Photocatalytic Degradation of Chlorinated Phenoxyacetic Acids by a New Buoyant Titania-Exfoliated Graphite Composite Photocatalyst

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A new class of floating composite photocatalysts for water purification is introduced. The composite material is comprised of exfoliated graphite support, titania photocatalyst, and sol-gel-derived methyl silicate binder. The catalyst composition was optimized for the degradation of rhodamine B dye. The photodegradation performance of the optimized catalyst was compared with supported titania film and P-25 titania suspension for the degradation of chlorophenoxyacetic acids. The photodegradation of the coated catalyst was between 50% and 95% of the activity of supported photocatalyst film.

Introduction

The photocatalytic oxidation of organic species in water by illuminated titania involves two simultaneous processes: oxidation of the target compound and reduction of dissolved oxygen.¹⁻³ To promote photocatalytic oxidation of organic impurities in water, four components-light, oxygen, the target compound, and the photocatalyst-should meet at one place. Light is supplied either by intense artificial light sources or by solar irradiation. Solar photochemical reactors usually contain shallow reaction basins or flowing thin films of the contaminated solution. The titania photocatalyst is present either in suspension or in the form of coated films on the bottom of the reactor.^{4,5} However, for purification of water in deep water or waste-water reservoirs and for purification of oil slicks and floating pollutants, titania particles are not applicable because titania will sink and disappear at the bottom of the aquatic system. Thus, to prevent loss of the titania and to concentrate the titania where it is most likely to be needed-at the liquid-air interface-buoyant catalysts are needed. Serpone and co-workers⁶ and Heller and co-workers^{7,8} introduced the coated hollow glass beads, Dagan and Tomkiewicz proposed floating titania aerogels,9 and our group proposed methyl silicate floating composites.¹⁰ An apparent drawback of titania-coated beads is the gradual detachment of titania particles from the beads by collisions and hydrodynamic turbulence. Titania aerogels are not hydrophobic, and thus once wetted, they will sink in water. In the present article we introduce a novel buoyant photocatalyst and show that the fact that the buoyant support is not transparent had surprisingly little effect on the activity of the composite photocatalyst.

The rate of the overall photocatalytic process is determined by light intensity distribution in the reactor. It was shown in ref 11 that photodegradation process can be described as a pseudoheterogeneous reaction between the light and the species in solution with an effective reaction rate constant K:

$$dC/dt = -K(S/V)C$$
, where $K = kI^n$ (1)

The effective reaction surface in this case is the illuminated cross section of the solution (*S*). *V* stands for the volume of solution, *I* is the radiation intensity (<400 nm), *n* is an effective reaction order with respect to light intensity (1 > n > 0.5), and

C is the concentration of the target compound in solution. Since the bandgap of titania is about 3 eV, only radiation with wavelength shorter than 400 nm can be utilized in the process. The effective reaction rate constant *K* reaches saturation at high concentration of suspended titania, when the titania concentration is sufficient to capture all useful light. Further increase of titania concentration results in absorption of light by the upper layers of the suspension, leaving the deeper sections of the reaction vial in darkness. Increasing the concentration of the titania suspension therefore does not increase further the degradation rate. The above approach enables one to compare the degradation rates observed with titania suspensions and supported titania on the basis of a given illuminated cross section reactor area and maximal utilization of light. Since the light absorption coefficient of titania is rather high ($\lambda = 350$ nm, α = 1.4×10^5 cm⁻¹¹²), only a small fraction of the titania in both concentrated titania suspensions and supported titania films is active, and therefore, an opaque support can be used instead of the glass beads or methyl silicate supports for manufacturing floating catalysts.

The goal of the present work was to present a new type of buoyant titania-coated photocatalysts based on a coating of porous, floatable matrix containing both closed and open pores. The open pores provide surface roughness and penetration of titania into the porous matrix and thus provide higher stability against erosion. The closed pores are expected to provide floatation. In this case, collisions of particles will not affect the catalytic properties because erosion of the particle surface will reveal new photocatalytically active TiO₂ sites.

