

# Photoassisted Decomposition of Salicylic Acid on TiO<sub>2</sub> and Pd/TiO<sub>2</sub> Films

Valeriy Sukharev, Aaron Wold, Yu-Ming Gao, and Kirby Dwight

*Department of Chemistry, Brown University, Providence, Rhode Island 02912*

Received January 30, 1995; in revised form June 2, 1995; accepted June 7, 1995

A marked increase in the activity of a Pd/TiO<sub>2</sub> catalyst toward the decomposition of salicylic acid was observed compared to that measured for a pure TiO<sub>2</sub> film. The observed difference in activity of Pd/TiO<sub>2</sub> vs pure TiO<sub>2</sub> films was in accordance with predictions made from the Langmuir-Hinshelwood model. This study further confirmed Bard's model that the metal cocatalysts provide additional sites for electron transfer to oxygen. © 1995 Academic Press, Inc.

## INTRODUCTION

The application of illuminated semiconductors for the decomposition of organic contaminants in water has been successfully used for a wide variety of compounds. In many cases complete mineralization of organic compounds has been achieved (1–3). Several mechanisms have been proposed in order to understand the initial steps of the semiconductor-mediated photodecomposition of organic compounds (4). These mechanisms can be summarized as (i) direct oxidation of organic molecules by holes from the semiconductor valence band and (ii) generation of hydroxyl radicals by water decomposition which can then oxidize the organic compounds.

In a photocatalytic process, the reaction rate of the holes must be balanced by a corresponding rate of removal of electrons. An increase in the electron concentration within a system will result in an increase in the electron-hole recombination and a decrease in the observed activity of the catalyst. Heller and Gerischer (5, 6) have calculated the rate of electron removal from the TiO<sub>2</sub> particles to oxygen molecules dissolved in aqueous solution. The model calculations were corroborated indirectly from experimental evidence involving changes in oxygen concentration in the system. They have shown that the rate of electron transfer can be both yield- and rate-controlling in photocatalytic processes (6). Indeed, it has been shown that electrons can accumulate on slurried TiO<sub>2</sub> particles resulting in a decrease in the activity of the catalyst. It was shown that even in oxygen saturated solutions electrons

persist on the slurried particles for at least 1 min (7). Hoffmann and co-workers, in their investigations on TiO<sub>2</sub> photoreactivity and size quantization (8), have found that the charge-carrier recombination lifetime and the interfacial electron-transfer rate constant correlated with the photo-oxidation quantum efficiency obtained for aqueous chloroform in the presence of TiO<sub>2</sub>. It was shown that photogenerated holes, which escaped band-gap recombination, were transferred to the sorbed electron donor within nanoseconds. The results obtained on electron transfer from the surface of TiO<sub>2</sub> particles are applicable to TiO<sub>2</sub> thin films. However, it is essential that the grain size be kept small in order to minimize bulk electron accumulation. This accumulation would favor electron-hole recombination. For both TiO<sub>2</sub> particles and thin films the molecular oxygen dissolved in solution plays the role of reagent-bonding of the photogenerated electrons (5–7). It was found (8–10) that photocatalytic activity is nearly completely suppressed in the absence of oxygen and the steady-state concentration of oxygen has a profound effect on the rate of photocatalyzed decomposition of organic compounds. Despite the fact that the rates and efficiencies of photoassisted degradation of organic substances are improved in the presence of oxygen, they remain relatively slow in the case of a pure TiO<sub>2</sub> catalyst. Gerisher and Heller (6) have postulated two possible mechanisms in order to explain this observation. First, the interaction of the overlapping oxygen *pπ* orbitals with the 3*d* orbitals of the transition metal is weak and hence electron transfer to the dissolved oxygen is retarded. The second possibility is a low rate of electron transfer from traps on the surface or subsurface region of the semiconductor to the oxygen molecules. There are some possibilities to improve the efficiency of such catalytic processes based on the addition of inorganic oxidizing species such as peroxydisulfate, periodate, or peroxides (3). Electrical biasing can also be used to withdraw the photogenerated electrons before they recombine with the holes (11, 12). Finally, modification of the semiconductor surface by means of the formation of surface electronic states that strongly interact with O<sub>2</sub> can be achieved with metal atoms

