

Chemistry and Applications of Photocatalytic Oxidation of Thin Organic Films

ADAM HELLER

Department of Chemical Engineering, The University of Texas at Austin, Austin, Texas 78712-1062

Received May 2, 1995

Introduction

Thin films of organic contaminants can be photocatalytically oxidized on TiO₂-coated surfaces. The thickness of the organic layer oxidized per day is 1–5 μm, a rate sufficient for maintaining the cleanliness of a surface when the flux of contaminant is not excessive. Thus it is practical, through photocatalytic coatings, to maintain clean windows or windshields, strip finger marks off walls, reduce the density of colonies of microorganisms on hospital walls, and, with buoyant photocatalyst-coated ceramic microbubbles, oxidatively strip oil sheens off water. The initial reactions of the photogenerated hole–electron pair in humid air are $h^+ + H_2O \rightarrow \cdot OH + H^+$ and $e^- + O_2 + H^+ \rightarrow \cdot OOH$. The $\cdot OH$ (hydroxy) radical abstracts hydrogen from the organic molecule, to form an organic radical and water. The organic radical combines with a molecule of oxygen to form an organoperoxy radical. Two molecules of oxygen are thus activated per absorbed photon, one combining with the organic radical, to form an organoperoxy radical, the second with the photogenerated electron and a proton, to form a hydroperoxy radical. Combination of the organoperoxy radical with the hydroperoxy radical produces a labile organohydroperoxide that decomposes to products. In the photocatalytic oxidation of benzene in humid air such decomposition produces little or no phenol. CO₂ is evolved early in the oxidation reactions, while most of the reactant is still intact. Because of their oxygen-rich intermediates, photocatalyzed oxidation reactions of contaminant films in sunlight can be cleaner than their non-photocatalyzed weathering reactions.

Commercial products and processes having photoelectrochemically active surfaces are now entering the market. On the basis of joint research with Fujishima, Hashimoto, and their colleagues at the University of Tokyo, the Japanese company TOTO developed and is marketing tiles for operating rooms and other hospital applications. Colonies of pathogenic microorganisms do not persist on these, even under low-level irradiance from common fluorescent lamps.¹ Tiles are also being developed by TOTO for use in public restrooms, where they reduce the count of colonies of microorganisms and eliminate odors.^{2–3} The effort led by Fujishima and Hashimoto involves ISK,⁴ the largest TiO₂ producer of Japan and Southeast

Adam Heller received his M.Sc. (chemistry and physics, 1957) and Ph.D. (chemistry, 1961) from the Hebrew University, Jerusalem, where he studied under E. D. Bergmann. He was appointed to the Ernest Cockrell, Sr., Chair in Engineering at The University of Texas at Austin in 1988. Earlier he headed the Electronic Materials Research Department of AT&T Bell Labs. He was elected to the National Academy of Engineering in 1988, was awarded an Honorary Doctorate of Uppsala University, Sweden, in 1991, and has received awards of the American Chemical Society and The Electrochemical Society.

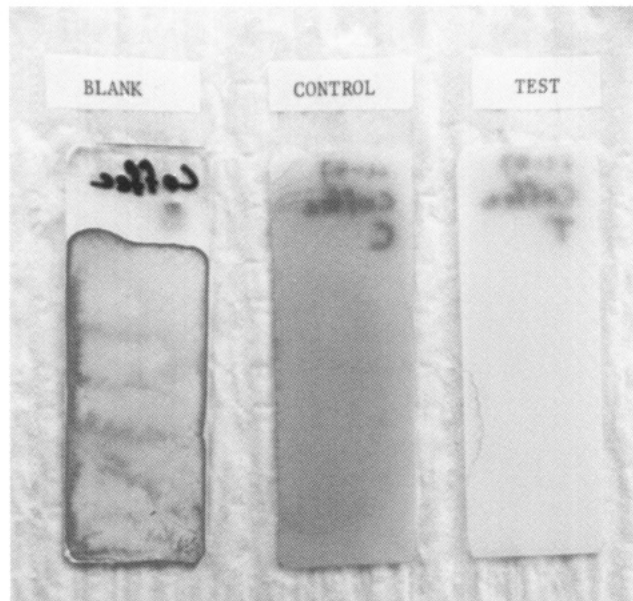


Figure 1. Photooxidative cleaning of a coffee stain on a photocatalytic surface coating based on a nonoxidizable binder of TiO₂ crystallites. Left: Coffee stain on latex paint after 105 min exposure to sunlight. Center: The stain on the photocatalytic coating after 105 min without exposure to sunlight. Right: As in the picture in the center, after 105 min exposure to sunlight. Courtesy EHC, Alameda, CA.

Asia, and Takenaka, one of Japan's major construction companies with interests in deodorizing, mold-preventing, and self-cleaning architectural surfaces.⁵ Independently, Toyota patented photocatalytic air cleaners for cars.^{6,7} E. Heller & Co. of Alameda, CA, is developing binders of photocatalyst particles that, unlike conventional binders of pigment particles in common paints, are not readily degraded through photocatalytic oxidation. Its technology is the basis for photooxidatively self-cleaning (Figure 1) and biocidal coatings that under light will clean thin films of organic stains from walls and keep these free of

(1) Ogawa, T.; Saito, T.; Unno, K.; Hasegawa, K.; Yoshioka, Y.; Tsubochi, N.; Hosoi, S.; Katayama, T.; Fujishima, A.; Hashimoto, K. Japanese Patent 07000462, Jan 6, 1995.