The exfoliated graphite^{13,14} material of very high porosity and superb floatability was chosen as a model of porous carrier for titania. Exfoliated graphite (EG) is produced by rapid heating of an intercalated graphite compound to $700-1200^{\circ}$ C. Intercalation is usually performed by treatment of natural graphite in a mixture of concentrated sulfuric and nitric acids. Heating of intercalated graphite results in evaporation of the intercalate and consequent expansion of graphite crystallites along their *c*-axes by up to several hundred times. Exfoliated graphites are widely used as thermal insulators and grease composition components, and they can also be pressed to form foils, gaskets, and seals. So despite the fact that light reflection by graphite is relatively poor (approximately 30% at 350 nm wavelength¹⁵), it was chosen as a model floating support. Titania (P-25 of Degussa) was chosen as a model semiconducting material

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SCHEME 1



top. Results are reported per illuminated cross-sectional area of vial or per unit of apparent surface area of titania film. The test solutions were buffered by 0.01 N Borax (pH 9.2). The Xe lamp was equipped with dichroic mirror and a glass filter to produce a 300–400 nm band-pass filter. Light intensity hitting the target cell was adjusted by use of an Ophir thermopile light intensity monitor, Nova 03A-P-CAL (Jerusalem, Israel). Unless otherwise stated, the illuminated vial was kept at a constant temperature of 25° C regulated by a water jacket and a thermostat.

In all cases, to ensure lack of direct UV photolysis, blank experiments were carried out by irradiation of the test solution. The concentrations of the chlorinated phenoxyacetic acids and rhodamin B were monitored by periodic sampling of 2 mL samples during the course of the experiment and determination of their concentrations by a Varian, Cary 1E UV-vis spectrophotometer equipped with a diffuse reflectance accessory. Concentrations of the target compounds were determined by monitoring the light absorption peaks at 269, 279, 283, and 288 nm for PhAc, Cl-PhAc, 2,4-D, and 2,4,5-T, respectively. The concentration of Rh-B was determined by monitoring the absorbance at 543 nm. Total organic carbon (TOC) measurements were performed using a Dohrmann DC-80 automated laboratory TOC analyzer. The initial solution was used as a standard. Concentration of Cl⁻ was determined by titration of the acidified solution with 0.01 N AgNO₃, using a Metrohm 673 titroprocessor with combined silver electrode Model 6.0404.100. The quantitation of TOC and Cl⁻ was done by destructive tests and required large volumes. Therefore, a separate test was conducted for each data point and the whole test solution was taken for analysis at the end of every experiment.

Determination of the organic intermediates of the photooxidation of 2,4-D was conducted using a straightforward solvent extraction procedure and by diazomethane esterification followed by GC/MSD analysis. Briefly, 4 g NaCl (Frutarom, Israel) was added to 20 mL sample. The sample was then acidified with nitric acid (Palacid Ltd., Israel) to pH 2 and mixed with 2 mL of methyl tert-butyl ether (MTBE, Sigma), and 69 ppb of 1,2,3-trichloropropane was added as an internal standard. The organic phase was collected in a 3 mL vial, dried over sodium sulfate (Frutarom, Israel), and concentrated under helium flow to 0.1 mL. A quantity of 5 μ L of the concentrated solution was injected for GC analysis. Diazomethane esterification was conducted using 50 μ L of the concentrated solution and 50 μ L of diazomethane-saturated MTBE solution, which was prepared from N-methyl-N-nitroso-p-toluenesulfonamide according to standard methods.²³ An RTX-1 column, 30 m \times 0.32 mm, 1 μ m film thickness, was used. The oven temperature program was as follows: initial temperature = $40 \,^{\circ}$ C, 1 min; first ramp, 5 °C/min to 180 °C; second ramp, 10 °C/ min to 210 °C; third ramp, 30 °C/min to 240 °C; final hold time = 4 min. The oncolumn injector was kept 3 °C higher than the oven temperature at all times.

