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Hammett Study on the TiO_2-Catalyzed Photooxidation of *Para*-Substituted Phenols. A Kinetic and Mechanistic Analysis

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The TiO_2-catalyzed photooxidation of phenol, *p*-methoxyphenol, *p*-cresol, *p*-fluorophenol, *p*-chlorophenol, *p*-bromophenol, 4-hydroxyacetophenone, α,α,α-trifluoro-*p*-cresol, *p*-cyanophenol, and *p*-iodophenol were investigated. The decay kinetics of the substituted phenols are consistent with the Langmuir−Hinshelwood (L−H) kinetic model. Although a variety of substituents were employed the changes in the L−H kinetic parameters are relatively small. The relationship among Hammett constants and the kinetic parameters suggest that a number reaction pathways may be involved in the degradation.

Introduction

There is considerable concern over the increasing number of reports on hazardous materials entering and contaminating the Nation's groundwater and surface water.[1,2] The uses of photochemical and oxidative technologies for the destruction of organic pollutants in groundwater have received considerable attention recently.[3−5] Titanium dioxide (TiO_2)-catalyzed photodegradation is particularly attractive because TiO_2 is an effective, photostable, reusable, inexpensive, nontoxic, and readily available catalyst. Over the past decade, vigorous research has demonstrated that essentially all chlorinated aliphatics, chlorinated aromatics, several pesticides, herbicides, surfactants, and dyes are completely photooxidized in the presence of TiO_2 to innocuous products such as water, carbon dioxide, and mineral acids.[6,7] While this technology is approaching commercialization and a wide variety of organics have been decomposed there are still important fundamental questions to be answered.[6−8]

Photoexcitation of TiO_2 generates an electron/hole pair, creating the potential for both reduction and oxidation processes to occur at the surface of the semiconductor. The positions of the valence and conduction bands of anatase TiO_2 at pH = 1 relative to SCE are −0.1 and +3.1 V, respectively.[9,10]

There are a number of possible reaction pathways involving direct and indirect reactions of substrates dissolved in aqueous solutions with photoexcited TiO_2. Hydroxyl radical formation upon irradiation of TiO_2 has been observed.[11,12] Once formed, the hydroxyl radical can react with a variety of substrates. Two probable reaction pathways of hydroxyl radicals with organic substrates are hydroxyl radical addition and hydrogen abstraction. Both reaction pathways are expected to give oxidized products in solutions saturated with oxygen, eq 1.

$$^{\bullet}\text{OH} \xrightarrow{\text{substrate}} \text{substrate}_{\text{ox}} \tag{1}$$

In the absence of water or in competition with water in aqueous solutions, the substrate can undergo direct electron transfer to the photogenerated holes to yield a radical cation.[13−15] The radical cation can then react with water or oxygen to form an oxygenated product, eq 2.

$$\text{substrate} + h^{+} \rightarrow \text{substrate}^{\bullet +} \xrightarrow{\text{oxygenation}} \text{substrate}_{\text{ox}} \tag{2}$$

While hole-catalyzed formation of substrate radical cation and hydroxyl radical-mediated pathways are vastly different processes, the two give similar product distributions in oxygenated aqueous solutions, thus making distinction of the processes difficult.

Another important consideration in the TiO_2-photocatalyzed reactions of substrates is the adsorption onto the surface of the semiconductor particle. Although it has been reported that adsorption is critical for the generation of reactive intermediates, there is still uncertainty as to the role adsorption plays and how it ultimately effects the reaction pathways[16,17] (e.g., Lawless et al. have reported direct observation of hydroxyl radicals bound to the surface of the TiO_2,[11] but whether subsequent reactions occur at the surface or in solution remains unclear). While the chemical reactions occurring in the TiO_2-photocatalyzed reactions of organic substrates appear complicated, distinction and evaluation of the operative pathways is of critical importance for the

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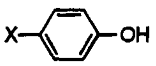

X = H, OCH_3, CH_3, F, Cl, Br, I, CF_3, $COCH_3$, CN

Figure 1. *Para*-substituted phenols used in the TiO_2 study.

development and optimization of this process as an innovative treatment technique.