(2) Watanabe, T.; Kitamura, A.; Kojima, E.; Hashimoto, K.; Fujishima, A. Patent WO 9411092, May 26, 1994.

(3) Watanabe, T.; Kitamura, A.; Kojima, E.; Nakayama, C.; Hashimoto, K.; Fujishima, A. Photocatalytic Activity of Titanium Dioxide Thin Film under Room Light. *Trace Met. Environ.* **1993**, *3* (Photocatalytic Purification and Treatment of Water and Air), 747–51.

(4) Murasawa, S. *Denki Kagaku oyobi Kogyo Butsuri Kagaku* **1995**, *63*, 9.

(5) Ogawa, T.; Yoshioka, Y.; Tsubouchi, N.; Saido, T.; Hasegawa, T.; Fujishima, A.; Hashimoto, K., Japanese Patent JP 92-252931, Sept 22, 1992.

(6) Suzuki, K. Photocatalytic air purification on titanium dioxide coated honeycomb support. *Trace Met. Environ.* **1993**, *3* (Photocatalytic Purification and Treatment of Water and Air), 421–34.

(7) Suzuki, K. *Toyota Chuo Kenkyusho R&D Rebyu* **1993**, *28*, 47.

pathogenic organisms and mildew. At The University of Texas at Austin we are forming transparent and abrasion resistant photocatalyst films on glass that, upon exposure to sunlight, oxidatively strip thin layers of organic contaminants.⁶ Light-scattering films of city and highway grime, from incineration of refuse, from the exhaust of trucks and older cars, and from power and industrial plants, deposit on windshields. These might be oxidatively stripped off the photocatalytic windshields when a car is parked outdoors. These actual and future applications of photoelectrochemistry are based on novel understanding that follows 22 years of intensive research begun after the petroleum shortage of 1973. That research was aimed primarily at photoelectrochemical solar cells where, as in photocatalysis, ions or molecules at semiconductor surfaces were oxidized or reduced by photogenerated holes or electrons. The 1973 petroleum shortage nearly coincided with the 1972 report of Fujishima and Honda on photoassisted electrolysis of water at a potential below the thermodynamic hydrogen-evolution potential of 1.23 V.⁹ Following it, my colleagues and I at ATT Bell Laboratories built in 1977 the first moderately efficient (9%) electrical power generating electrochemical solar cell,¹⁰ and we reached by 1978 12% solar to electrical conversion efficiency,¹¹ and, by 1981, 12% efficiency in hydrogen-generating cells.^{12,13} The groups of Lewis and Licht have since built electrical power generating electrochemical solar cells reaching 16% efficiency,^{14,15} and a recent nanocrystalline TiO₂/redox dye based photoelectrochemical cell of Graetzel and co-workers¹⁶ is entering Swiss-made portable electronic devices.

Electrochemical solar cells did not impact, however, on the supply or cost of either electrical power or fuels. Sunlight is diffuse, and the large area of these and other solar cells, as well as of solar collectors that focus their light on smaller cells, makes the solar systems expensive. For this reason no solar air and water decontaminating reactors are in commercial production, even though it is established that organic contaminants can be photocatalytically oxidized on TiO₂,¹⁷⁻²⁸ that toxic metals can be photoreductively precipitated on TiO₂,^{29,30} and that carbon tetrachloride can be photoreductively activated and converted to

CO₂ on TiO₂.³¹ For high throughputs the solar processes require large-area concentrators or reactors,³² raising their cost beyond that of competing, nonsolar processes.³³

Because of the high cost of large-area reactors, we concentrated on applications where reactor size and the diffuse nature of sunlight were not limiting, particularly applications where the photoactive surface was inexpensive, or was large and already in place.³⁴⁻⁴¹ In this context we had to understand the mechanisms of environmentally relevant photocatalytic oxidation processes, so as to reduce the risk of generating photooxidation products that were more toxic than their precursors.⁴¹⁻⁴⁵ We considered the sunlight-assisted cleaning of sheens of organic contaminants on water³⁵⁻⁴¹ and photocatalyst-coated glasses that in sunlight oxidatively cleaned themselves of organic films.⁸ For cleaning of oil and other organic sheens on water we used buoyant photocatalytic TiO₂-coated hollow ceramic microbubbles that accelerated their oxidation in sunlight.³⁴⁻⁴¹ For photocatalytically self-cleaning glasses we formed, from a stable sol, adherent films of nanocrystalline TiO₂ that did not scatter visible light.⁸

(24) Pichat, P.; Guillard, C.; Maillard, C.; Amalric, L.; D'Oliveira, J. C. Titanium dioxide photocatalytic destruction of water aromatic pollutants: intermediates; properties-degradability correlation; effects of inorganic ions and titanium dioxide surface area; comparisons with hydrogen peroxide processes. *Trace Met. Environ.* **1993**, *3*, (Photocatalytic Purification and Treatment of Water and Air), 207-23.

(25) Mills, A.; Davies, R. H.; Worsley, D. *Chem. Soc. Rev.* **1993**, *22*, 417.