Preparation of Supported Titania Films. TiO₂ films were prepared by repeated dip coating of glass slides with a titania P-25 suspension mixed with sol-gel precursors of methyl silicate binder. The coated films were dried at 80 °C for 3 min after each dipping step. The following protocol was used. Glass slides were degreased in methanol and chromic acid and dried before the coating step. The coating sol contained 20 mL methanol, 0.2 g of TiO₂ P-25, an appropriate amount of methyltrimethoxysilane (MTMOS), and 1 N HCl solution. The amount of acid was set to provide a 4.5:1 water-to-Si ratio. The sol was allowed to age for 3 h in a closed vessel before coating was performed.

because of its high photocatalytic reactivity. Methyl silicate (Ormosil) was used as a binder of the titania to the EG support.

The activity of buoyant catalyst was measured for the photocatalytic oxidation of rhodamine B (Rh-B) and chlorinated phenoxyacetic acids, namely, 2,4,5-trichlorophenoxyacetic acid (2,4,5-T), 2,4-dichlorophenoxyacetic acid (2,4-D), and 4-chlorophenoxyacetic acid (Cl-PhAc) (see Scheme 1). The degradation mechanisms of 2,4-D on floating photocatalysts was compared to P-25 Degussa catalysts and previous studies.

2,4,5-T and 2,4-D are widely used broad-leaf herbicides. The degradation of halogenated phenoxyacetic acids and their reaction intermediates by irradiated P-25 titania,^{16–18} by Fenton reagent,^{19,20} and by UV irradiation^{16,21} was recently studied. Rh-B is often used as a model compound in studies of photocatalytic activity.²² The selection of these compounds as target compounds was at least partly motivated by their stability under near-UV radiation and their easy quantitation by spectrometric methods.

Experimental Section

Reagents. Rhodamin B and methyltrimethoxysilane were purchased from Aldrich. 2,4,5-Trichlorophenoxyacetic acid and 2,4-dichlorophenoxyacetic acid were supplied by Applied Science Lab. Corp., and 4-chlorophenoxyacetic acid (Cl-PhAc) and phenoxyacetic acid (PhAc) were supplied by Aldrich. Titania photocatalysts, P-25 Degussa, were donated by Degussa Corp. The powder was suspended in a test solution and sonicated for 5 min before use. Triply distilled water was used throughout.

Apparatus. Scanning electron microscope (SEM) studies and electron probe analysis were conducted using a JEOL 840 microscope. Energy dispersive spectrum was taken on EDS LINK 10000 calibrated on Co and operated on 20 kV. BET surface area measurements were carried out using a Micromeritics Gemini II 2370 surface area analyzer. Measurements were carried out using nitrogen as the adsorbent. Desorption isotherms were used for quantitation. Instron 4502 was used for strain-stress studies of powders. A HP5890 gas chromatograph equipped with an electron impact (EI) mass selective detector HP5971 and a cool on-column injector was used for determination of reaction intermediates.

Photooxidation Experiments. The photooxidation experiments were carried out by exposing 100 mL of aerated, stirred, buffered aqueous solution of the target substances and the photocatalyst to the irradiation of a 300 W Oriel ozone-free Xe lamp. The catalysts were introduced either as sonicated P-25 titania sol, as a coated glass slide, or as a layer of floating photocatalyst. The test vial was uniformly illuminated from

Phenoxyacetic Acids

Preparation of Exfoliated Graphite–Titania Composite Photocatalysts. Exfoliated graphite was used as a porous support for the photocatalyst. It was prepared by thermal exfoliation of commercial intercalated graphite compound (bisulfate graphite). Exfoliation of bisulfate graphite (Asbury Graphite Co., U.S.) was carried out by heating it to 1000 °C for about 20 s. Material produced this way had approximately 20 g/L bulk density, 20 m²/g BET surface area, and 10–15% volume of closed pores, as it was estimated in ref 24. The volume of closed pores was calculated by subtracting the volume of open pores from the total volume of powdered particles.

