead causing only a subtle graying of the catalyst. Furthermore, while catechols are known to form charge-transfer complexes with TiO_2,[13,14] we are not aware of any reports of such complexes with trichlorophenols. Yet, we have strong evidence that TCP does form a charge-transfer complex on the P25 surface.

Electron paramagnetic resonance (EPR) spectra were obtained by Hurum et al.[15] of an aqueous slurry containing P25 and TCP maintained at 5 K. The relevant portions of that work are summarized here as follows. A background scan was performed in the dark. The sample was then scanned while being illuminated by a Xe arc lamp behind a long-pass filter. Even when light wavelengths shorter than 495 nm were excluded and band-gap excitation was impossible, the EPR spectra showed trapped electrons on both the anatase and rutile phases, and a TCP-derived organic radical. As the cutoff wavelength was decreased, all unpaired electron signals increased, especially those of TiO_2-bound excited electrons. When all wavelengths above 420 nm were permitted, the rutile and anatase electron signals were very strong, even though there was no band-gap excitation. These results required TCP and TiO_2 together; no electron signals were observed for TiO_2 by itself under sub-band-gap illumination. Nor were any radicals observed in a TCP/P25 system in darkness. These observations indicate the photoinduced direct transfer of electrons from TCP to the conduction band of TiO_2, i.e., a charge-transfer complex.

Diffuse reflectance UV−vis spectra of P25 and of P25 exposed to TCP are consistent with a charge-transfer complex (Figure 5a). Absorbance of P25 with TCP matches that of clean P25 at wavelengths above 520 nm. From 520 nm to the onset of band-gap excitation at 410 nm, the absorbance of P25/TCP increases linearly with decreasing wavelength, while absorbance of P25 remains flat. Since TCP by itself does not absorb in this range, we attribute the absorbance to a charge-transfer complex. In contrast, the spectra of anatase and anatase/TCP are identical; anatase does not form a charge-transfer complex with TCP (Figure 5b). We ensured that the differences between the P25 and P25/TCP spectra were not due to products of TCP reaction triggered by ambient light or by the beam of the spectrophotometer. After the P25/TCP sample was scanned, the sample was exposed to ambient light for 5 min, then scanned an additional five times. There was no significant change in the spectrum. Also, while the diffuse-reflectance spectral feature showing charge transfer between P25 and TCP resembles that reported for P25 and catechol,[14] there is no evidence in the literature that phenols can be converted to catechols upon dark chemisorption on TiO_2. In the data shown in Figure 5a, the baseline of the P25/TCP spectrum has been slightly displaced (by 0.03 absorbance units) to facilitate a comparison of the spectra. As additional controls, DR spectra were taken of TCP and H_2O on alumina (a model unreactive metal oxide) and on rutile. No features were observed that would provide evidence for a visible light-activated charge-transfer complex on either material (data not shown).

The existence of a charge-transfer complex indicates the photoexcitation and transfer of an electron from TCP directly into the conduction band of TiO_2. This process directly produces TCP radicals. Since chlorophenols

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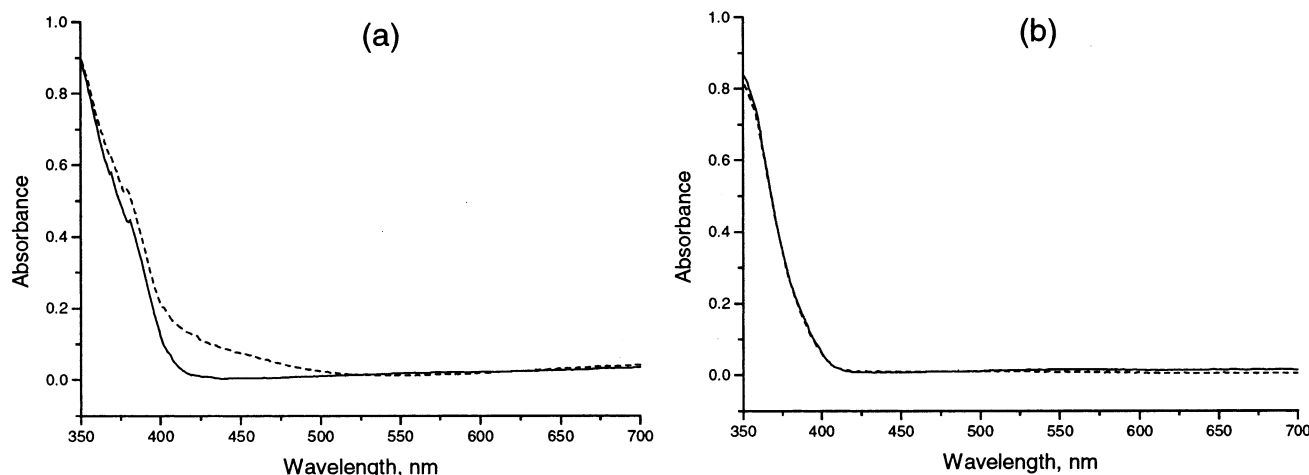
Figure 5. Diffuse reflectance UV−vis spectra of (a) P25 and (b) anatase, with (dashed) and without (solid) adsorbed TCP.
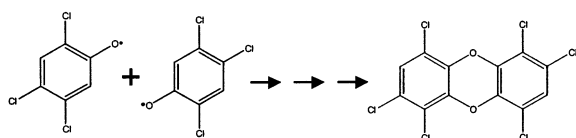

Figure 6. Dimerization of two trichlorophenoxyl radicals.

typically adsorb to TiO_2 via the phenolic oxygen,[16,17] the resulting radical is likely a trichlorophenoxyl species. Reaction between nearby trichlorophenoxyl radicals results in different products than those produced by band-gap excitation. In contrast, UV photocatalysis generates hydroxyl radicals, which favor attack at ring positions C-3 and C-6 over formation of a phenoxyl radical through hydrogen abstraction from the phenolic hydroxyl group or attack at C-1 followed by dehydration.[18] Indeed, the product mixture observed under sub-band-gap illumination is consistent with a mechanism involving reactions of two or more trichlorophenoxyl radicals to form fused compounds (see Figure 6). Direct excitation of TiO_2 in the presence of chlorinated aromatics tends to produce the familiar products of hydroxyl radical attack, e.g., hydroxylated, partially dechlorinated aromatic compounds and ring cleavage products.[2] No such species were detected under sub-band-gap energy illumination.

