ARTICLES

Heterogeneous Photocatalytic Decomposition of Benzoic Acid and Adipic Acid on Platinized TiO₂ Powder. The Photo-Kolbe Decarboxylative Route to the Breakdown of the Benzene Ring and to the Production of Butane

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The heterogeneous photocatalytic decomposition of adipic acid in deaerated aqueous solutions containing a suspension of platinized TiO₂ (anatase) powder leads to the formation of CO₂ and butane with lesser amounts of valeric acid and negligibly small quantities of oligomeric materials. A mechanism for this photo-Kolbe reaction, which yields different products than the electrochemical Kolbe reaction, is proposed. The photodecomposition of benzoic acid in oxygen-containing solution at platinized TiO₂ was also investigated. The reaction product is predominantly CO₂, with intermediate production of salicylic acid and phenol. A mechanism for the reaction based on photogeneration of hydroxyl radicals and adsorption of intermediates on the powder surface is proposed.

Introduction

Semiconductor materials are currently of much interest in electrochemical systems which can utilize solar energy for the production of electricity or useful chemical species. Recently semiconductor powders suspended in solution have been used to carry out heterogeneous photocatalytic and photosynthetic processes.[1] For example, applications of particulate semiconductors, e.g., TiO₂ and ZnO, to photocatalytic oxidation of cyanide,[2,3] sulfite,[3] acetate,[4] and other substances[5,6] have demonstrated the versatility and ease of application of these methods. Recent studies from this laboratory have shown that irradiation of reaction mixtures containing suspended platinized TiO₂ (Pt/TiO₂) powders can promote several photocatalytic and photosynthetic reactions, such as the photo-Kolbe reaction, in which acetic acid is decomposed to methane and carbon dioxide,[4,6] and even the photosynthesis of amino acids from methane–ammonia–water mixtures.[7] To extend the scope of synthetic methods at illuminated semiconductor powders, we describe here the heterogeneous photooxidation of benzoic acid on Pt/TiO₂ powders in the presence of oxygen, and also the heterogeneous photocatalytic decomposition of adipic acid in deaerated aqueous solution.

The oxidation of benzoic acid has been demonstrated by the thermal decomposition of the cupric or molybdenum salt to phenol and carbon dioxide,[8] by the radiolysis of aqueous solutions of benzoic acid or benzoate to monohydroxylated compounds and carbon dioxide derived from the carboxyl group,[9–11] and by the Kolbe electrolysis in nonaqueous solvents to products due to the intermediacy of benzoyloxy and/or phenyl radicals.[12] We report here that the photocatalytic oxidation of benzoic acid in aqueous solutions containing suspended Pt/TiO₂ powders involves the breakdown of the benzene ring through the addition of hydroxyl radicals to aromatic rings (unlike the usual electrochemical Kolbe reactions described above).

The electrolysis of dicarboxylic acids in aqueous media has been reported to yield olefins and alcohols, containing two carbons less than the starting material.[13] We report here the heterogeneous photocatalytic decomposition of adipic acid, a six-carbon saturated aliphatic dicarboxylic acid, on Pt/TiO₂ to yield n-butane, valeric acid, and CO₂ (eq 1). This predominant decarboxylation reaction to

$$HO_2C(CH_2)_4CO_2H \xrightarrow{-CO_2} CH_3(CH_2)_3CO_2H \xrightarrow{-CO_2} C_4H_{10}$$
$$(1)$$
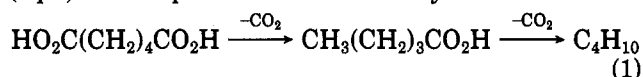
yield an uncoupled alkane thus follows previous studies from this laboratory in which unactivated monocarboxylic acids at ambient temperature are decomposed efficiently to the corresponding alkanes in a reaction pathway different from the electrochemical one.

Experimental Section

Materials. Benzoic acid (reagent grade, Matheson, Coleman and Bell), salicylic acid (reagent grade, Baker and Adamson), sodium hydroxide (analytical reagent grade, Mallinckrodt Chemicals), barium hydroxide (reagent grade, Matheson, Coleman and Bell), and adipic acid (reagent grade, Baker Chemical Co.) were used without

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further purification. Triply distilled water was used to prepare aqueous solutions. All solvents and other chemicals used were reagent or spectrophotometric grade and were used without further purification. The cation exchange resin (Dowex 50W-X8, Baker Chemical Co.) was used after swelling with triply distilled water and exchanging Na^+ ions with H^+ ions. The platinized TiO_2 powders were made by photodecomposition of hexachloroplatinic acid onto TiO_2 powders (reagent grade, Matheson, Coleman and Bell, 125–250 μm) and contained 10% platinum by weight.[14]

Apparatus. A 2500-W Xe–Hg lamp (Model UF30KK, Christie Electric Corp., Los Angeles, CA), operated at 1600 W, was used as the light source for all preparative runs; a 450-W Xe lamp with Model 6242 power supply (Oriel Corp., Stamford, CT) served in several analytical runs. The reaction cell with a flat window for irradiation and the water bath were both of Pyrex; the bath temperature usually was set to 27 ± 1 °C. Irradiation was performed by illuminating the sample (a stirred suspension of typically 100 mg of powder in 25 mL of solution) through the water bath and the reaction cell. GC–mass spectra of reaction gases were obtained with an automated gas chromatograph/EI-CI mass spectrometer system (Finnigan, Model 2000). Infrared spectra were taken on a Beckman IR-9 spectrophotometer. UV–visible spectra were recorded with a Cary Model 14 spectrophotometer. Electrochemical experiments were performed by using a PAR Model 173 potentiostat (Princeton Applied Research, Princeton, NJ) and a PAR Model 173 universal programmer. Fluorescence measurements were made with an Aminco-Bowman spectrophotofluorometer.