deposited on the  $\text{TiO}_2$  surface (6, 13). Indeed, the situation changes when a small quantity of a metal, such as Pd, Au, Ag, or a metal oxide such as  $\text{WO}_3$  or  $\text{MoO}_3$ , is added onto the surface of the  $\text{TiO}_2$  photocatalyst (7, 13, 14). Bard and co-workers have indicated (13) that the increase in photocatalytic activity of a metal/ $\text{TiO}_2$  catalyst is caused by the additional sites present on such materials. These additional sites result in a more efficient utilization of photogenerated electrons in the reduction of  $\text{O}_2$ .

In this study, the role played by Pd particles, dispersed onto a  $\text{TiO}_2$  surface is investigated by the determination of the photodegradation kinetics of salicylic acid. The photoassisted decomposition of salicylic acid is measured as a function of the concentration of air dissolved in an aqueous solution of this acid in two cases: a pure  $\text{TiO}_2$  film and a  $\text{TiO}_2$  film loaded with Pd particles. The comparative studies of these two dependencies were found to be consistent with the possible mechanism for the Pd cocatalyst action proposed by Bard and co-workers (13). Salicylic acid was chosen as a prototype molecule for its low volatility, sufficient solubility in water, and well-known UV-special characteristics.

## EXPERIMENTAL SECTION

### Preparation of $\text{TiO}_2$ Films

Titanium(IV) oxide films coated the inside of Pyrex tubes by an ultrasonic nebulization and pyrolysis technique (15). The deposition apparatus has been described by Wold and co-workers (16). The reactor used in this investigation was heated by means of a two-zone mirror furnace (Transtemp. Co., Chelsea, MA). Dipropoxy-titanium-bis(acetylacetonate) was used as a precursor for the preparation of these thin films. It was synthesized according to Yamamoto and Kambara's method (17). An alcohol solution of 0.1 M dipropoxy-titanium-bis(acetylacetonate) was nebulized by a commercial ultrasonic humidifier (Holmes Air) and carried into a Pyrex tube with an inside diameter of 2 cm by argon. The Pyrex tube used for the deposition of the film was held parallel to the carrier gas flow in the furnace and was rotated by a low-speed motor to achieve best uniformity. To obtain a 2-cm wide band of film, the remainder of the tube was masked with an aluminum foil. Typical reaction parameters were: deposition temperature, 500°C; argon flow rate, 2.8 liter/min; distance between nozzle and front edge of the film, 7.5 cm. Under such conditions, a film of 350 nm in thickness could be grown in 10 min using 6 ml of precursor solution. All deposited films were postannealed under a flowing oxygen atmosphere at 500°C for 20 min.

### Photochemical Decomposition of Palladium(II) Chloride on $\text{TiO}_2$ Films

Palladium(II) chloride was reduced onto titanium(IV) oxide films by photochemical decomposition in a manner

similar to that reported by Papp *et al.* (18). An aqueous  $1 \times 10^{-3} M$  palladium(II) chloride solution (30 ml) was added to the Pyrex tube coated inside with a transparent  $\text{TiO}_2$  film. The tube was then irradiated with four commercial fluorescent lamps (VITA-LITE full spectrum natural light, 15 W) arranged parallel to the reactor axis. Palladium(II) chloride was decomposed onto the titanium(IV) oxide film, and the thickness of the palladium layer increased with the duration of irradiation. The irradiated sample was then rinsed with distilled water to remove the remainder of palladium(II) chloride on the film. The films prepared by this method were analyzed by X-ray diffraction in a previous investigation (18). In the diffraction pattern of an as-deposited film of 0.42  $\mu\text{m}$  in thickness on a Pyrex substrate, four broad peaks at 25.3°, 48.2°, 55.3°, and 70.6° could be identified. They correspond to (101), (200), (211), and (220) reflections of the anatase phase of titanium(IV) oxide, respectively. X-ray diffraction of a film prepared with a sufficiently high concentration of palladium to be detected by X-ray analysis indicates that the palladium is deposited as elemental palladium.