(26) Matthews, R. W. Photocatalysis in water purification: possibilities, problems and prospects. *Trace Met. Environ.* **1993**, *3* (Photocatalytic Purification and Treatment of Water and Air), 121-38.

(27) Fox, M. A. The role of hydroxy radicals in the photocatalyzed detoxification of organic pollutants: pulse radiolysis and time-resolved diffuse reflectance measurements. *Trace Met. Environ.* **1993**, *3* (Photocatalytic Purification and Treatment of Water and Air), 163-7.

(28) Serpone, N.; Terzian, R.; Minero, C.; Pelizzetti, E. *Adv. Chem. Ser.* **1993**, *238*, 281.

(29) Prairie, M. R.; Stange, B. M.; Evans, L. R. Titanium dioxide photocatalysis for the destruction of organics and the reduction of heavy metals. *Trace Met. Environ.* **1993**, *3*, (Photocatalytic Purification and Treatment of Water and Air), 353-63.

(30) Prairie, M. R.; Evans, L. R.; Stange, B. M.; Martinez, S. L. *Environ. Sci. Technol.* **1993**, *27*, 1776.

(31) Hilgendorff, M.; Hilgendorff, M.; Bahnemann, D. W. *Proceedings of Symposium on Environmental Aspects of Electrochemistry and Photoelectrochemistry*: Electrochemical Society: Pennington, NJ, 1993; p 112.

(32) Pacheco, J.; Prairie, M.; Evans, L.; Yellowhorse, L. *Proc. Intersoc. Energy Convers. Eng. Conf.* **1990**, *25*, 141.

(33) Jakob, L.; Oliveros, E.; Legrimi, O.; Braun, A. M. Titanium dioxide photocatalytic treatment of water. Reactor design and optimization experiments. *Trace Met. Environ.* **1993**, *3*, (Photocatalytic Purification and Treatment of Water and Air), 511.

(34) Jackson, N. B.; Wang, C.-M.; Luo, Z.; Schwitzgebel, J.; Ekerdt, J. G.; Brock, J. R.; Heller, A. *J. Electrochem. Soc.* **1991**, *138*, 3660.

(35) Rosenberg, I.; Brock, J. R.; Heller, A. *J. Phys. Chem.* **1992**, *96*, 3423.

(36) Heller, A.; Nair, M.; Davidson, L.; Schwitzgebel, J.; Luo, Z.; Norrell, J. L.; Brock, J. R.; Ekerdt, J. G. *Proceedings 1993 International Oil Spill Conference (Prevention, Preparedness, Response)*, p 623.

(37) Nair, M.; Luo, Z.; Heller, A. *Ind. Eng. Chem. Res.* **1993**, *32*, 2318.

(38) Heller, A.; Brock, J. R. In *Aquatic and Surface Photochemistry*; Helz, G. R.; Zepp, R. G.; Crosby, D. G., Eds.; Lewis Publishers: Boca Raton, 1993; pp 427-436.

(39) Heller, A.; Schwitzgebel, J.; Pishko, M. V.; Ekerdt, J. G. *Proceedings of Environmental Catalysis Symposium (Waste Water Treatment)*; Rose, T. L.; Murphy, O.; Rudd, E., Conway, B. E., Eds.; The Electrochemical Society: Pennington, NJ, 1994; Vol. 94-19, p 1.

(40) Heller, A.; Nair, M.; Davidson, L.; Luo, Z.; Schwitzgebel, J.; Norrell, J.; Brock, J. R.; Lindquist, S.-E.; Ekerdt, J. G. *Trace Met. Environ.* **1993**, *3*, 139-53.

(41) Schwitzgebel, J.; Ekerdt, J. G.; Gerischer, H.; Heller, A. *J. Phys. Chem.* **1995**, *99*, 5633.

(42) Gerischer, H.; Heller, A. *J. Electrochem. Soc.* **1992**, *139*, 113.

(43) Gerischer, H.; Heller, A. *J. Phys. Chem.* **1991**, *95*, 5261.

(44) Wang, C.-M.; Heller, A.; Gerischer, H. *J. Am. Chem. Soc.* **1992**, *114*, 5230.

(45) Sitkewitz, S.; Heller, A. *New J. Chem.*, in press.

(8) Paz, Y.; Luo, Z.; Rabenberg, L.; Heller, A. *J. Mater. Res.*, in press.

(9) Fujishima, A.; Honda, K. *Nature (London)* **1972**, *238*, 37.

(10) Chang, K. C.; Heller, A.; Schwartz, B.; Menezes, S.; Miller, B. *Science* **1977**, *196*, 1097.

(11) Heller, A.; Parkinson, B. A.; Miller, B. *Rec. 13th IEEE Photovoltaic Spec. Conf.*; Institute of Electrical and Electronics Engineers: New York, 1978; p 1253.

(12) Heller, A.; Vadimsky, R. G. *Phys. Rev. Lett.* **1981**, *46*, 1153.

(13) Heller, A.; Aharon-Shalom, E.; Bonner, W. A.; Miller, B. *J. Am. Chem. Soc.* **1982**, *104*, 6942.