Product Analysis. (a) A typical preparative experiment for the photooxidation of benzoic acid consisted of illuminating 25 mL of a solution containing 0.305 g (0.10 M) of benzoic acid, 10 mL of 0.20 M NaOH, distilled water, and 100 mg of 10% platinized TiO_2 powder kept in suspension by bubbling oxygen through the solution. The gases produced during the irradiation under O_2 were collected in a mercury-containing gas volumetric apparatus.[15] After termination of photolysis, a directly attached, evacuated gas sample cell for use in analysis by GC–mass spectrometry was filled with the gas mixture in the volumetric apparatus. The rate of carbon dioxide evolution was determined gravimetrically in another preparative run. The reaction gases were swept out of the reaction vessel with a stream of oxygen and were bubbled through a saturated solution of $Ba(OH)_2$ in 0.2 M sodium hydroxide. The precipitated $BaCO_3$ was filtered off, washed with distilled water, dried at 120 °C, and weighed. The reaction mixture, which had a yellow–brown color after irradiation, was brought to pH 10 with 0.2 M NaOH and then extracted with ether. No neutral material and organic bases resulted from the ether layer. The aqueous layer was then extracted with carbon tetrachloride after being acidified to pH 1–2 with 1 M HCl. A small amount of resinous brown solid (solid 1) formed at the interface between the CCl_4 and aqueous layers. The carbon tetrachloride layer was dried over Na_2SO_4 and carefully removed under reduced pressure at room temperature to give unreacted benzoic acid with mp 119–121 °C (122–123 °C for standard sample). The aqueous layer was extracted again with ether. The ether layer obtained here was treated by the same procedure as that of the CCl_4 layer described above to give a resinous yellowish solid (solid 2). Na^+ ions in the

aqueous layer were exchanged with H^+ ions through a column of cation exchange resin, and a resinous shiny brown (solid 3) was obtained. For the determination of hydroxylated intermediates, a fluorimetric method was employed, as follows. The reaction mixture was extracted with carbon tetrachloride after being acidified to pH 1–2 with 1 M HCl to remove colored products into the aqueous layer. The CCl_4 layer was extracted with 5 wt % sodium bicarbonate, and then the aqueous layer, adjusted to pH 5, was examined in the spectrophotofluorometer.

(b) Fenton Reactions: The reaction between Fenton's reagent and benzoate were carried out as described by Cier et al.[16] Benzoic acid (5 mmol) and NaOH (5 mmol) were dissolved in 75 mL of H_2O. The reaction chamber was a one-compartment cell fitted with three side arms (one for nitrogen gas input, one for gas output, and the other with a septum for injecting reagents). The aqueous benzoate solution prepared above was put in the reaction chamber and deaerated for 30 min; 5 mmol of $FeSO_4$ was then added to the solution. After the solution became clear, 10 mmol of H_2O_2 (~1.13 mL of 30% H_2O_2) was injected slowly into the reaction chamber with a syringe. After a reaction time of ~30 h, the CO_2 gas generated and the product mixture were collected, separated, and analyzed as described above.

(c) A typical experiment for the photooxidation of adipic acid was performed as follows. In a Pyrex cell connected to a gas volumetric system, 25 mL of a mixture of 0.365 g (0.10 M) adipic acid, 12.5 mL of 0.2 M sodium hydroxide, triply distilled water, and 100 mg of 10% platinized TiO_2 powder was irradiated with a 2.5-kW Xe–Hg lamp (operated at 1.6 kW) while stirring at 45 °C. Before and during irradiation the mixture was deaerated with purified nitrogen. After irradiation for 40 h, the gaseous products, which were collected in a gas buret, were analyzed by GC–mass spectrometry. The identities of the products were confirmed by comparison with a standard sample. The yield of CO_2 was determined quantitatively by trapping as $BaCO_3$ in a separate experiment. After irradiation the colorless reaction mixture, which had an unpleasant odor, was adjusted to pH 10 with 0.2 M NaOH and extracted with ether. The aqueous layer was acidified to pH 1–2 with 1 M HCl and then extracted with a large amount of benzene. The aqueous layer was further extracted with ether to yield unreacted adipic acid (mp 148–150 °C compared to 149–151 °C for a standard sample).[17] The benzene layer was dried over Na_2SO_4 and evaporated under reduced pressure at 40 °C to give a liquid product. The infrared spectrum of the liquid product was identical with that of a standard sample of valeric acid with strong absorption at wave numbers (cm^{-1}) of 530–560, 950, 1120, 1235, 1295, 1430, 1735, and 3000.