### Measurement of Photocatalytic Activity

The photocatalytic activities of titanium(IV) oxide films were evaluated by degradation of salicylic acid. An aqueous  $6 \times 10^{-5} M$  salicylic acid solution (30 ml) was added to a Pyrex tube whose inside surface was coated with a  $\text{TiO}_2$  film. The sample to be measured was then irradiated with a 150 W Xenon short arc lamp whose output was passed through a Pyrex filter. The differential absorbance at 296 nm (absorption peak of salicylic acid) was measured using a Perkin-Elmer 552 A spectrophotometer. The change in concentration of salicylic acid of the irradiated sample as a function of time was compared with the reference sample of distilled water. The generation of carbon dioxide was measured by means of a carbon dioxide electrode (Orion 950200).

The dependencies of photocatalytic activity on the concentration of oxygen dissolved in aqueous solutions of salicylic acid were measured in the apparatus shown in Fig. 1. Different concentrations of dissolved oxygen were obtained by bubbling different air-argon gaseous mixtures through the solution. The flow rate of these gaseous mixtures was 110 ml/min. This flow rate was maintained during the entire process. In addition to providing a chosen oxygen concentration, the continuous gas stream also minimized possible diffusion problems. The measurements of the degradation rates of salicylic acid when different air-argon gas mixtures were bubbled through the solution were carried out under identical experimental conditions. The catalyst surface was regenerated each time before activity measurement. After each measurement, the Pyrex tube was filled with distilled water and the film was irradiated by

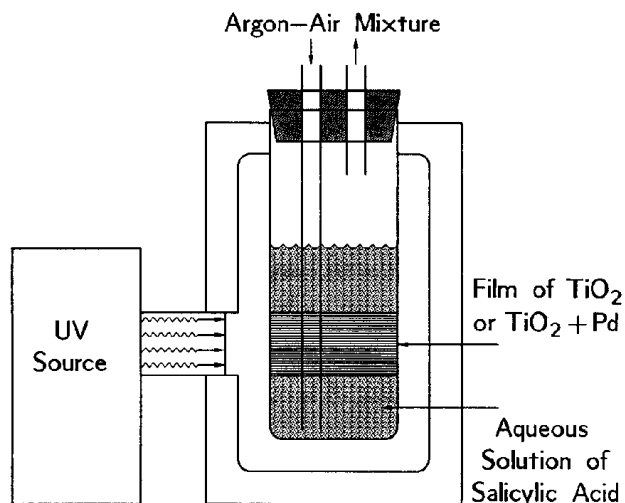


FIG. 1. Apparatus for catalyst photoactivity measurements.

the four commercial fluorescent lamps. The reproducibility of the value of salicylic acid adsorption taking place in the dark when argon was bubbled through the solution was chosen as the criteria for full surface regeneration. In this study, the films were all irradiated for the same amount of time and changes in the concentration of salicylic acid as a function of oxygen concentration were compared with the values obtained from the reference sample.

## RESULTS AND DISCUSSION

Wang *et al.* (7) have shown that the rate-limiting step in the photocatalytic destruction of some organic compounds by Pd coated TiO<sub>2</sub> particles is the transfer of electrons from the TiO<sub>2</sub> to oxygen dissolved in solution. In this study, the oxygen concentration dependencies of the rates of photoassisted decomposition of salicylic acid on an uncoated TiO<sub>2</sub> film and one loaded with some quantity of Pd were investigated. All experiments have been made in the cell shown in Fig. 1. The oxygen concentration in solution could be changed by means of bubbling different air-argon gaseous mixtures and the composition of these mixtures was varied from pure argon to pure air.