The formation of chlorinated multi-ring products is peculiar to the charge-transfer reaction mechanism. Dioxins, an undesirable class of byproducts, are not normally formed by the hydroxyl attack mechanisms that predominate in conventional band-gap-excitation photocatalysis. In fact, dioxins are known to be destroyed by this process.[19] An experiment was conducted to verify that UV photocatalysis does not produce the coupling products but rather degrades them. Two $TCP/TiO_2/H_2O$ slurries were exposed to light of $\lambda > 415$ nm. One slurry was extracted and analyzed by GC-MS, and the usual chlorinated polymers were observed. The other slurry was treated in a photocatalytic reactor with high-intensity UV light. The treated TiO_2 had the pure white appearance of a fresh TiO_2/H_2O slurry, without any of the discoloration typical of a P25/TCP slurry exposed to visible light. This TiO_2 was extracted and analyzed, and no chlorinated

products were observed by GC-MS. To ensure that the technique used in separating and extracting the catalyst following photocatalysis did not result in a false negative, a control photocatalytic treatment experiment was performed where the UV lamp was never turned on. Chlorinated coupling products were detected in the extract of this untreated TiO_2.

A second mechanism exists that may also contribute to sub-band-gap reaction on P25: Degussa P25 exhibits limited intrinsic activity under visible light. A photocurrent action spectrum of P25 by Cao et al.[20] showed very low but nonzero response of P25 to light wavelengths as high as 550 nm. Intrinsic sub-band-gap activity can be explained by defect sites. An ideal semiconductor has zero density of states within the band gap, but a real semiconductor may have localized defect sites with energies that lie inside the band gap. Some sites would be populated with electrons and some would be unpopulated, depending on their positions with respect to the Fermi level of the semiconductor. Excitations between defect sites, from a populated defect site to the conduction band, or from the valence band to an unpopulated defect site, would all occur at sub-band-gap energies.[21−23] Nevertheless, given that the intrinsic photoresponse of P25 to visible light is so low and that the reaction products are consistent with the charge-transfer mechanism, the readily observable charge-transfer complex of P25 and TCP accounts for the vast majority of photocatalytic transformation of TCP under sub-band-gap energy light.

It is important to note that neither of these sub-band-gap activation mechanisms operates on either pure-phase anatase or rutile. The marked difference between P25 and either pure phase with respect to dark adsorption points to sites on P25 that are chemically different from those on pure anatase or pure rutile. This is consistent with a literature report[4] showing that adsorption of 4-chlorophenol to P25 was mostly chemisorption, whereas adsorption to anatase was primarily physisorption. Available data allow many possible scenarios that explain the different chemistry of P25 and pure-phase TiO_2. The most obvious feature of P25 that the pure phases lack is an anatase−rutile interface; the most logical location of sites unique to P25 is at these interfaces. We propose that the

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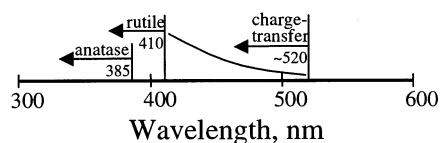(23) Stimming, U. *Langmuir* **1987**, *3*, 423−428.

Figure 7. Wavelength regimes for photoreactions on P25.

close association of anatase and rutile phases in P25 gives rise to surface states at which there is efficient electronic overlap between TCP molecules and TiO_2, and that photoinduced charge transfer takes place at these sites. Changes in band structure at these phase boundaries may also lead to more energetically favorable electronic transfer processes than those that can occur on pure anatase or rutile. The combination of efficient wave function overlap and energetically favorable transitions allows the charge-transfer complexes observed only on P25 in these experiments.

Conclusions

Our results provide insight into the surface activity of Degussa P25. In the dark, P25 adsorbs much more TCP than pure-phase TiO_2: dark adsorption is significant on P25 but undetectable on pure anatase or rutile. The TCP on P25 is subject to a variety of reaction mechanisms under ultraviolet and visible illumination that do not occur on pure-phase anatase or rutile. We can identify three distinct wavelength regimes for photoreaction of P25 with TCP (Figure 7). Below 385 nm, band-gap excitation of anatase and/or rutile occurs. Between 385 and 410 nm, rutile excitation followed by electron transfer to anatase traps dominates. Above 410 nm, TCP is degraded by charge transfer between TCP and TiO_2, and to a lesser extent by sub-band-gap charge separation in TiO_2, leading to the formation of radical species. On anatase, photoreaction is driven only by band-gap excitation. Pure-phase rutile shows a complete lack of activity under the fluorescent lighting used, probably due to rapid charge recombination.

While the products of visible light-induced transformation of TCP on P25 are undesirable, they are destroyed under UV light. Our results show a set of conditions to avoid in the case of TCP photocatalysis, but more broadly, they suggest the use of light wavelength to control photocatalytic reactions on P25 and select for desired products. While only small amounts of polymeric products were found in our experiments, it may be possible to synthesize desirable polymeric products from adsorbed organics on P25 under illumination conditions targeted to activate charge-transfer complexes. Conversely, charge-transfer can be avoided with appropriate optical filters when its products are undesirable.