(14) Tufts, B. J.; Abrahams, I. L.; Santangelo, P. G.; Ryba, G. N.; Casagrande, L. G.; Lewis, N. S. *Nature (London)* **1987**, *326*, 861.

(15) Licht, S.; Peramunage, D. *Nature (London)* **1990**, *345*, 330.

(16) Graetzel, M. J. *Sol-Gel Sci. Technol.* **1994**, *2*, 673.

(17) Pelizzetti, E.; Pramauro, E.; Minero, C.; Serpone, N. *Waste Manage.* **1990**, *10*, 65.

(18) Ollis, D. F.; Turchi, C. *Environ. Prog.* **1990**, *9*, 229.

(19) Ollis, D. F.; Pelizzetti, E.; Serpone, N. *Environ. Sci. Technol.* **1991**, *25*, 1522.

(20) Matthews, R. W. *Pure Appl. Chem.* **1992**, *64*, 1285.

(21) Hoffmann, M. R.; Martin, S. T.; Choi, W.; Bahnemann, D. W. *Chem. Rev.* **1995**, *95*, 69.

(22) Herrmann, J. M.; Guillard, C.; Pichat, P. *Catal. Today* **1993**, *17*, 7.

(23) Serpone, N.; Pelizzetti, E.; Hidaka, H. Identifying primary events and the nature of intermediates formed during the photocatalyzed oxidation of organics mediated by irradiated semiconductors. *Trace Met. Environ.* **1993**, *3* (Photocatalytic Purification and Treatment of Water and Air), 225-50.

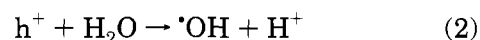
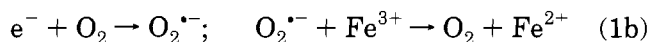
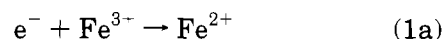
Manufacturers of TiO₂ have traditionally aimed at reducing the photoactivity of pigments.⁴⁶⁻⁴⁹ Photoactivity was unwelcome in TiO₂ pigments because photocatalytic activity led to oxidation of organic polymeric binders in paints and thus to their chalking. Photoactivity also limited the usefulness of nanocrystalline TiO₂ particles in applications as diverse as UV-absorbing cosmetic sunscreens and overcoatings. The understanding gained in the 22 years of intensive research on photoelectrochemistry contributed to the design of less photoactive pigments for nonchalking paints.⁴⁹

In considering environmental applications of photocatalysts, two issues invariably surfaced. One concerned the adequacy of the rate of the oxidation reaction, i.e., its ability to cope with the flux of the contaminant. When this flux exceeded the rate of conversion to volatile oxidation products, not only was the process insufficient for its intended purpose, but the photocatalyst was often fouled by nonvolatile UV-blocking partial oxidation products. The second concerned intermediates and byproducts of the photocatalytic oxidation reaction. Beyond being of scientific interest, understanding of the mechanism of the photocatalytic oxidation reactions provided the only means for addressing the potential hazard of generating and releasing intermediates and byproducts that were more toxic than the reactants themselves. It also accounted for the beneficial short-lived bactericidal and fungicidal intermediates that were not desorbed or released, but diffused only on the surfaces that were photodisinfected. Such intermediates are present on wall coverings where the count of colonies of pathogens is reduced and on surfaces of coatings that prevent mildew and rot of wood.

Mechanism of the Air Oxidation Reactions of Thin Organic Films on Water

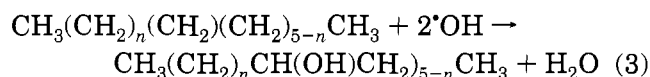
In our study of the photocatalytic processes whereby films of aliphatic hydrocarbons, alcohols, ketones, carboxylic acids, and aldehydes were photooxidized on n-TiO₂ coated buoyant glass microbubbles on water,³⁴⁻⁴¹ we were particularly interested in the role of oxygen,⁴¹⁻⁴⁴ the time dependent concentrations of the various intermediates, and the rates of O₂ consumption and CO₂ evolution in the photocatalytic oxidation reactions and their dependence on irradiance, pH, salinity of water, and O₂ partial pressure. The most important conclusion of these studies was that oxidation was mostly by oxygen, not by photogenerated holes (electron vacancies, h⁺), nor by their initial

reaction product with water, •OH radicals. Although valence band holes of anatase phase TiO₂ nanocrystallites were required for the oxidation to be initiated, the actual oxidizer was molecular oxygen. Furthermore, not only holes but also photogenerated electrons were essential in the oxidation of reactants other than aldehydes.⁴¹ The essential roles of O₂ became apparent when we attempted the photooxidation of thin organic films of *n*-octane, 3-octanol, 3-octanone, or *n*-octanoic acid on water (0.5 M NaCl) in the presence of 0.02 M Fe³⁺, but in the absence of air. Under conditions where the reactions in the presence of air generated CO₂ and other oxidation products, there was no significant photooxidation in the absence of air, even though the concentration of the electron-capturing Fe³⁺ was 80-fold higher than that of O₂ in air-saturated water. The rate of CO₂ production was negligibly slow when charge neutrality on the TiO₂ particles was maintained by the photogenerated electrons' being captured by reactions 1a or 1b. Neither

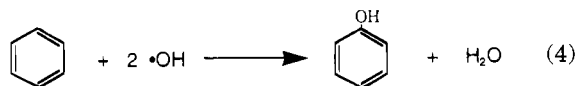


the holes nor the •OH radicals generated by reaction 2 were adequate for the oxidation to proceed when the photogenerated electrons were captured by Fe³⁺ directly (1a) or indirectly (1b).