We investigated a variety of substituted phenols. Phenols and phenolic compounds pose a significant threat to the environment and are commonly found as dilute contaminates in groundwater and surface water.[18,19] TiO_2-mediated photodecomposition and complete mineralization studies have been carried out on several substituted phenols, but a single study comparing the photodecomposition of monosubstituted phenols at identical experimental conditions has not been previously reported.[6] The electronic properties of the substituents ranged from strong electron-donating to strong electron-withdrawing. The effects of substituents on the kinetics and reaction mechanisms of *para*-substituted phenols on irradiated TiO_2 are reported herein. Hammett correlations have been used in an attempt to better understand the reaction mechanisms initiated by photoexcited TiO_2.

Results and Discussion

Kinetic Studies. A number of substituents were employed in order to encompass a wide variety of electronic effects. The TiO_2-catalyzed photooxidations of phenol, *p*-methoxyphenol, *p*-cresol, *p*-fluorophenol, *p*-chlorophenol, *p*-bromophenol, 4-hydroxyacetophenone, α,α,α-trifluoro-*p*-cresol, *p*-cyanophenol, and *p*-iodophenol were investigated, Figure 1. Unsubstituted phenol was used as the model/reference compound.

In a representative experiment, the semiconductor powder was suspended in an oxygenated aqueous solution of the phenol. Sonication was used to obtain effective dispersion of the semiconductor particles. The suspensions were irradiated at wavelengths which did not directly excite the phenols. The disappearance of each phenol was monitored by gas chromatography. The initial reaction rates were calculated assuming a pseudo-first-order reaction rate. Extreme care was taken to ensure uniform experimental conditions during rate determinations. A plot of concentration vs time for the first 10–20% of degradation was constructed for each phenol at a number of different initial concentrations. These results are summarized in Table 1.

Several controls were run to establish the degradation as photocatalytic. There is no degradation of the phenols in the presence of TiO_2, without irradiation, and high percent recoveries obtained for the dark controls imply there is little dark adsorption of the phenols onto the TiO_2 surface. When irradiated in the absence of the photocatalyst, TiO_2, there was negligible degradation as a result of direct photolysis or photooxidation of the phenols.

While a variety of models have been derived to describe the kinetics of semiconductor photocatalysis,[20-23] the most commonly used model is the Langmuir–Hinshelwood (L–H) kinetic model.[24,25] The L–H model relates the rate of surface-catalyzed reactions to the surface covered by the substrate and has been used to suggest reactions between adsorbed reactants. The model is indicative of apparent kinetics and good for predictive purposes.[25]

A mathematical representation of the Langmuir–Hinshelwood model is given by eq 3, where k' is the

$$1/\text{rate} = 1/k' + 1/k'K[\text{subst}] \qquad (3)$$

apparent reaction rate constant and K is the apparent adsorption equilibrium constant of the substrate onto the surface of the semiconductor. For the purposes of our studies, a well-mixed oxygen headspace was maintained and constant dissolved oxygen concentrations are assumed. The assumption that rates are pseudo-zero-order in oxygen is justified under such conditions.[25] The Langmuir–Hinshelwood kinetic parameters, K and k', were determined for each phenol from the initial decomposition rate of the phenol as a function of concentration, Table 2.