The buoyant photocatalysts were prepared by coating the exfoliated graphite particles with TiO₂ P-25 and methyl silicate binder. The coating protocol was as follows. A quantity of 25 mL of methanol, an appropriate amount of TiO₂ P-25, and an appropriate amount of methyltrimethoxysilane were mixed and sonicated for 5 min to ensure dispersion of titania. Then 0.5 g EG was added and the mixture was stirred. A quantity of 1 M HCl was added to hydrolyze the methyltrimethoxysilane at a 4.5:1 water-to-silicon ratio. The mixture was allowed to hydrolyze for 3 h in a closed vessel and then was cast in a Petri dish. The color of the particles was changed from black to gray by the coating step. After drying at room temperature for 20 h, the photocatalysts were heat treated for 30 min at 300° C to remove residual methanol. When a high concentration of titania (more than 33%) was used, particles formed agglomerates that could be separated only by mechanical chopping. It takes 1 g of 1:1:1 Ormosil:TiO₂:EG catalyst to cover 60 cm² surface area of a solution with one layer of particles. The observed degradation rates are related per unit surface area of solution covered by particles of photocatalyst.

The photocatalysts were used in several repeated degradation tests with no loss of activity during consecutive series of tests. The photocatalyst retained full floatability even after 3 weeks of solar illumination. Freshly prepared particles were hydrophobic, and visual inspection could not reveal wetting by the solution. After 2-4 h of irradiation partial wetting of the particles occurred. This was also accompanied by increased photoactivity. This change of activity is ascribed to an increase of the active surface by wetting. The illumination oxidized some of the methylsiloxane groups that are close to the titania active sites and thus reduced the hydrophobicity. Similar increase of the water contact angle and wettability was indeed observed also for titania–Ormosil films that were deposited on glass slides.

Results and Discussion

Physical Characterization. SEM micrographs of exfoliated graphite-titania photocatalyst particles TiO₂:Ormosil:EG = 1:1:1 are presented in Figure 1. Figure 1A presents typical micrographs of composite photocatalysts taken in a back-scattered mode. Figure 1B presents a micrograph of the cross section of a typical particle. The brightness of the picture is roughly proportional to concentration of TiO₂ (as verified by X-ray microanalysis). The very bright sites are composed of droplets of TiO₂-Ormosil composite, and the darker sites correspond to bare graphite surfaces or deep cracks. Examination of the cross section of the cross section of the particle, Figure 1B, shows that TiO₂ coating is not confined to the outer surface of the exfoliated graphite and that the coating is also taking place on the inner surface of the macropores. Results of X-ray microanalysis are presented in Table 1.

Table 1 indicates that the average concentrations of TiO_2 and Ormosil at the outer surface and inside the particle are roughly the same, though the variability in concentration of the titania





Figure 1. SEM micrograph of a floating catalyst particle taken in backscattering mode: (A) general view; (B) cross section of an exfoliated graphite—titania composite particle. Composition is TiO₂:Ormosil:EG = 1:1:1.

is much larger than the variability in the distribution of the binder. Microanalysis of a bright site (TiO₂-rich site, Table 1) indicates enrichment of TiO₂ over the Ormosil binder, while analysis of a typical dark site at the cross section (TiO₂-poor, Table 1) shows enrichment of Ormosil. Exfoliated graphite is highly hydrophobic, but it is readily wetted by methanol. During the coating step open pores of the exfoliated graphite are filled with the TiO₂–Ormosil–methanol suspension. Hydrolysis and condensation of the methyltrimethoxysilane leaves a network of Ormosil + TiO₂ coating on the surface of the graphite particles.