Results

Photocatalytic Decarboxylation of Benzoic Acid on Platinized TiO_2 Powders. Illumination of suspensions of platinized TiO_2 powders in aqueous benzoic acid/sodium benzoate mixtures in the presence of oxygen leads to the observable evolution of carbon dioxide. After the illumination was stopped, the gaseous products, which were collected in a gas volumetric system, were analyzed by GC–mass spectrometry: the mass spectrum m/e (rel intensity) consisted of signals due to CO_2, 44 (44.9%) and 16 (11.5%), with background signals due to O_2, 32 (100%),

(14) Kraeutler, B.; Bard, A. J. *J. Am. Chem. Soc.* 1978, *100*, 4317.
(15) This gas volumetric system was identical with that reported in ref 4.

(16) Cier, A.; Nofre, C.; Ranc, M.; Lefier, A. *Bull. Soc. Chim. Fr.* 1959, 1523.
(17) The ether layer obtained here was dried over anhydrous sodium sulfate and evaporated carefully under reduced pressure at room temperature to give a white crystal, adipic acid.

TABLE I: Heterogeneous Photocatalytic Carbon Dioxide Evolution under Illumination at Platinized TiO$_2$ Powder and Control Experiments

Pt/TiO$_2$ powder	soln compn[a]	conditions	amount of CO$_2$ evolved, mmol	rate of CO$_2$ evolved, mmol/h
yes	0.020 M HBz, 0.080 M NaBz in water	3–96 h illuminated under O$_2$	0.350–4.10	~5.0 × 10^{-2}
yes	0.020 M HBz, 0.080 M NaBz in water	72 h in the dark under O$_2$	0.0182	2.5 × 10^{-4}
yes	0.020 M HBz, 0.080 M NaBz in water	58 h illuminated under N$_2$	0.0238	4.1 × 10^{-4}
yes	0.10 M HBz in benzene	72 h illuminated under O$_2$	0.162	2.3 × 10^{-3}
yes	0.125 M HBz, 0.125 M tetra-n-butylammonium benzoate in acetonitrile	48 h illuminated under O$_2$	0.304	6.3 × 10^{-3}
yes	0.020 M HBz, 0.080 M NaBz, 0.10 M K$_3$Fe(CN)$_6$ in water	19.5 h illuminated under N$_2$	0.147	7.54 × 10^{-3}
no[b]	0.060 M NaBz in water	Fenton's reagent	0.40	

[a] HBz is benzoic acid; NaBz is sodium benzoate. [b] With Fenton's reagent (0.06 M FeSO$_4$ and 0.12 M H$_2$O$_2$). In addition to CO$_2$ 0.12 mmol of phenol and 6.8 × 10^{-3} mmol of salicylic acid were formed.

and air contaminents, nitrogen, 28 (27.9%), and water, 18 (4.9%). No benzene signals were obtained. The only gaseous product evolved under illumination was thus CO$_2$. The CO$_2$ yield (determined as BaCO$_3$) as a function of the time of illumination at 27 ± 1 °C, as shown in Figure 1, gives a CO$_2$ evolution rate of 0.05 mmol/h. From the yellow–brown reaction mixture the unreacted benzoic acid was recovered by the separation procedure described in the Experimental Section. The amount of the unreacted benzoic acid was also determined by titration of the solution. Following the procedure of Kaeding,[18] the CCl$_4$ layer obtained in the separation procedure was titrated to the thymol blue end point with a standard solution of 0.2 M NaOH. The results from the gravimetric and titrimetric methods agreed to within ~10%. The mole ratio of the CO$_2$ evolved to the benzoic acid consumed (from the titration results) is shown in Figure 1. It increased from the value of ~1.8 after 3-h illumination to values above 4. Three kinds of resinous solids, solids 1–3, were also obtained in the separation of the reaction mixture. Analysis of these products produced after 3-days illumination of benzoic acid/benzoate solution with Pt/TiO$_2$ powders showed that the 1.76 mg of yellowish solid 2 was soluble in ether and that the 23.2 mg of shiny brown solid 3 was soluble in water and methanol. All resinous products were insoluble in CCl$_4$. The infrared spectra of thin films of these solids showed the OH frequency at 3480 cm^{-1}, accompanied by two broad absorption waves at 2700 and 3120 cm^{-1}, and the C=O frequency at 1725 cm^{-1} with a shoulder at 1630 cm^{-1}.[19] The infrared spectrum was very similar to that of phenolic resin[20] particularly in the region of wavenumbers higher than 1100. Thus the resinous products all appear to be the same kind of hydroxylated polymer containing carbonyl groups.