Hammett Studies. The reactivity of aromatic compounds, including phenols, can be drastically affected by the electronic nature of substituents. Hammett constants represent the effect different substituents have on the electronic character of a given aromatic system. Correlations of Hammett constants with different reaction characteristics have been used to obtain information about reaction intermediates and mechanisms.[26] Although Hammett correlations have been used primarily for reactions occurring in homogeneous solutions, successful applications for heterogeneous systems have also been reported.[27,28] A Hammett correlation between aromatic olefins and the relative rates of photooxidation on photoexcited TiO_2 surfaces in nonaqueous solutions has been reported as evidence for hole-catalyzed reactions.[28] A correlation between electron-donating and electron-withdrawing *para*-substituents of phenol and the relative rates of reaction of hydroxyl radicals in aqueous media has also been reported.[29]

Since Hammett correlations have been independently reported for hydroxyl radical-mediated and hole-catalyzed reactions under specific conditions, if either of these pathways is dominant in the TiO_2-catalyzed photodegradation of substituted phenols an analogous correlation is expected. A variety of Hammett constants, Table 3, were used in an attempt to establish a correlation with the Langmuir–Hinshelwood kinetic parameters for the *para*-substituted phenols. A good correlation is observed

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Table 1. Initial Reaction Rates as a Function of Concentration for *Para*-Substituted Phenols on Photoexcited TiO_2 in Aqueous Solution (pH = 3)

substituent	initial concn[a] (mM × 10^2), [initial rate[b] (M/min × 10^5)]
H	182.1, [2.44]; 89.5, [1.77]; 63.3, [1.73]; 53.8, [1.59]; 46.1, [1.66]; 36.4, [1.36]
p-OCH_3	178.7, [2.70]; 86.0, [2.07]; 62.1, [1.78]; 52.7, [1.38]; 45.9, [1.55]; 36.7, [1.23]
p-CH_3	180.0, [2.10]; 53.8, [1.50]; 38.0, [1.36]; 30.5, [1.24]; 47.8, [1.32]; 81.6, [1.71]
p-F	183.4, [3.81]; 184.0, [3.83]; 92.4, [3.14]; 64.8, [2.37]; 55.5, [2.49]; 45.9, [2.28]; 37.1, [1.86]
p-Cl	192.5, [2.52]; 91.1, [1.82]; 70.4, [1.54]; 62.7, [1.63]; 51.7, [1.34]
p-Br	187.6, [1.80]; 88.2, [1.32]; 61.0, [1.15]; 53.0, [1.15]; 44.6, [1.03]; 36.0, [9.66]
p-I	181.3, [1.38]; 125.0, [1.04]; 88.2, [0.879]; 75.1, [0.780]; 50.5, [0.611]; 49.7, [0.590]; 39.7, [0.497]
p-CF_3	187.8, [2.12]; 89.3, [1.65]; 56.9, [1.47]; 40.8, [1.34]
p-$COCH_3$	176.0, [1.66]; 134.8, [1.78]; 89.2, [1.65]; 60.5, [1.28]; 52.6, [1.07]; 45.9, [0.946]
p-CN	254.4, [1.64]; 173.9, [1.30]; 140.5, [1.16]; 104.3, [0.853]; 91.4, [0.717]; 81.1, [0.717]

[a] The concentrations were measured from a standardization curve devised from aqueous extractions, and the reported concentrations were not absolute, but relative to the maximum that could be extracted under our experimental conditions. Any reaction with a recovery of less than 90% at time = 0 min was not used in the kinetic analysis. [b] Estimated error in the measurement of the initial rate is <8% based on results from duplicate runs.

Table 2. Langmuir–Hinshelwood Kinetic Parameters for TiO_2-Catalyzed Photodegradation of *Para*-Substituted Phenols

substituent (X)	linear fit[a]	k' (M min^{-1}) × 10^5	K (M^{-1})	$\log(k'_X/k'_H)$	$\log(K_X/K_H)$
H	0.942 (6)	2.7	2900	0.00	0.00
p-OCH_3	0.960 (6)	3.9	1300	0.16	−0.35
p-CH_3	0.958 (6)	2.3	3600	−0.07	0.094
p-F	0.981 (6)	5.1	1600	0.28	−0.26
p-Cl	0.977 (5)	3.4	1300	0.11	−0.35
p-Br	0.980 (6)	2.0	2300	−0.12	−0.096
p-I	0.998 (7)	2.4	700	−0.052	−0.64
p-$COCH_3$	0.949 (6)	2.8	1200	0.023	−0.39
p-CF_3	0.979 (4)	2.4	3000	−0.052	0.014
p-CN	0.975 (6)	5.4	200	0.030	−1.20

[a] The correlation coefficient, *r*, for the best least-squares fit line representing the experimental data. The number in parentheses represents the number of data points used for each plot.