The comparative results of this study can be seen from Fig. 2. Curves 1 and 2 represent the change in concentration of salicylic acid with irradiation time for a pure TiO<sub>2</sub> film and a TiO<sub>2</sub> film loaded with Pd, respectively. Regions (a) indicate the decrease in concentration of salicylic acid when argon is bubbled into the cell which is kept dark. Regions (b) show the change in acid concentration when argon is bubbled into the cell when illuminated. Gas mixtures of different air to argon ratios were used to obtain the changes shown in regions (c). The cell was illuminated during these periods. It can be seen that the original decrease in salicylic

acid concentration (in the dark under argon) was due to adsorption of salicylic acid onto the surface of TiO<sub>2</sub> or Pd/TiO<sub>2</sub>. It can be seen from Fig. 2 (a) that after 20 min of intensive argon bubbling the adsorption of salicylic acid reached saturation and no further change occurred. Cunningham and Al-Sayyed found (19) that under different experimental conditions, i.e., the use of slurried TiO<sub>2</sub> particles, adsorption saturation occurred after 1 hr. The zero activity shown for irradiation of the TiO<sub>2</sub> film when argon was bubbled through the solution (curve 1, region b) is in agreement with the results of other investigators (7, 10-12). However, the initial irradiation of the TiO<sub>2</sub> film loaded with Pd under an argon atmosphere was accompanied by a significant decrease in salicylic acid concentration. This change was saturated after approximately 10 min. This additional decrease in salicylic acid concentration can arise from photoadsorption. The possibility of photoadsorption in such systems has been previously mentioned by Cun-

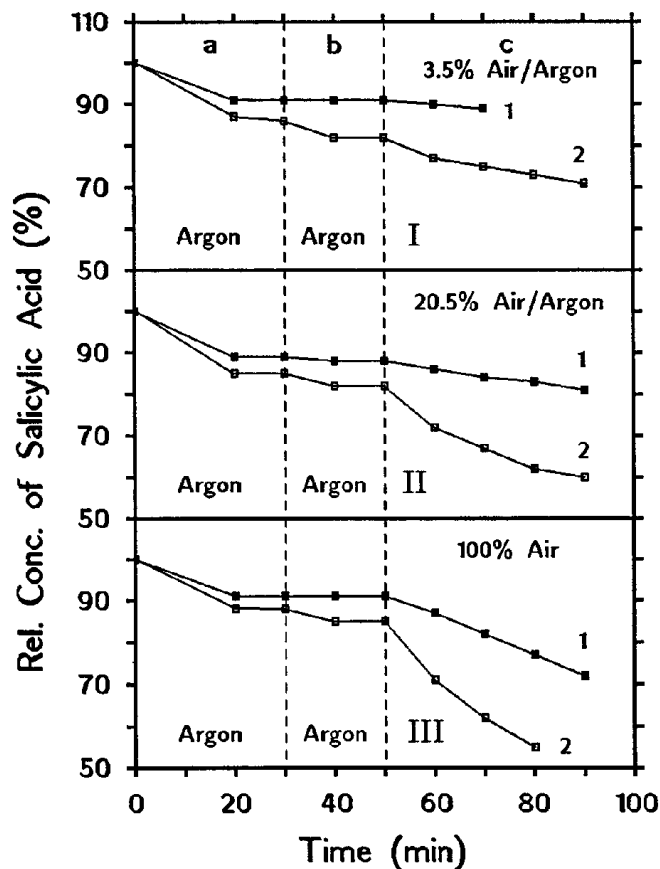


FIG. 2. The changes in concentration of salicylic acid caused by various origins. Curve 1 is a bare TiO<sub>2</sub> film, curve 2 is a TiO<sub>2</sub> film loaded with Pd. Region (a) adsorption of salicylic acid when argon was bubbled through the solution; (b) photodecompositions of salicylic acid under the argon bubbling; (c) photodecompositions of salicylic acid under the bubbling different air-argon mixtures with the following air concentrations: (I) 3.1%; (II) 20.5%; (III) 100%.