In a separate experiment, the yellow–brown reaction mixture after acidification was directly extracted with ether. After being dried over sodium sulfate and after careful removal of most of the solvent, the concentrated ether solution was examined by gas chromatography (SE-30 column). No peaks corresponding to benzene, biphenyl, or phenyl benzoate were obtained.
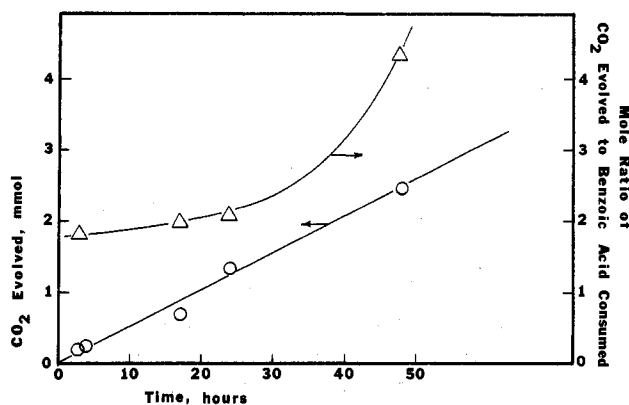
(18) Kaeding, W. W. *J. Org. Chem.* 1961, *26*, 3144.
(19) Except for these absorption peaks, some distinct absorption peaks were also observed at 660, 725, 785, 1135, 1250, 1295, 1400, and 1445 cm^{-1}.
(20) Referred to as phenol–resorcinol–formaldehyde resin (0.5:0.5:0.6, alkaline condensed); Hummel, D. O.; Schall, F. "Infrared Analysis of Polymers, Resins and Additives—An Atlas"; Wiley-Interscience: New York, 1969; Vol. I, Part 2, spectrum number 321.
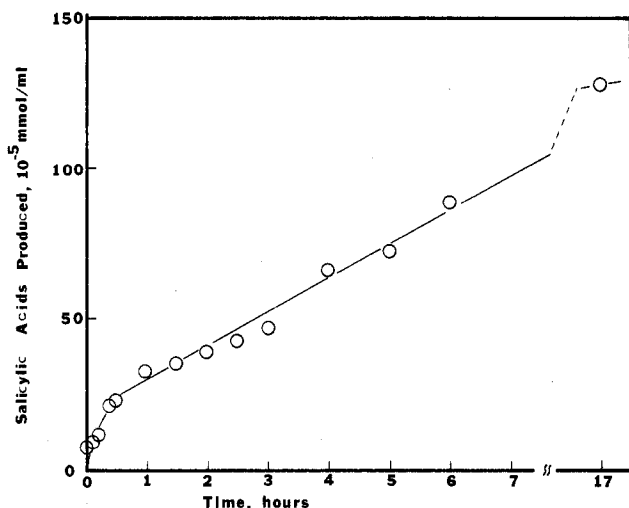

Figure 1. CO$_2$ yield (circles) and the mole ratio of CO$_2$ evolved to benzoic acid consumed (triangles) as functions of the time of illumination. Oxygen-saturated aqueous solutions containing 20 mM benzoic acid and 80 mM sodium benzoate with 100 mg of suspended 10% platinized anatase powder were irradiated with a 2.5-kW Xe lamp (operated at 1.6 kW) at 27 °C.

A fluorimetric technique was used to identify and determine any hydroxylated benzoates.[9] The reaction mixture, after removal of the brownish resinous products, showed an excitation spectrum maximized at 303 nm and an emission peak at 408 nm. The positions of the peaks and the shapes of the spectra are identical with those of standard salicylic acid solutions. No p-hydroxybenzoate was found. The fluorescence spectrum of salicylic acid was shown to be unaffected by the presence of unreacted benzoic acid, so that the concentration of salicylic acid in an illuminated sample could be derived form the maximum fluorescence emission intensity relative to that of the standard sample. The yield of salicylic acid thus obtained is shown in Figure 2. The initial formation rate (for ~30 min) of salicylic acid was 0.5 μmol/(h mL); this rate decreased to ca. one-fifth of the initial value at longer times.

Several control experiments were carried out to eliminate possible effects of sample contamination and to investigate other paths for photodecarboxylation of benzoic acid under O$_2$. Passing oxygen for 72 h in the dark through the same solution with Pt/TiO$_2$ under otherwise identical conditions as the irradiation experiments showed only a negligible amount of CO$_2$ production (less than 5.1 × 10^{-3} times that under the illumination, see Table I). A 58-h illumination under the same conditions but under nitrogen also produced a negligible amount of carbon dioxide (8.2 × 10^{-3} times that under oxygen). Two experiments in

Figure 2. Salicylic acid yield as a function of the time of illumination. Experimental conditions same as in Figure 1.
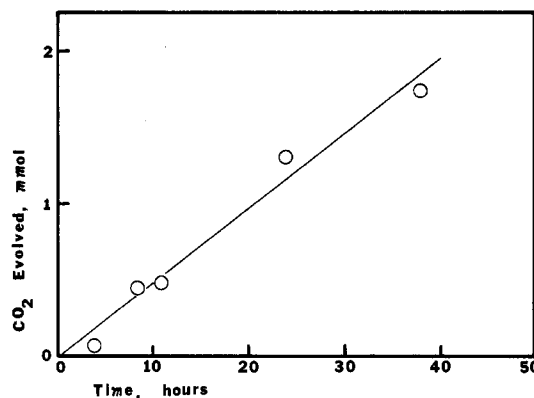

Figure 3. CO_2 yield as a function of the time of illumination of 37.5 mL of 0.067 M deoxygenated adipate solutions with 100 mg of suspended 10% platinized anatase powders irradiated with a 2.5-kW Xe lamp (operated at 1.6 kW) at $\sim$40 °C.