The Ormosil plays several roles in this catalyst. First, it serves as a binder for TiO₂, both inside and outside the graphite particle. Second, the Ormosil interpenetrates the catalyst and increases its rigidity. Thus, on one hand it increases the erosion resistance and on the other hand, once the catalyst is eroded or broken, a fresh TiO₂-Ormosil layer is exposed, all that without losing the closed pores and without affecting the buoyancy of the composite material. Figure 2 depicts results of Instron compression tests of unmodified EG, Ormosil-modified EG (1: 1.5), and floating catalyst (TiO₂:Ormosil:EG = 1:1:1), which demonstrate the increased toughness by the coating procedure. Table 2 presents the BET surface areas of the P-25 titania, EG, and the coated EG. The table suggests that most of the surface area of the composite catalyst is contributed by the methyl silicate binder and that the titania contributed less than 30% of the surface area of the composite photocatalyst. Stability of the methyl-Ormosil binder under UV radiation was investigated by sunlight exposure (noon time UV radiation = 3.7 mW/cm^2 for <400 nm wavelength) of a powdered composite catalyst (titania:Ormosil = 1:4) for 7 days. The FTIR peak at 1276cm⁻¹, characteristic of the methyl-silicon bond remained

	site of analysis			
compound	outer surface	outer surface	cross-section	inner section
	average	TiO ₂ -rich spot	average	TiO ₂ -poor spot
Ormosil, % weight	20.6	28.7	22.1	23.9
TiO ₂ , % weight	15.8	45.2	16.6	9.4

^a Sum of TiO₂ + Ormosil content is less than 100%; graphite and interference of surface topology make up the rest.





Figure 2. Curves from Instron compression tests of powders: (1) exfoliated graphite; (2) Ormosil-coated exfoliated graphite (EG:Ormosil = 1:1); (3) floating catalyst (Ormosil:EG:TiO₂ = 1:1:1). The cylinder cross section is 2 cm², the full piston path length is 50 mm, and the velocity is 10 mm/min.

unaffected. This indicates that degradation of the Si-C bond is (at most) confined to the vicinity of the titania particles and the bulk methyl-Ormosil remained intact after prolonged exposure.

Photocatalytic Activity. Optimization of a three-component photocatalyst was based on the photocatalyzed oxidation rate of Rh-B. Two sets of compositions were prepared. The first contained a constant ratio of EG:Ormosil = 1 and variable TiO_2 content, and in the second, the $TiO_2:EG = 1$ was kept constant and the Ormosil content was changed. Photodegradation rates for Rh-B are presented in Figures 3 and 4. In all cases the photodegradation of Rh-B followed first-order rate laws. Typical degradation curves are shown in the insert of Figure 4. Figure 3 shows that increasing the TiO_2 content in the photocatalyst improves the photocatalytic activity. The relative increase is sharp at low concentrations of TiO₂ but levels off at higher titania content. The activity saturation indicates full coverage of the particle surface by titania. Similar saturation of the photocatalytic activity at high titania coverage was observed for titania-coated glass beads.⁸ The data scattering for the titania-rich catalysts is ascribed to agglomeration of catalyst particles during the preparation step, which causes poor reproducibility. The dependence of the photocatalytic activity on the Ormosil concentration is shown in Figure 4. The increase of activity of the floating catalyst when the Ormosil content in the photocatalyst was increased is ascribed to better coating of the surfaces of particles by TiO_2 + Ormosil and thus smaller losses of light by absorption by the uncoated graphite. Based



Figure 3. Dependence of the Rh-B photodegradation rate constant (per unit of illuminated surface area) on composition of floating catalyst. Composition is Ormosil:EG = 1 with variable TiO₂ content. Irradiation intensity is 60 mW/cm².



Figure 4. Dependence of the Rh-B photodegradation rate constant (per unit of illuminated surface area) on composition of floating catalyst. Catalyst composition is EG:TiO₂ = 1 with variable Ormosil content. Irradiation intensity = 60 mW/cm². Insert shows concentration—time curves. Volume is 100 mL; initial concentration is 0.02 mM; illuminated surface area = 18 cm².

on the above measurements, the optimal composition of the photocatalyst was taken as TiO_2 :Ormosil:EG = 1:1:1.