Table 3. Tabulation of Hammett Constants

substituent (X)	σ_p[a]	σ[b]	$\sigma+$[c]	σI (Hine)[c]	σI (Taft)[c]	σI (Grob)[c]
H	0.00	0.00	0.00	0.00	0.00	0.00
p-OCH_3	−0.28	−0.27	−0.78	0.27	0.23	0.31
p-CH_3	−0.14	−0.17	−0.31	−0.04	−0.05	−0.02
p-F	0.15	0.06	−0.07	0.50	0.50	0.46
p-Cl	0.24	0.23	0.11	0.46	0.47	0.44
p-Br	0.26	0.23	0.15	0.44	0.45	0.47
p-I	0.28	0.18	0.13	0.39	0.38	0.41
p-$COCH_3$	0.47	0.50			0.27	0.29
p-CF_3	0.53	0.54		0.45		
p-CN	0.70	0.66	0.66	0.56	0.59	0.55

[a] Reference 30. [b] Reference 31. [c] Reference 26.

among the L–H reaction rate constant (k') and σ_p, as well as $\sigma+$, for the monohalogenated phenols, as shown in Figure 2. These correlations[30] suggest that monohalogenated phenols follow analogous photodecomposition mechanisms and may involve the formation of a positively charged reaction center. The limited correlation observed for the non-halophenols may be the result of several competing reactions occurring simultaneously (e.g., reactions occurring directly with the aromatic ring and at the side chain). The L–H kinetic parameter, k', changes systematically with the electronic influence, σ_p and $\sigma+$, of the individual halophenols.

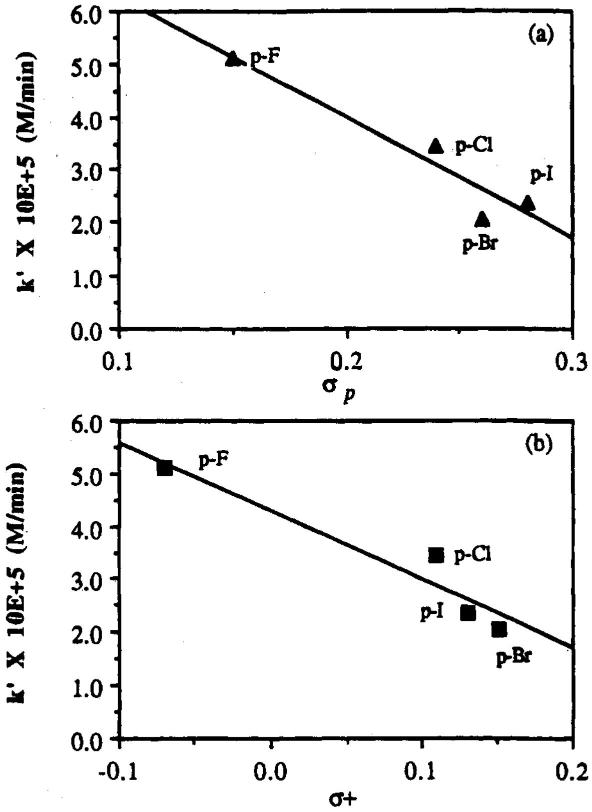

Figure 2. Plots of the Langmuir–Hinshelwood reactivity constants, k', vs Hammett constants for *p*-halophenols.