nonaqueous solvents were performed as follows. A solution of benzoic acid in benzene under oxygen was illuminated and produced only a trace amount of CO_2 ($\sim$10^{-2} times that in water). However, a solution of benzoic acid/tetra-n-butylammonium benzoate in acetonitrile under illumination yielded a small amount of CO_2 (12.7% of that in water). When potassium ferricyanide was added to the deaerated aqueous solution containing benzoic acid/benzoate and Pt/TiO_2, which was then illuminated under nitrogen, CO_2 was produced in an amount $\sim$15.1% of that under oxygen. Thus the photodecomposition rate under nitrogen increased by 18.4 times when potassium ferricyanide was present in the solution. Preliminary experiments concerning the reactions between Fenton's reagent, which produces hydroxyl radicals, and benzoate showed that carbon dioxide, phenol, and hydroxylated benzoate were the major products (Table I). This demonstrates the possibility of at least the initial stages of the photodecomposition process occurring by attack of $\cdot$OH on benzoic acid and intermediates.

Photocatalytic Decarboxylation of Adipic Acid on Pt/TiO_2 Powders. Similar to the behavior of benzoic acid mentioned above, illumination of suspension of Pt/TiO_2 powders in aqueous adipic acid solutions leads to the observable evolution of CO_2. After irradiation for 40 h, the gaseous products were analyzed by GC–mass spectrometry. The mass spectrum for the separated gas components showed signals corresponding to carbon dioxide, m/e 44; n-butane, m/e (relative intensity) 43 (100), 41 (31.8), 42 (15.1), 58 (14.0), 39 (11.7); and hydrogen, respectively. The identity of n-butane was confirmed by comparison with a standard sample (43 (100), 41 (27.2), 42 (12.8), 58 (16.8), 39 (9.6)). No additional gaseous reaction products such as cyclobutane or butene were obtained. The amount of CO_2 evolved (determined as $BaCO_3$ in a separate experiment) as a function of time of irradiation is shown in Figure 3. The rate of production of CO_2 was constant at 50 μmol/h. After irradiation the colorless reaction mixture was analyzed as mentioned in the Experimental Section. Only adipic acid and valeric acid were present in significant amounts. An analysis of the products showed that the ratio of adipic acid reacted/CO_2 evolved/valeric acid produced/n-butane produced was 1.0:1.75:0.25:0.76. Several control experiments in the absence of Pt/TiO_2 and without irradiation[21] under similar conditions as described
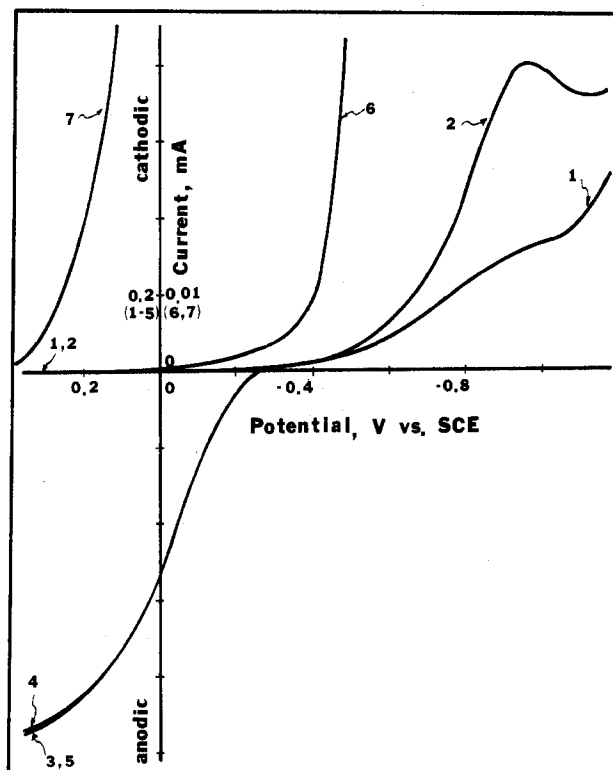

Figure 4. Voltammetric curves at Pt and n-type TiO_2 single crystal electrodes. A 450-W Xe lamp with a water filter was used as the light source. Scan rate, 100 mV/s. Initial potentials at positive extremes. (1) TiO_2 in the dark under N_2; 0.5 M $NaClO_4$ containing 20 mM benzoic acid and 80 mM sodium benzoate. (2) TiO_2 in the dark under O_2; same solution as in 1. (3) TiO_2 in the light under N_2; same solution as in 1. (4) TiO_2 in the light under O_2; same condition as in 1. (5) TiO_2 in the light under N_2; 0.5 M $NaClO_4$. (6) Pt; under N_2; same solution as in 1. (7) Pt; under O_2; same solution as in 1.

above resulted in only minute amounts of CO_2 corresponding to $\sim$6 μmol/h.