Demonstration of the capability of the buoyant photocatalyst to perform useful photooxidation and comparative evaluation of the floating photocatalyst relative to titania films and titania suspensions were performed taking the photodegradation of the chlorophenoxyacetic acid family as a test case. To compare the performance of the suspended catalysts and the two forms of supported photocatalysts (in buoyant and film forms) based on a common basis, it was important to ascertain first that the degradation of the phenoxyacetic acids on these catalysts follows the same reaction rate laws (eq 1) and has a similar reaction

floating catalyst



Figure 5. LN–LN plot of the concentration derivative with time as a function of light intensity for photodegradation of 60 mL of 50 ppm 2,4-D in presence of 0.3 g floating catalyst with TiO_2 :Ormosil:EG = 1:1:1.



Figure 6. Arrhenius plot of the degradation rate of 2,4-D by titaniacoated glass slide. Composition is TiO₂:Ormosil = 6; S = 9.2 cm²; volume is 60 mL; light intensity = 60 mW/cm²; slope of the curve = 3350 K; correlation coefficient $R^2 = 0.92$.

mechanism (the latter will be addressed in the next section). Indeed, for all three forms of catalysts, the degradation rate obeyed a linear dependence on the concentrations of the chlorophenoxyacetic acids and evaluation of the degradation dependence on light intensity gave for all three types of catalysts approximately 1/2-order dependence. In all cases the LN-(degradation rate) vs LN(illumination intensity) yielded straight lines with correlation coefficients R > 0.94 (Figure 5). Halforder dependence on the irradiation intensity is often encountered in low quantum yield photodegradation processes.^{2,3,25,26} The energy of activation was determined for the degradation of 2,4-D on thin titania film (TiO₂:Ormosil = 6). Arrehnius type dependence with a relatively high activation energy (E =27.8 kJ/mol) was observed (Figure 6). This value is commensurate with reported values for the activation energy of the degradation of 4-chlorophenol (20.6 kJ/mol²⁷). Agitation of the solution did not improve the kinetics, which confirmed that the photodegradation is not dependent on outer diffusion control.

Figures 7–9 depict the photodegradation of the chlorophenoxyacetic acids on the three types of photocatalysts. Photodegradation curves of 2,4,5-T, 2,4-D, and Cl-PhAc by illuminated floating catalyst are shown in Figure 7. The composition of the catalyst was TiO₂:EG:Ormosil = 1:1:1 by weight. The weight of floating catalyst (0.3 g) was adjusted to cover entirely the water—air interface of the reaction vial (18 cm²) with approximately one layer of particles. It can be seen that the degradation rates follow a first-order rate law for all compounds (linear regression coefficients greater than 0.99 was observed



Figure 7. Concentration changes during irradiation of 100 mL of 50 ppm 2,4,5-T and of 2,4-D or Cl-PhAc acids in presence 0.3 g floating catalyst. Photocatalyst composition is TiO₂:Ormosil:EG = 1:1:1. Irradiation intensity = 60 mW/cm². Slopes of the curves are 1/min: [2,4-D] - 0.0027, $R^2 = 0.994$; [2,4,5-T] - 0.002, $R^2 = 0.999$; [Cl-PhAc] - 0.0014, $R^2 = 0.999$.



Figure 8. Concentration changes during irradiation of 100 mL of 50 ppm 2,4,5-T and of 2,4-D, Cl-PhAc, and Ph-Ac acids in the presence of 4 mg TiO₂ P-25. Illuminated surface area = 18 cm². Irradiation intensity = 60 mW/cm². Slopes of the lines are (1/min): [2,4-D] – 0.0011, $R^2 = 0.997$; [2,4,5-T] – 0.004, $R^2 = 0.95$; [Cl-PhAc] – 0.0066, $R^2 = 0.998$; [Ph-Ac] – 0.0022, $R^2 = 0.98$.

in all cases). The rate of photodegradation of the chlorinated phenoxyacetic acids obeyed the following order: 2,4-D > 2,4,5-T > Cl-PhAc. The kinetics of photodegradation of chlorinated phenoxyacetic acids on P-25 suspension is shown in Figure 8. It can be seen that the first-order reaction rate law is still valid, but the order of activity of the phenoxyacetic acids is 2,4-D > Cl-PhAc > 2,4,5-T. Figure 9 demonstrates that the photodegradation of the three model compounds on titania film proceeded at approximately the same rate (K = 0.016 cm/min).