The Hammett plots suggest similar reaction mechanisms, and addition of hydroxyl radical followed by elimination of the halide has been proposed to explain dehalogenation of halosubstituted phenols.[32] While the rates of degradation are expected to parallel the relative carbon–halogen bond strengths if halide elimination is the rate-determining step, the actual initial degradation rates for *para*-substituted halophenols follow the opposite trend. Apparently, the predominant mechanism does not involve simple carbon halide bond cleavage. The formation of an intermediate in which the relative bond strengths of the carbon halide bonds are strongest to weakest in the following order, C–I > C–Br > C–Cl > C–F, may be the result of a complex between the halide and the TiO_2, a radical intermediate, or an excited-state intermediate. We propose the involvement of such an intermediate to rationalize the observed relative reactivities of the *p*-halophenols.

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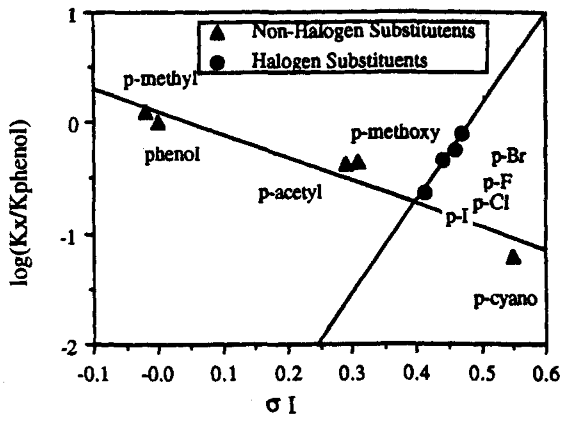

Figure 3. Plots of the Langmuir–Hinshelwood adsorption equilibrium constants, K, vs the Hammett constants, σI, for *para*-substituted phenols.

A correlation between the apparent adsorption equilibrium constant, K, of *para*-substituted phenols and the inductive/field effect of the substituents was also observed. Although the Hammett plot of log (K_X/K_H) vs σI shows a poor correlation when considering all the substituted phenols, when the halogens and the remaining substituents are evaluated separately, good correlations are observed. (p-CF_3 is not included as a σI value has not been reported.)

These correlations suggest that the halo- and nonhalophenols exhibit different adsorption mechanisms. The halophenol may be adsorbing onto the TiO_2 through a charge transfer type complex whereas the non-halophenol adsorption may be the result of hydrogen bonding and/or a π interaction.

The similarity among the apparent reaction constants, k', for *para*-substituted phenols seems to support the claims of Turchi and Ollis that for a given reactor these disappearance rates are similar despite the different functionalities of the substrates.[25] Although they also suggested that the L–H kinetic parameter, k', should be dependent on the type of TiO_2 comparison of their studies with our investigations using different TiO_2 showed similar y-intercepts ($1/k'$). This may be coincidental or suggest an independence on the semiconductor's physical and electronic properties.[25]

Turchi and Ollis also suggested that the equilibrium rate constant, K, should be proportional to a second-order homogeneous reaction rate constant ($k_{OH^\cdot}$) for the two reacting species; if the substrate is absorbed when it reacts with the hydroxyl radical, then K would reflect its adsorptive properties. We could only find a limited number of absolute rate constants $k_{OH^\cdot}$ for hydroxyl radicals with *para*-substituted phenols in aqueous media in the literature, Table 4.

Figure 4 suggests a correlation between $k_{OH^\cdot}$, absolute homogeneous reaction rates of hydroxyl radical with the phenols, and the product of the L–H kinetic parameters, $k'K$. Although a good correlation among relative rates of hydroxyl radical addition to *para*-substituted phenols and various Hammett constants has been reported,[29b] the limited correlation observed in the plots of the Hammett constants vs the absolute rate constants, $k_{OH^\cdot}$, may be due to the fact that these $k_{OH^\cdot}$ values were measured by different groups under different experimental conditions. Despite these factors, there is a reasonable correlation between the observed L–H kinetic parameters and second-order hydroxyl radical rate constants.