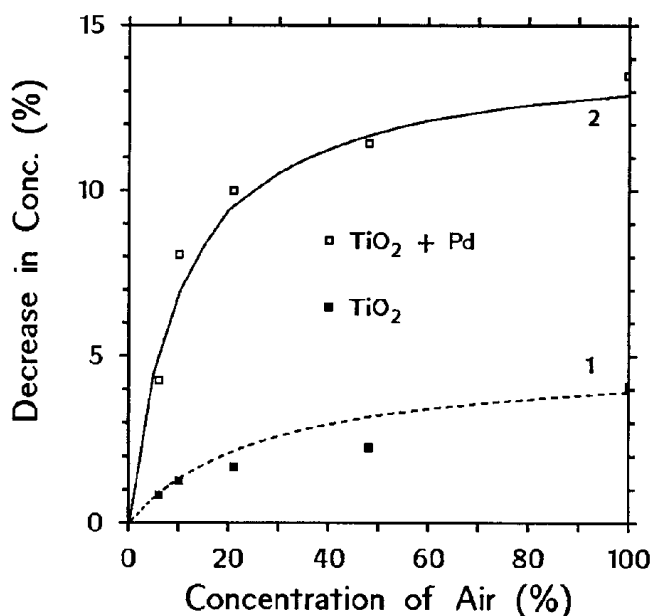


FIG. 3. The rate of decomposition of salicylic acid vs concentration of air in the gaseous mixture bubbling through the solution (10 min irradiation). Curves 1 and 2 are calculated in accordance with the Langmuir-Hinshelwood model. Curve 1 corresponds to a pure TiO<sub>2</sub> film and curve 2 to a Pd/TiO<sub>2</sub> film.

ningham and co-workers (19, 20). When the cell with Pd/TiO<sub>2</sub> was purged with an air/argon gas mixture and illuminated (Fig. 2, region c), a decrease in the concentration of salicylic acid was observed. This decrease was due to the photodecomposition of organic acid. Variation of the air concentration, shown in Fig. 2, resulted in a variation of the photodecomposition rate, which is dependent on the amount of oxygen present in the gas mixture. Regions (c) clearly indicate that the activity of the catalyst is solely dependent on the presence of oxygen in solution.

The data plotted in Fig. 2 indicate there is a marked increase in the activity of the Pd/TiO<sub>2</sub> catalyst toward decomposition of salicylic acid compared to uncoated TiO<sub>2</sub>. The comparative data shown for the two films were obtained under corresponding conditions. Hence the increase in observed activity must be associated with the role of palladium on the surface of the TiO<sub>2</sub> film.

There is considerable controversy concerning the correlation of absorbance spectra data with complete decomposition of the organic acid. In this study it was found that from the data shown in Fig. 2 (region C) for a pure TiO<sub>2</sub> film there was approximately 17% degradation of salicylic acid. In a separate controlled experiment 20% degradation of salicylic acid corresponded to a total conversion to CO<sub>2</sub> of 18 ± 3%. Under the conditions of these experiments there appears to be rapid oxidation of salicylic acid to CO<sub>2</sub>. This is in agreement with the results reported by Matthews (2).

Figure 3 shows the rate of decomposition of salicylic acid as a function of air concentration. The observed concentration changes were obtained from the changes in intensity of the absorption peak at  $\lambda = 296$  nm after 10 min of irradiation. These changes are plotted for irradiated catalysts as a function of air concentration in various argon-air mixtures. For an undoped TiO<sub>2</sub> film, the decrease in salicylic acid concentration increases with increasing concentration of air. This is in agreement with the experimental results of Mills *et al.* (10). For a Pd/TiO<sub>2</sub> film it can be seen that there is a rapid initial increase in activity as a function of air concentration followed by a slower increase when the concentration of air in gas mixture exceeds 20%. It can be seen from comparison of these two curves that above ~30% air concentration in the bubbling gas mixture the curves become parallel. This indicates that the same mechanism of salicylic acid photodegradation occurred when the concentration of dissolved oxygen exceeds ~30%.

It can be seen from Fig. 3 that the initial rate of decomposition of salicylic acid  $R \sim (\Delta C/\Delta t)$  depends on the partial pressure of oxygen in the bubbling gas. The solid lines shown in Fig. 3 were calculated in accordance with the Langmuir-Hinshelwood kinetic model (1-3)

$$R \sim K_{O_2} C_{O_2} / (1 + K_{O_2} C_{O_2}).$$

The best fit of these plots has been obtained with a value of adsorption equilibrium constant  $K_{O_2} = 0.18$  kPa<sup>-1</sup> for a pure TiO<sub>2</sub> film and  $K_{O_2} = 0.41$  kPa<sup>-1</sup> for a TiO<sub>2</sub> film loaded with Pd. It should be noted that the  $K_{O_2}$  value for a pure TiO<sub>2</sub> film is similar to the previously reported value obtained from TiO<sub>2</sub> powder (10). It should be noted that the relation between these photochemical-type constants and the real adsorption constants is unknown (21). However, the solid lines in Fig. 3 calculated with these values of  $K_{O_2}$  are in a good agreement with the experimental results. The increased value of  $K_{O_2}$  for a Pd/TiO<sub>2</sub> film compared to a pure TiO<sub>2</sub> film supports Bard's model (13) that a metal cocatalyst can provide additional sites for interaction between photogenerated electrons and "adsorbed" oxygen.