All three catalysts exhibit a deviation from the Hammett law. The Hammett equation²⁸ predicts that the reactivity of the compounds increases with the number of chlorine substituents on the aromatic ring. However, similar deviations from Hammett's prediction were reported for the degradation of halophenols. Pichat and co-workers²⁷ reported the following order of activity for the degradation of chloro-substituted phenols by illuminated P-25 titania: 2,4-dichlorophenol > 2,4,5-trichlorophenol > 4-chlorophenol. El-Ekabi and co-workers²⁹ reported that an equimolar unbuffered mixture of 2,4,5-T, 2,4-dichlorophenol, and 4-chlorophenol exhibited approximately the same degradation rate by illuminated film of titania P-25.

The first-order rate law for degradation of chlorinated phenoxyacetic acids, which was observed in our work for both suspended and supported TiO_2 , indicates that the surface concentration in all cases was proportional to volume concentra-



Figure 9. Concentration changes during irradiation of 60 mL of 50 ppm solution of 2,4,5-T and of 2,4-D or Cl-PhAc with titania-coated film. Composition is TiO₂:Ormosil = 3. S = 8.7 cm². Irradiation intensity = 60 mW/cm². Slopes of curves are (1/min): [2,4,5-T] - 0.0023, $R^2 = 0.998$; [2,4-D] - 0.0023, $R^2 = 0.999$; [Cl-PhAc] - 0.0026, $R^2 = 0.999$.

tion. However, that does not mean that the proportionality constant is the same for all acids. So deviation from the Hammett law may be ascribed to preferential adsorption of the 2,4-D on titania. However, the adsorption of all three compounds on titania at pH 9 is very low. Our attempts to evaluate the adsorption isotherms of chlorinated phenoxyacetic acids on TiO₂ at concentrations that are relevant to this report were unsuccessful because of their very low adsorption ($<1 \mu g/g$ P-25 titania). This is understandable, since the point of zero charge (PZC) of titania is pH 6.3, and thus, both the target compounds and the titania surface are negatively charged at basic pH.

The changes of the relative degradation rates due to changes in the form of the photocatalysts are probably caused by changes in adsorption of the compounds or their reaction intermediates on the hydrophobic catalysts. At this time we do not know whether the changes in the relative lability are caused by the graphite support or by the Ormosil, but it is clear that the support is affecting to some extent the mechanism of the reaction.

Comparison of the photocatalytic activity of the coated plate with the activity of the floating catalyst shows that activities of particles of composition TiO_2 :Ormosil:EG = 1:1:1 range between 48% and 94% of the activity of the film (for 2,4-D and Cl-PhAc, respectively). The relatively small difference in activity shows that most of the outer surface of the particles is covered by TiO_2 and that only a small fraction of the light is lost in gaps between particles of floating catalyst and by absorption by bare graphite. The activity of P-25 suspension was only 2-5 times larger than that of the supported catalysts.

Mechanism and Reaction Intermediates. Figure 10 presents concentration changes during photocatalytic oxidation of 2,4-D by a P-25 suspension. The photocatalytic oxidation is a complicated multistage process. The decay of the UV absorption peak indicates only the disappearance of the initial compound. This process under conditions of Figure 10 is characterized by a half-life of approximately 20 min. The halflife of Cl⁻ release is approximately 110 min, and the half-life of TOC removal is approximately 13 h, that is, approximately 40 times longer than the half-life of the initial 2,4-D acid.