Table 4. Comparison of the $k_{OH^\cdot}$, L–H Kinetic Parameters, and σ for *Para*-Substituted Phenols

substituent	$k_{OH^\cdot}$ (L/mol·s) × 10^{-10}	log($k'K$)	σ^e
p-OCH_3	2.6[a]	−1.305	−0.27
p-CH_3	1.2[b]	−1.082	−0.17
phenol	1.8[c]	−1.108	0.00
p-Cl	7.6[d]	−1.353	+0.23

[a] Reference 33. [b] Reference 34. [c] Reference 35. [d] Reference 36. [e] Reference 31.

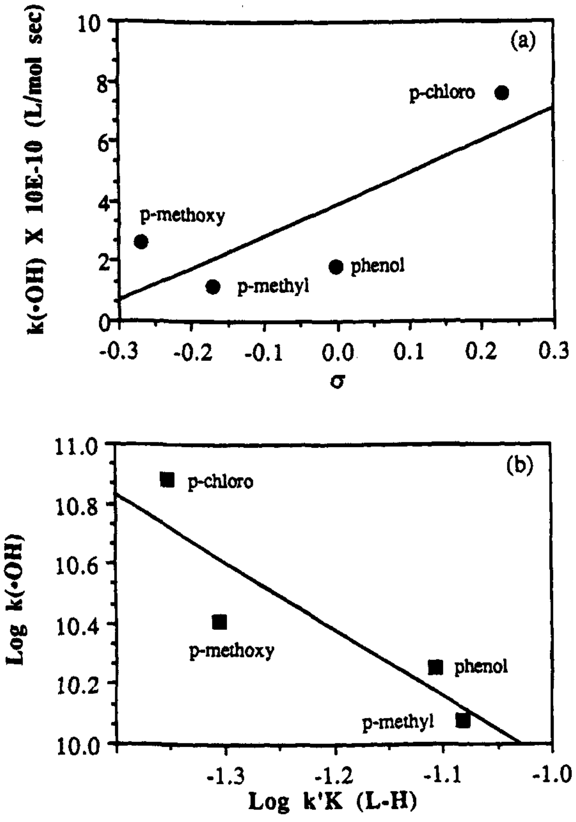

Figure 4. Plots of the absolute hydroxyl radical rate constants, $k(^\cdot OH)$, vs Hammett constants and Langmuir–Hinshelwood kinetic parameters for several *para*-substituted phenols.

The correlation between the L–H kinetic parameters and the $k_{OH^\cdot}$ support predictions[25] that TiO_2-catalyzed photodegradation of organic substrates in oxygenated aqueous media is controlled by the generation of hydroxyl radicals and diffusion (adsorption/desorption) of the substrate at the solid–liquid interface.

Conclusions

The TiO_2-catalyzed degradations of p-substituted phenols were investigated. The decay kinetics of the substituted phenols are consistent with the Langmuir–Hinshelwood (L–H) model. Although a variety of substituents were employed the changes is the L–H kinetic parameters are relatively small. The y-intercept of the Langmuir–Hinshelwood plots and, therefore, the apparent reactivity constant, k', for the studied phenols appear to be independent of substituent effects for nonhalophenols. A direct relationship between the k' and

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different Hammett constants was observed for *para*-substituted monohalogenated phenols. Hammett correlations were also observed for *K*, the L−H adsorption equilibrium constant, suggesting different adsorption modes for the halogenated and nonhalogenated para monosubstituted phenols. The relationship among Hammett constants and the kinetic parameters strongly suggests that a number of different reaction pathways, depending on the electronic nature of the substituent, are involved in the TiO_2-catalyzed photodegradation of *para*-substituted phenols. The effects of pH on the kinetic parameters of degradation and the determination of absolute rate constants for hydroxyl radicals with the substituted phenols are currently under investigation.