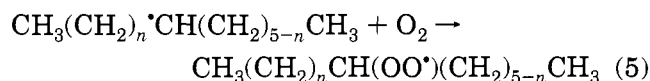
We also found that the dominant photocatalytic oxidation reactions involved only one hole and one electron, i.e., resulted in excitation of a TiO₂ reaction domain by one photon. In the photocatalytic air oxidation of *n*-octane films on water, only traces of octanols were found among the intermediates. Octanols should have been major products if two holes, or one hole and one spontaneously injected electron,⁵⁶ had been involved (reaction 3). Similarly, in a study



of the photocatalytic air oxidation of benzene on nanocrystalline TiO₂ coated surfaces,⁴⁵ we did not detect any phenol that might have been produced by two-hole or two-•OH radical oxidation (reaction 4).



From these results we deduced that, as in combustion reactions, the organic radicals, such as the octyl radical from reaction 3 or the radical generated by the one-hole oxidation of benzene, promptly combined with O₂ to form an organoperoxy radical as shown in reaction 5 for the octyl radical. This radical, produced



in a sequence involving a single hole, reacted with the

(56) Gerischer, H. *Electrochimica Acta*, in press.

(46) Heller, A.; Degani, Y.; Johnson, D. W., Jr.; Gallagher, P. K. *J. Phys. Chem.* **1987**, *91*, 5987.

(47) Voelz, H. G.; Kaempf, G.; Klaeren, A. *Farbe + Lack* **1976**, *82*, 805.

(48) Voelz, H. G.; Kaempf, G.; Fitzky, H. G.; Klaeren, A. *ACS Symp. Ser.* **1981**, *151*, 163.

(49) Jacobson, H. W., E. I. du Pont de Nemours and Co. European Patent 244180, Nov 4, 1987.

(50) Sclafani, A.; Palmisano, L.; Davi, Eugenio *J. Photochem. Photobiol.* **1991**, *56*, 113.

(51) Anpo, M.; Aikawa, N.; Kubokawa, Y.; Che, M.; Louis, C.; Gianello, E. *J. Phys. Chem.* **1985**, *89*, 5689.

(52) Von Sonntag, C. *The Chemical Basis of Radiation Biology*; Taylor and Francis: London, 1987; pp 60, 67-8.

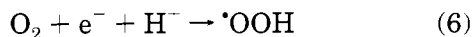
(53) Bartlett, P. D.; Guaraldi, G. *J. Am. Chem. Soc.* **1967**, *89*, 4799.

(54) Bennett, J. F.; Brown, D. M.; Mile, B. *Trans. Faraday Soc.* **1970**, *66*, 397.

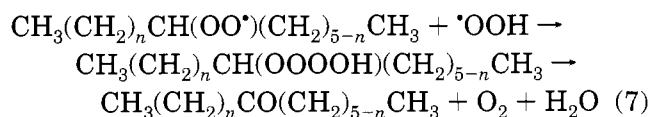
(55) Howard, J. A. Self Reaction of Alkylperoxy radicals in Solution. In *Organic Free Radicals*; Pryor, W. A., Ed.; ACS Symposium Series 69; American Chemical Society: Washington, DC, 1978; p 41.

one electron reaction product, the hydroperoxy radical ($\cdot\text{OOH}$). Evidently, at the moderate irradiance and high photocatalyst surface area in our experiments, there were only one hole and one electron within their diffusion zone, near the site where the photon was absorbed. Consequently, only one $\cdot\text{OH}$ radical and one $\cdot\text{OOH}$ radical were generated both in this zone and in the diffusion zone of the $\cdot\text{OH}$ radical. Products of reactions involving two electrons, two holes, a hole and an injected electron,⁵⁶ or two of the initially produced radicals were found only in trace amounts.

Though adding 0.02 M Fe^{3+} to aerated solutions drastically reduced the rates of CO_2 generation from *n*-octane, 3-octanol, 3-octanone, and *n*-octanoic acid, it did not affect the rate of CO_2 generation from *n*-octanal. This suggested that not only the photogenerated holes but also electrons were required for most, but not all, photocatalytic oxidation reactions. Suppression of photocatalytic oxidations on TiO_2 by Fe^{3+} in homogeneous aqueous solutions has been described by Sclafani et al.,⁵⁰ who ascribed the effect to UV absorption by the Fe^{3+} ions. Because in our systems the photocatalyst was on buoyant low density (0.4 g cm^{-3}) microbubbles, floating on the surface of water, UV absorption could not have been the reason for the suppression of the rate of CO_2 evolution. We explained the observed suppression by involvement of electrons in the photocatalytic oxidation reaction. It has been known, particularly from earlier ESR studies of Anpo et al.,⁵¹ that photogenerated electrons react with adsorbed O_2 on TiO_2 to form superoxide radical anions protonated below pH 4.7 to hydroperoxy radicals (reaction 6). We proposed that the hydroperoxy