Scheme 2 demonstrates the degradation pathways of 2,4-D on floating catalyst based on aromatic intermediates identified by GC/MSD. Figure 11 depicts the dynamics of formation of the most abundant aromatic reaction intermediates. Since in most cases standards were unavailable, quantitation was based on the abundance of the products relative to the abundance of 2,4-D. Our studies were conducted at pH 9 and compared to



Figure 10. Relative concentration changes of 2,4-D, Cl^- and TOC during irradiation of 100 mL of sample with S = 18 cm². Initial conditions are 50 ppm 2,4-D acid, 4 mg TiO₂, irradiation intensity of 60 mW/cm².



Figure 11. Dynamic evolution of the 2,4-D photodegradation intermediates. Numbers corresponds to compounds in Scheme 2 and are the following: 1 = 2,4-D; 2 = 2,4-dichloro-6-hydroxyphenoxyacetic acid, 3 = 5,7-dichloro-1,4-benzodioxan-2-one, 5 = 2,4-dichlorophenol, 6 = 3,5-dichloro-1,2-hydroquinone

SCHEME 2



results at pH 4.2. The same intermediates were identified for the floating and suspended catalysts.

Pathway $1 \rightarrow 2 \rightarrow 3$ represents the oxidative hydroxylation of 2,4-D, which is expected at the α position, which allows further lactone formation. Pichat and co-workers¹⁶ also found compound **3** (5,7-dichloro-1,4-benzodioxan-2-one) but attributed it to an artifact of the high-temperature gas chromatography. Pignatello²⁰ also identified compound **3**, but both researchers did not identify intermediate 2. Our findings clearly indicate that compound 3 is not an artifact, since the methylation reaction employed in our studies impedes the cycle-closing reaction. Additionally, the use of cool on-column injection precludes hightemperature reactions in the injector. Theoretically, such reactions could occur also in the capillary column itself, but that would have led to the formation of a very broad peak, which was not observed in our studies. In fact, the lactone peak had a regular shape. Pichat,¹⁶ Pignatello,²⁰ and also Barbeni et al.¹⁸ (who studied the degradation of 2,4,5-T) correctly inferred the formation of the hydroxylated intermediate, compound 2, though this was identified only in the current studies probably because of the higher sensitivity gained by the cool on-column injector. A second oxidation pathway involves the oxidative decarboxylation of the aliphatic chain either directly to dichlorophenol (compound 5) or most probably to a 2,4-dichlorophenol formate intermediate (compound 4). The mechanism of photooxidative decarboxylation was originally suggested for aliphatic acids by Yoneyama, Bard, and co-workers³⁰ (see eq 2, $R = X_1X_2X_3Ph$, where X_1 , X_2 , and X_3 are H or Cl).

$$R-OCH_{2}COO^{-} + p^{+} \rightarrow R-OCH_{2} + CO_{2}$$
$$R-OCH_{2} + O_{2} \rightarrow R-OCH_{2}OO^{\bullet} \rightarrow R-OC(O)H + OH^{\bullet}$$
$$R-OC(O)H + H_{2}O \rightarrow R-OH + HCOO^{-} + H^{+}$$
(2)

Compound **4** detected by Pichat,¹⁶ Pignatello,²⁰ and Barbeni¹⁸ in acid media was not found under our experimental conditions (pH 9), but we identified it in pH 4 studies. This suggests that the hydrolysis of the phenolic ester, **4** to the corresponding phenol, **5** is much faster under basic condition than in acid media. Pichat and co-workers¹⁶ identified also 2,4-dichloromethoxybenzene as a reaction byproduct, but in our studies it was found only after methylation of the reaction mixture as a methylated derivative of **5**, while unmethylated samples did not show even traces of the 2,4-dichloromethoxybenzene. Compound **5** can be further oxidized to form 3,5-dichloro1,2-hydroquinone (**6**) as anticipated by the previous studies.¹⁶

Note that the initial degradation pathway from 1 to 3 does not lead to TOC reduction, which explains the lag time in the reduction of TOC (Figure 10). In contradistinction chlorides start to accumulate from time zero because of the reductive as well as the oxidative pathways.

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