Electrochemical Measurements. As shown in previous studies,[4,6] the photocatalytic activity of suspended powders can be correlated with the behavior of semiconductor electrodes in photoelectrochemical (PEC) measurements.[4,6] The current–potential (i–V) behavior of a rutile single crystal electrode in an aqueous solution (pH $\sim$5) containing 20 mM benzoic acid, 80 mM sodium benzoate, and 0.5 M sodium perchlorate as the supporting electrolyte is shown in Figure 4. In the dark, only a very small anodic current was observed on TiO_2 electrodes both in deaerated and in oxygen-saturated solutions (curves 1 and 2). Note,

(21) The control experiment in the dark was carried out with bubbling N_2 for 1 day. No CO_2 was precipitated as $BaCO_3$.
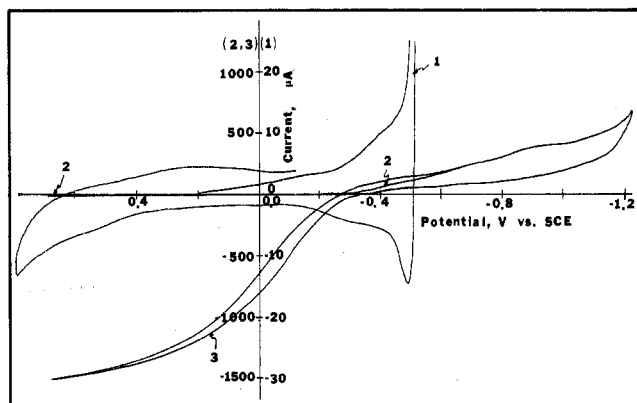
Figure 5. Current–potential curves at Pt and n-TiO$_2$ single crystal electrodes in 0.5 M NaClO$_4$ solutions containing 0.10 M adipic acid half-neutralized with NaOH. A 450-W Xe lamp fitted with a water infrared filter was the light source. Scan rate, 100 mV/s. (1) On Pt; initial potential, 0.20 V vs. SCE. (2) On n-TiO$_2$ in the dark; initial potential, -0.31 V vs. SCE. (3) On n-TiO$_2$ in the light; initial potential, -0.31 V vs. SCE. Curves 2 and 3 use the left-handed current scale and curve 1 uses the right-handed scale.

however, that in oxygen-saturated solutions, the TiO$_2$ electrodes showed higher cathodic background currents than in deaerated solutions, presumably because of oxygen reduction. Under illumination, the anodic current was substantially enhanced. The onset potential, V_{on}, of the photocurrent and the shape of the anodic photovoltammetric curves were essentially unaffected by the absence or the presence of oxygen or the benzoic acid/benzoate mixture (curves 3–5), with $V_{on} \sim -0.30$ V vs. SCE. Following the principles for photocatalyst design discussed previously,[1b,c] where the rate of reaction at the catalyst powder is determined by the system operating at a potential where the anodic and cathodic currents are equal in magnitude, TiO$_2$ powder alone, even in the presence of oxygen, is not expected to be a very efficient catalyst. The role of Pt was examined by observing the i–V curves of a Pt electrode in these solutions. The reduction of protons on Pt in the presence of benzoic acid occurs at potentials more negative than -0.40 V vs. SCE (curve 6), so that H$^+$ reduction, even at Pt, is not a useful photocatalyst half-reaction, as opposed to the results on aliphatic carboxylates. The reduction of oxygen on Pt (curve 7) occurs at potentials much more positive than either V_{on} or the potentials at which reduction of oxygen on TiO$_2$ occurs. Thus, the photocatalytic activity of TiO$_2$ powder for the oxidation of benzoic acid is substantially enhanced by the presence of Pt and oxygen.

The current–potential behavior of a rutile single crystal electrode in an aqueous solution (pH $\sim$5) containing 0.10 M adipic acid half-neutralized with NaOH and 0.5 M sodium perchlorate as the supporting electrolyte is shown in Figure 5. Thus, the photoinduced oxidation of adipic acid (presumably as the adipate ion) on an illuminated n-type TiO$_2$ rutile single crystal electrode takes place at slightly more negative potentials than the reduction of protons on platinum (see curves 1 and 3). Therefore, the photooxidation of adipate ions on n-type TiO$_2$ and the reduction of protons on platinum can easily take place simultaneously at the two electrodes under short-circuit conditions, i.e., without applied potential. Moreover, the photooxidation of n-valeric acid, the intermediate in the photooxidation of adipic acid to n-butane, on TiO$_2$ and the reduction of protons on platinum can also be rationalized by similar voltammetric curves. Thus, as in previous studies,[4,6] the Pt/TiO$_2$ powders act as a multitude of small, short-circuited electrode systems.

Discussion

In the presence of oxygen, several n-type semiconductor powders have been shown to behave as photocatalysts and promote the oxidation of substrates.[1-6] Irradiation of a semiconductor with light of energy higher than the band gap results in creation of holes in the semiconductor valence band (VB) and electrons in the conduction band (CB) followed by trapping of the separated charges in shallow traps (tr) at the powder–solution interface (eq 2 and 3); As recently discussed in connection with the
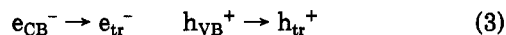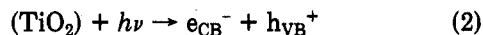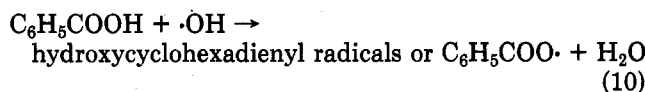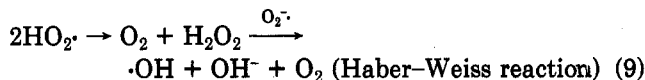
$$(\text{TiO}_2) + h\nu \rightarrow e_{CB}^- + h_{VB}^+ \tag{2}$$