## CONCLUSION

It has been shown that Pd/TiO<sub>2</sub> catalysts are more effective than pure TiO<sub>2</sub> catalysts in promoting the photodecomposition of salicylic acid. In this study the experimental values of the initial rates of acid decomposition were in agreement with calculated values obtained from the Langmuir-Hinshelwood model. Calculation of the adsorption equilibrium constants has indicated that the increased value of this constant for Pd/TiO<sub>2</sub> supports Bard's model

that the role of a metal cocatalyst in the reaction of photo-assisted decomposition of organic compounds in aqueous solutions is to provide sites for more efficient utilization of photogenerated electrons in the reduction of O<sub>2</sub>.

#### ACKNOWLEDGMENTS

The authors thank R. Kershaw and A. Orlov for help in the preparation of the samples. This research was supported by the National Science Foundation under Grant DMR 9016302.

#### REFERENCES

1. D. F. Ollis, E. Pelizzetti, and N. Serpone, *Environ. Sci. Technol.* **25**, 1523 (1991).
2. R. W. Matthews, *J. Phys. Chem.* **91**, 3328 (1987).
3. M. A. Fox and M. T. Dulay, *Chem. Rev.* **93**, 341 (1993).
4. E. Pelizzetti and C. Minero, *Electrochim. Acta* **38**, 47 (1993); and references therein.
5. H. Gerischer and A. Heller, *J. Electrochem. Soc.* **139**, 113 (1992).
6. H. Gerischer and A. Heller, *J. Phys. Chem.* **95**, 5261 (1991).
7. C-M. Wang, A. Heller, and H. Gerischer, *J. Am. Chem. Soc.* **114**, 5230 (1992).
8. S. T. Martin, H. Herrmann, W. Choi, and M. R. Hoffmann, *J. Chem. Soc. Faraday Trans.* **90**, 3315 (1994).
9. M. Barbeni, E. Pramanro, and E. Pelizzetti, *Nouv. J. Chim.* **8**, 544 (1984).
10. A. Mills, C. E. Holland, R. H. Davies, and D. J. Worsley, *Photochem. Photobiol. A: Chem.* **83**, 254 (1994).
11. K. Vinodgopal, S. Hotchandani, and P. V. Kamat, *J. Phys. Chem.* **97**, 9040 (1993).
12. D. H. Kim and M. A. Anderson, *Environ. Sci. Technol.* **28**, 479 (1994).
13. I. Izumi, W. W. Dunn, K. O. Wilbourn, F. R. Fan, and A. J. Bard, *J. Phys. Chem.* **84**, 3207 (1980).
14. A. Wold, *Chem. Mater.* **5**, 280 (1993).
15. Y.-M. Gao, P. Wu, K. Dwight, and A. Wold, *J. Solid State Chem.* **90**, 228 (1991).
16. W. W. Xu, R. Kershaw, K. Dwight, and A. Wold, *Mater. Res. Bull.* **25**, 357 (1990).
17. A. Yamamoto and S. Kambara, *J. Am. Chem. Soc.* **79**, 4344 (1957).
18. J. Papp, H.-S. Shen, R. Kershaw, K. Dwight, and A. Wold, *Chem. Mater.* **5**, 284 (1993).
19. J. Cunningham and G. Al-Sayyed, *J. Chem. Soc. Faraday Trans.* **90**, 3315 (1994).
20. J. Cunningham and B. K. Hodnett, *Chem. Soc. Faraday Trans. 1* **77**, 2777 (1981).
21. J. Cunningham and G. Al-Sayyed, *J. Chem. Soc. Faraday Trans.* **86**, 3935 (1990).