Methods and Materials

Chemicals. Phenol was purchased from Fisher Scientific (Purified Grade), and *p*-methoxyphenol, *p*-cresol, *p*-fluorophenol, *p*-chlorophenol, *p*-bromophenol, 4-hydroxyacetophenone, α,α,α-trifluoro-*p*-cresol, *p*-cyanophenol, and *p*-iodophenol were purchased from Aldrich Chemical Co. Deionized water pH = 3.0 (pH was adjusted with 0.1 N HCl) and chloroform (Fisher Scientific, Certified A.C.S.) were the solvents used throughout this study. The photocatalyst was titanium dioxide, Degussa P25 lot no. RV2186.

Photoreactor. A Rayonet photochemical chamber reactor Model RPR-100 (purchased from Southern New England Ultraviolet Co.), fitted with 16 low-pressure mercury lamps blazed at 350 nm, a Rayonet Merry-Go-Round (Model-RMA-500), and a cooling fan, was used to irradiate several samples simultaneously. Reactions vessels were 50-mL screw cap, Corex, round-bottom tubes. Each sample was magnetically stirred throughout irradiation, and the solution temperatures were maintained at 40 ± 2 °C.

Analyses. The degradation of the phenols was followed with a Hewlett-Packard gas chromatograph 5890 equipped with an FID detector and a J & W Scientific DB-1 (30 m × 0.25 mm, 0.25 μm) column. The temperature program started at 40 °C for 5 min and increased at 20°/min to 220 °C with a final time of 5 min. The temperature of the injector was 200 °C, and that of the detector was 220 °C. The head pressure was 14.1 psi; the purge was off at 0.0 min, on at 1.5 min. The gas flows were 375 mL/min for air, 30 mL/min for N_2 + He (carrier), and 30 mL/min for H_2. A standard calibration curve was prepared for the analysis of each phenol.

General Photoylsis and Extraction Procedure. A 50-mL aliquot of deionized water pH = 3.0 was placed in a round-bottom Corex tube; a determined volume of this water was removed and replaced with an equal volume of an aqueous stock solution (0.1 M prepared in deionized water pH 3.0) of the phenol to be studied. Then, 5 mg of TiO_2 (0.1 g/L) was added, and the mixture was sonicated (43 kHz) for 5 min to achieve a homogeneous suspension. After sonicating, the mixture was cooled to 22 °C with an ice−water bath while being stirred. A 5-mL aliquot of the mixture was filtered, using a 10-mL gas tight syringe and a 0.45-mm PTFE acrodisk, into a 40-mL extracting vial, followed by the filtration of two separate 5-mL aliquots of deionized water pH = 3.0 to rinse the syringe and acrodisk. A 10-mL aliquot of deionized water pH = 3.0 was added to the extracting vial as well as a 5-mL aliquot of $CHCl_3$ to bring the total volume to 30 mL. The resulting solution was shaken in an Orbit Shaker (3 min at 300 rpm), and the $CHCl_3$ layer was pipetted into an amber autosampler vial to be chromatographed. Standardization curves were continuously checked with authentic samples to insure the validity of the results.

The remaining solution was purged with O_2 for 1 min after every hour of irradiation. A control reaction was purged with N_2 for 5 min initially and after every hour of irradiation. After purging, the mixture was equilibrated to 40 °C prior to irradiation. Following irradiation, the mixture was rapidly cooled to 22 °C with an ice−water bath while stirring, and then a 5−mL aliquot was taken to be analyzed as above. The sampling times were 0, 5, 10, 15, and 30 min for the kinetic studies carried out at different concentrations; the control reactions were usually sampled at 0, 15, 30, 60, 120, and 240 min. Control reactions were carried out and analyzed to assess the effect, if any, of irradiation in the presence of TiO_2 and O_2 or N_2, irradiation without TiO_2 (direct photolysis) in the presence of O_2, and no irradiation at all (kept in the dark at 40 °C) in the presence of TiO_2 and O_2. The controls were carried under dilute conditions (~detection limit) where small changes are most pronounced.

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