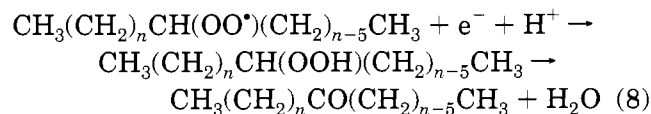


radicals reacted with the hole-generated organoperoxy radicals of reaction 5 to form labile hydrotetraoxides⁴¹ that decomposed to products (reaction 7). When the



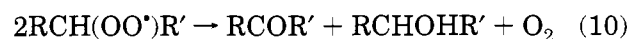
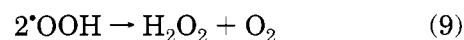
superoxide radical anion (reaction 1) or its protonated form, the hydroperoxy radical, was oxidized by Fe^{3+} , the labile hydrotetraoxide could not be formed. Therefore, the rate of oxidation decreased drastically.

Reaction 7 explained why octanols were not found and why the only initial products in the oxidation of *n*-octane were the three possible octanones. An alternative explanation that was consistent with the suppression of the photoactivity by Fe^{3+} would have involved the photogenerated electrons themselves (reaction 8). However, we were unable to detect the



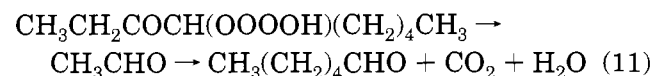
intermediate organohydroperoxides and, more importantly, we could not explain the products of 3-octanone films on water, or of benzene in air, by reactions other than those involving $\cdot\text{OOH}$ and organohydrotetraoxides.

While hydrotetraoxides are new to researchers of photocatalysis, they have been long known to radiation chemists.⁵²⁻⁵⁵ There are similarities and differences between tetraoxide-involving radiolytic processes and those on TiO_2 nanocrystallites. Both involve electrons: hydrated electrons in radiolysis and conduction band electrons in photocatalysts. Furthermore, both involve $\cdot\text{OH}$ radicals. The important difference is that in radiolysis, where reactions start in spurs, the initial and transient density of hydrated electrons and $\cdot\text{OH}$ radicals can be transiently higher than on illuminated nanocrystalline semiconductors. Consequently, products of combination of identical hydrated-electron-generated hydroperoxy radicals (reaction 9) or identical $\cdot\text{OH}$ -generated radicals like the octylperoxy radicals (reaction 10) can dominate in radiolysis. Both reactions 9 and 10 proceed via labile tetraoxide intermediates, hydrogen tetraoxide in the case of reaction 9 and a dialkyl tetraoxide in the case of reaction 10.⁵²



Because on TiO_2 nanocrystallites the concentration of radicals below $\sim 3 \text{ mW cm}^{-2}$ UV irradiance is low, the dominant intermediate is the organohydrotetraoxide formed upon combination (reaction 7) of the two dissimilar radicals in the same reaction zone near the site of absorption of a photon, the hydroperoxy radical from reaction 6 and the organoperoxy radical from reaction 5.

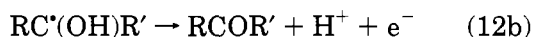
Through invoking organohydrotetraoxide intermediates we were able to account for all of the observed products and for the absence of those that were not found in the photocatalytic oxidation reactions of *n*-octane, 3-octanone, and *n*-octanoic acid films on water, and also in the photocatalytic gas phase oxidation of benzene. In the case of 3-octanone, where one photon led to incorporation of two O_2 molecules, the hydrotetraoxide decomposed to CO_2 and aldehydes (reaction 11), accounting for the observed early evolution of CO_2 , while most of the ketone was still intact.



The observed oxidation products of *n*-octanoic acid were explained by decarboxylation by $\cdot\text{OH}$ radicals, yielding a heptyl radical that reacted with O_2 to form the heptylperoxy radical, which reacted with the hydroperoxy radical to produce heptyl hydrotetraoxide. The tetraoxide oxidized and decarboxylated a second molecule of octanoic acid. CO_2 , 1-heptanol, and *n*-heptanal were produced initially at a 2:1:1 ratio.⁴¹

In the oxidation of 3-octanol, the initial major oxidation product was 3-octanone. In this case a process proposed by Gerischer,⁵⁶ known to occur on metal and semiconductor electrode surfaces, where currents can be "doubled" upon electrooxidation of an organic compound, could have been significant, if the initially produced radical (reaction 12a) injected an electron into the TiO_2 conduction band (reaction 12b), to be further oxidized. Because this sequence does not require molecular oxygen, it should have proceeded

also if the photogenerated electrons were captured by Fe^{3+} . We found, however, that the photocatalytic oxidation of 3-octanol to 3-octanone does not proceed at an appreciable rate in the absence of O_2 and in the presence of 0.2 M Fe^{3+} , and that it is suppressed by 0.2 M Fe^{3+} in the presence of O_2 . Thus, the rate of electron injection by the initially formed organic radical is slower than its rate of combination with O_2 , and the rate of electron injection by the resulting organoperoxy radical is slower than the rate of its combination with the hydroperoxy radical.