$$e_{CB}^- \rightarrow e_{tr}^- \qquad h_{VB}^+ \rightarrow h_{tr}^+ \tag{3}$$
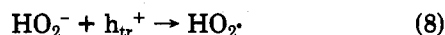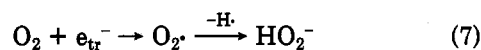
photo-Kolbe reaction at Pt/TiO$_2$ powder,[4] adsorbed species, e.g., OH$^-$, could also provide a site for trapping of the holes. These trapped carriers can recombine or the h_{tr}^+ can be scavenged by oxidizable species (for example, H$_2$O, H$_2$O$_2$, C$_6$H$_5$COO$^-$, or adipate ion), and e$_{tr-}$ by reducible species (for example, O$_2$ or H$^+$) in the solution. Thus the following reactions appear reasonable for the photooxidation of benzoic acid (adsorption of intermediates on the powder surface is possible, but is not specifically indicated in the equations below):

$$\text{OH}^- + h_{tr}^+ \rightarrow \cdot\text{OH} \tag{4}$$

$$\text{C}_6\text{H}_5\text{COO}^- + h_{tr}^+ \rightarrow \text{C}_6\text{H}_5\text{COO}\cdot \rightarrow \text{C}_6\text{H}_5\cdot + \text{CO}_2 \tag{5}$$

$$\text{H}^+ + e_{tr}^- \rightarrow \text{H}\cdot \tag{6}$$

$$\text{O}_2 + e_{tr}^- \rightarrow \text{O}_2\cdot \xrightarrow{-\text{H}\cdot} \text{HO}_2^- \tag{7}$$

$$\text{HO}_2^- + h_{tr}^+ \rightarrow \text{HO}_2\cdot \tag{8}$$

$$2\text{HO}_2\cdot \rightarrow \text{O}_2 + \text{H}_2\text{O}_2 \xrightarrow{\text{O}_2^-}$$
$$\cdot\text{OH} + \text{OH}^- + \text{O}_2 \text{ (Haber–Weiss reaction)} \tag{9}$$

$$\text{C}_6\text{H}_5\text{COOH} + \cdot\text{OH} \rightarrow$$
hydroxycyclohexadienyl radicals or C$_6$H$_5$COO$\cdot$ + H$_2$O
$$\tag{10}$$

The electrochemical measurements suggest that the reduction of H$^+$ on Pt and the reduction of O$_2$ at TiO$_2$ do not occur at a high enough rate at the potentials where photooxidation of benzoate takes place for these to be effective half-reactions at the catalyst particle. The role of the Pt for this reaction is thus to provide a site for the more efficient reduction of O$_2$ (eq 7). In fact the photodecarboxylation of benzoate does not occur to an appreciable extent in deaerated solutions containing Pt/TiO$_2$ (Table I).[22] The addition of ferricyanide to a deaerated solution to provide an alternate species which can be reduced causes decomposition of benzoate, but at a much smaller rate than in the presence of O$_2$. Thus, intermediates that form during the reduction of O$_2$ may also play a role in the oxidation process, as shown in reactions 7-9. Recent experiments involving spin trapping and electron spin resonance spectroscopic detection of intermediates formed during irradiation of Pt/TiO$_2$ in aqueous solutions have demonstrated the intermediacy of $\cdot$OH and HO$_2\cdot$.[23]

Since the mole ratio of CO$_2$ evolved to benzoic acid consumed is much larger than 1 (Figure 1), breakdown of the benzene ring must be occurring. This possibility has been confirmed by experiments on the photooxidation of aerated solutions of benzene, where CO$_2$ production has

(22) A negligibly small amount of CO$_2$ may result from the adsorbed oxygen on powders.
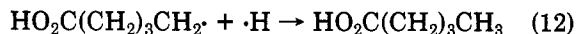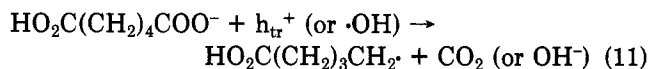
(23) Jaeger, C. D.; Bard, A. J. *J. Phys. Chem.* **1979**, *83*, 3746.