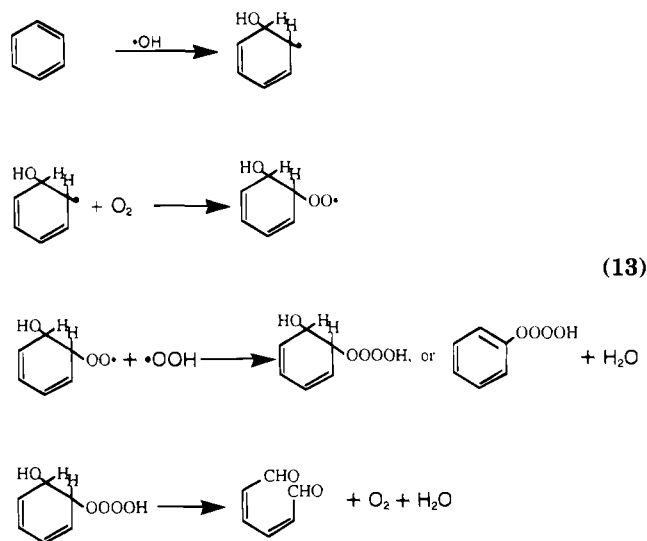


The photooxidation of *n*-octanal films on aerated water was quite different. From the fact that it was not inhibited by 0.02 M Fe^{3+} we deduced that the reaction did not involve the photogenerated electron or its product, the hydroperoxy radical.⁴¹ The number of O_2 molecules consumed in the photocatalytic oxidation of *n*-octanal in part of the experiments exceeded the number of photons absorbed, suggesting a hole-initiated or $\cdot\text{OH}$ radical initiated autocatalytic air oxidation process. The aldehyde was rapidly and efficiently oxidized to octanoic acid, which was further decarboxylated and oxidized.

Air oxidation of benzene in the gas phase produced only CO_2 .⁸ The volatile intermediates, if formed, reacted so rapidly that their steady state concentration was too low to measure with our GC-MS-FTIR system. The infrared spectrum of the nonvolatile intermediate that was found on the TiO_2 photocatalyst, after the reaction in the flow reactor was abruptly interrupted and when the level of benzene was high (10 ppm or higher), showed the presence of polymerized conjugated aldehyde functions and of their oxidation products: carboxylic acids. These observations were consistent with the process of reaction 13. The hole or $\cdot\text{OH}$ radical added to one of the double bonds to form a radical, which combined with O_2 , and then with the hydroperoxy radical, to form phenyl hydrotetraoxide. The hydrotetraoxide decomposed in a ring-opening reaction to form an unsaturated dialdehyde which, like *n*-octanal, was rapidly oxidized to an acid or, at excessive steady state surface concentration, polymerized and fouled the catalyst.

Oxidation of Crude Oil and Fuel Oil Films on Water

In the photocatalytic oxidation of thin oil films on water we used two types of buoyant microbubbles of 50–200 μm diameter, cenospheres and engineered glass bubbles. Their densities ranged from 0.3 to 0.9 g cm^{-3} , and their appearance, texture, and toxicology were not very different from those of fine white sand. Cenospheres, costing \$300–1500/ton, are part of the fly ash in coal-burning power plants and are collected by their electrostatic precipitators. They are separated in ponds by flotation. Engineered glass microbubbles are about 10-fold more expensive. The microbubbles were coated, by either of two simple processes, with photocatalytic, nanocrystalline TiO_2 particles. In one process, the water-wetted 30–150 nm diameter anatase or anatase–rutile TiO_2 particles,



consisting of smaller crystallites, were mixed with the microbubbles to form a paste, which was dried at 120 $^\circ\text{C}$, pulverized, and fired at 550 $^\circ\text{C}$ to bind the hydroxylated surfaces of the bubbles to those of the TiO_2 particles via Si–O–Ti bonds and loss of water.³⁴ The bubbles were then reactively coated with an organosilicone that made their hydrophilic surface oleophilic. Alternatively, the TiO_2 , the microbubbles, and methyltrimethoxysilane were bound through the polymer formed upon controlled hydrolysis of the silane and cured at 120 $^\circ\text{C}$ to form a durable oleophilic coating that withstood photocatalytic oxidation.³⁴

The solar ultraviolet irradiance at sea level when the sun is at zenith (air mass 1 or AM1 sunlight) is about 3.5 mW cm^{-2} , or 10^{-8} einsteins $\text{cm}^{-2} \text{s}^{-1}$. If one UV photon would cause the reaction of one O_2 molecule, then 1 ton of material consisting of CH_2 groups would be oxidized in AM1 sunlight in 1 day, when 1 ton of the bubbles is maximally spread on the oil, i.e., is 1 bubble thick. One ton of bubbles having diameters near 100 μm and a density of about 0.4 g cm^{-3} covers 20 000 m^2 at single-bubble layer thickness. Thus the bubbles could cause, in theory, the oxidation of a mass of oil equaling their own in 1 day. In practice, more than 10 photons were needed to react one O_2 molecule, wherefore the process takes 10–30 days even when the bubbles are maximally spread. The thickness of an oil layer on water is reduced, when fully covered with bubbles and when irradiated by AM1 sunlight, by about 5×10^{-4} cm each day. This rate of photooxidation is adequate for maintaining the surface of the water of a harbor, ship channel, coast, or lake free of an oily sheen, or for oxidative stripping of a film from minor spillage common in transfer of oil at marine terminals. It is also adequate for oxidation of an oil sheen resulting from leaching of sedimented oil residues from earlier spills or destruction of residues of pesticides or herbicides on rice paddies. However, at this rate the photocatalytic cleanup of thick (2–10 cm) layers of oil would take several years, unless they were burned first to a thin layer. Such burning is possible with the bubbles that, being gas filled, are thermal insulators and, thus, reduce convective cooling of the burning oil film. When we applied the bubbles at a 1:2 v/v bubble:oil ratio, the oil layer burned to a thickness of less than 1 mm, though their burning stopped at 3–4 mm when the bubbles were

not applied. The photocatalytic oxidation of the combustion-thinned residue could be completed in months.

The oleophilic bubbles promptly adsorptively aggregated oil, thereby reducing its toxicity to marine animals. Because the chemistry of heterogeneous photocatalytic oxidation via the labile organohydroxytetraoxides eliminated many of the byproducts of the photooxidation reactions that take place when oil weathers in the absence of the photocatalytic bubbles, a notable reduction in the toxicity of both crude oil and fuel oil contaminated water was observed. Cook and Pishko in two-month-long weathering tests monitored the toxicity of crude and fuel oils spilled on water, comprising also their photooxidation and weathering products. They used juvenile shrimp *Mysidopsis bahia*, a marine animal that is particularly sensitive to contaminants, for their tests.³⁹ Oil-contaminated water that was treated with the oleophilic photocatalytic microbubbles was less toxic to the juvenile shrimp than similarly contaminated, but normally weathering, water. Consistent with the proposed mechanism and in contrast with the natural weathering of aromatic hydrocarbons which produced phenols, polyphenols, and eventually tar—consisting of difficult to biodegrade phenol polymerization products—the dominant photocatalytic reactions on the bubbles were ring opening and produced less of the toxic phenolic intermediates. The shrinkage of the colored condensed aromatic ring compounds in the bubble-photocatalyzed reaction was readily seen with the eye, as the dark nonvolatile residue of crude oil turned colorless on the bubbles, while turning into the usual black tar when weathering in their absence.

Photocatalytically Self-Cleaning Glasses

Photocatalytically self-cleaning windows appear practical at this time.⁸ The issue we faced in their design was the simultaneous achievement of adequate photoactivity, subwavelength particle size for transparency, and bonding of the nanocrystalline TiO₂ photocatalyst to common soda lime glass, without excessive diffusion of, or reaction with, its components. The scattering of light by a nonuniform organic film of 100 nm average thickness is detected by the eye, resulting in glare when the sun is low or at night when illuminated by an oncoming car. Our objective was to photooxidize the 100 nm glare-causing film in 1 day or less, i.e., to achieve a rate of oxidation exceeding 10 nm/h. A key issue that we had to address was that of perfect transparency, i.e., the absence of light scattering by particles in the photocatalytic TiO₂ film. This required not only that the particles be much smaller than the shortest (400 nm) visible wavelength, preferably in the 3–5 nm range, but also that their size distribution be narrow. In addition, the films,

though thin, had to withstand normal cleaning, resisting, for example, abrasion by dry paper. Because the rate of oxidation of an organic film on a windshield of a car parked outdoors depended on the overlap integral of the terrestrial solar spectrum and the absorption spectrum of the thin photocatalyst film on the glass, the shift of the absorption spectra to shorter wavelengths, because of electron confinement in the small particles ("size quantization"), was not desirable.

We obtained the desired uniform size through partially hydrolyzing titanium triisopropoxide acetylacetonate to form a sol that was sufficiently stable to be stored for over a month. This sol was spun on glass that was first treated with hot sulfuric acid, so as to produce a sodium depleted surface layer. After controlled heating to 500 °C a photocatalytic, abrasion-resistant, transparent film of 60–100 nm thickness was formed. Under 2.4 mW/cm² irradiance by 365 nm light our test film, consisting of stearic acid, was oxidatively stripped off either side of the glass at a rate of 20 nm/h. This rate was only 3 times below the rate at which stearic acid was stripped off a thick light-scattering layer of Degussa P25 TiO₂, the most frequently used photocatalyst, and is adequate for elimination of the glare-causing organic contaminant films, at their usual rate of deposition.⁸

Conclusion

In environmental applications, where only thin films or small amounts of organic contaminants need to be oxidized, or when surfaces on which pathogenic microorganisms and mildew cannot thrive are sought, photocatalytic coatings of semiconducting oxides can be useful. Sheens of nonvolatile organic contaminants can be stripped from water; thin films of organic contaminants on glass can be eliminated through their photocatalytic oxidation; stains are cleaned off surfaces coated with photocatalytic coatings and paints, made with binders that are stable to photocatalytic oxidation; and the density of colonies of microorganisms is reduced on photocatalyst-coated surfaces.

Photocatalytic oxidation adds a lesser environmental burden through release of toxic partial oxidation intermediates than oxidation upon weathering, because two, four, and even eight electrons are transferred in the process initiated by a single electron-hole pair on a semiconducting crystallite. The photocatalytic oxidation process involves not only holes, but also electrons, and in part of the reactions a single photon activates two oxygen molecules.

We gratefully acknowledge the support of this work by the National Science Foundation and the Texas Advanced Technology Program.

AR9500271