Scheme I
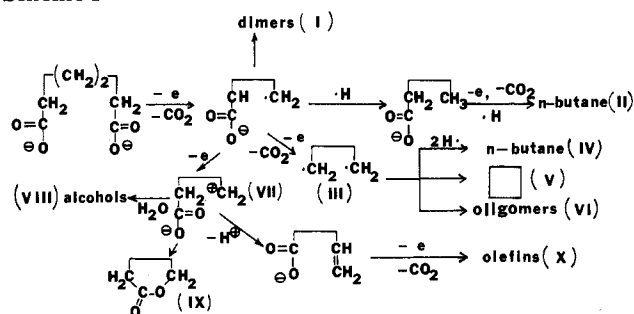
been established. Detailed studies of the photocatalytic decomposition of hydrocarbons at Pt/TiO_2 have been reported.[24] The mode of decomposition of the benzene ring has not been established. However, the detection of salicylic acid in the experiments described here suggests that attack by $\cdot OH$ radicals is a likely route. The probable role of $\cdot OH$ in these reactions is also supported by experiments showing the reaction of benzoic acid with Fenton's reagent as well as earlier studies on the radiolysis of benzoic acid solution.[10,11] The shape of the concentration–time profiles for salicylic acid production (Figure 2) can be qualitatively explained. The salicylic acid, which results from attack on the parent benzoic acid by $\cdot OH$, builds to a steady concentration, since it is produced from the benzoic acid whose concentration does not change significantly, and is also converted to more highly oxidized products (ultimately CO_2) by reaction with $\cdot OH$, holes, or other intermediates.

Note that the photocatalytic decarboxylation of benzoate differs from that found with acetate[4] and adipate under similar conditions (pH $\sim$5), where decomposition even in the absence of O_2 occurs. This implies that reaction 6 might be more favorable with aliphatic carboxylic acids than with aromatic acids. Although the observed onset potential for oxidation of adipic acid at n-TiO_2 is slightly more negative than for benzoic acid, this effect alone is probably insufficient to account for this difference in behavior. At this stage the most likely explanation is that aromatic intermediates in the benzoate system adsorb on the Pt sites and decrease the rate of the hydrogen evolution reaction. It is well-known that many adsorbed organic species can "poison" Pt electrodes toward proton reduction.[25] Note that only a small increase in the hydrogen overpotential can cause a significant decrease in the reaction rate at the Pt/TiO_2 powders. The lower molecular weight intermediates of adipic acid may never leave the TiO_2 sites and are less likely to poison the proton reduction reaction. Oxidation of the adipic acid might take place through the following reactions:

$$HO_2C(CH_2)_4COO^- + h_{tr}^+ \text{ (or } \cdot OH) \rightarrow$$
$$HO_2C(CH_2)_3CH_2 \cdot + CO_2 \text{ (or } OH^-) \quad (11)$$

$$H^+ + e_{tr}^- \rightarrow H \cdot \quad (6)$$

$$HO_2C(CH_2)_3CH_2 \cdot + \cdot H \rightarrow HO_2C(CH_2)_3CH_3 \quad (12)$$

The breakdown of valeric acid then follows a similar route, leading to butane.

The products found for the adipic acid oxidation are useful in providing information about the path of the photo-Kolbe reaction, since several possible routes are possible, as shown in Scheme I.

The Kolbe electrolysis of dicarboxylic acids has been reported to occur via carbonium ions (VII) and to produce alcohols (VIII), lactones (IX), and olefins (X).[13,26] Homogeneous photochemical reactions of dicarboxylic acids either in $FeCl_3$ solution[27a] or with uranyl salt as a sensitizer[27b] usually produce monocarboxylic acids. The results reported here showed that n-butane (II) was the predominant product during the photocatalytic decarboxylation of the adipic acid on Pt/TiO_2 with no cyclobutane (V) or oligomers (VI) obtained. This suggests that the diradical (III) was not formed. Whether any dimers (I) were formed is still not clear and bears further investigation. However their yield is very low, consistent with previous findings that radical intermediates react with $H \cdot$ or are reduced before extensive dimerization occurs. This probably can be attributed to the rather low surface density of adsorbed alkyl radicals at the prevailing light flux and catalyst surface area. The density of active sites on the catalyst powders may also be quite small.[28] The lifetime of these adsorbed radicals is also sufficiently small that further oxidation to the carbonium ion by another photogenerated hole does not occur. This accounts for the difference between the products of the electrochemical Kolbe reaction (olefins and alcohols)[13] or oligomers (e.g., the Brown–Walker reaction)[29] and those of the photo-Kolbe reaction. The absence of appreciable amounts of intermediates (e.g., valeric acid in the case of adipic acid and salicylic acid in the case of benzoic acid) in the oxidative breakdown probably indicates that they largely remain adsorbed on TiO_2 sites on the particles and are decomposed before they escape to the bulk solution.

Because the predominant photocatalytic breakdown of benzoic acid forms CO_2, and not the usual electrochemical Kolbe type intermediates, e.g., biphenyl and phenyl benzoate, such a process may be of use in the treatment of waste streams containing this intermediate, as has been suggested previously for removal of cyanide, sulfite,[3] and aliphatic carboxylates.[4]

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(25) See, e.g., Vetter, K. J. "Electrochemical Kinetics"; Academic Press: New York, 1967; pp 567–70.

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(28) Photoelectrophoresis experimetns on anatase powders have shown that the photogenerated positive charge carriers, presumably trapped at the interfacial sites, were $\sim$3500 electronic charges on a powder of diameter $\sim$1 μm. (See: Takahashi, A.; Aikawa, Y.; Toyoshima, Y.; Sujigara, M. *J. Phys. Chem.* 1979, *83*, 2854. Dunn, W. W.; Aikawa, Y.; Bard, A. J., manuscript in preparation).

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