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Spin Trapping and Electron Spin Resonance Detection of Radical Intermediates in the Photodecomposition of Water at TiO_2 Particulate Systems

Calvin D. Jaeger and Allen J. Bard*

Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712

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Spin trapping and ESR detection (with the traps α-phenyl *N*-*tert*-butyl nitrone and α-(4-pyridyl *N*-oxide) *N*-*tert*-butyl nitrone) were employed to detect free-radical intermediates formed during in situ irradiation of TiO_2 and platinized TiO_2 powders in aqueous solutions. Evidence for the production of hydroxyl radical (·OH) (formed in the oxidation of water) and perhydroxyl radical (HO_2·) (probably formed in a reduction step) is presented. Other spin adducts, attributed to decomposition reactions of the spin traps, were also found. The results suggest an important role for photogenerated ·OH in many photocatalytic and photosynthetic processes at TiO_2 powders.

Introduction

The photosynthetic and photocatalytic reactions occurring at TiO_2 (rutile) electrodes in electrochemical cells and at TiO_2 powders have been the subject of numerous studies.[1-8] For example, TiO_2 alone and platinized TiO_2 have been used to carry out a number of reactions, e.g., the photodecarboxylation of carboxylic acids[9] and the photooxidation of CN^-.[10] A single particle can be thought of as a short-circuited photoelectrochemical cell providing both the oxidizing and reducing sites for the reaction.[3] The presence of the platinum often serves to increase the efficiency for the overall reaction in the absence of an oxidant like oxygen, because it serves to lower the overpotential for the reduction of H^+.

The photoassisted decomposition of water in a TiO_2 (rutile)/Pt photoelectrochemical cell follows the overall reaction scheme

$$\text{TiO}_2 \qquad TiO_2 + h\nu \rightarrow e^- + h^+ \qquad (1)$$

$$\text{photoanode} \qquad 4h^+ + 2H_2O \rightarrow O_2 + 4H^+ \qquad (2a)$$

$$2h^+ + 2H_2O \rightarrow H_2O_2 + 2H^+ \qquad (2b)$$

$$\text{Pt electrode} \qquad 4e^- + 4H^+ \rightarrow 2H_2 \qquad (3)$$

For rutile electrodes a small bias must be applied to carry out the decomposition of water. At a platinized TiO_2 (anatase) particle, similar reactions can occur. The larger band gap for anatase (3.2 eV) compared to that of rutile (3.0 eV) provides the possibility of the reaction occurring to a small extent without external bias, as is indeed observed on $SrTiO_3$.[11-14] Many elementary steps can be proposed as paths to the overall reactions shown in eq 1–3; a number of possibilities are shown in Table I.

Although the overall energetics, stoichiometry, and product yields of these photoprocesses at TiO_2 have been studied extensively and appear to be well-understood, the details of the mechanisms of the processes and the intermediates produced in the elementary steps largely remain to be elucidated. One approach that appears promising for the detection of radicals produced in particulate systems is the application of spin trapping techniques with subsequent ESR observation. Spin trapping techniques, which have been widely used for the detection of short-lived radicals in homogeneous systems,[15] are based on the reaction

$$\text{radical·} + \text{spin trap} \rightarrow \text{spin adduct·} \qquad (4)$$

The following two spin traps are often used: (1) α-phenyl *N*-*tert*-butyl nitrone (PBN) and (2) α-(4-pyridyl *N*-oxide) *N*-*tert*-butyl nitrone (4-POBN).

TABLE I: Reactions Involving Water and Related Couples[a]

no.	reaction	E_{RED}[b] (pH 0)	E[b] vs. NHE (pH 7)
6	$O_2 + 4H^+ + 4e^- = 2H_2O$	1.229	0.815
7	$OH\cdot + H^+ + e^- = H_2O$	2.8	2.4
8	$H_2O_2 + H^+ + e^- = OH\cdot + H_2O$	0.72	0.31
9	$HO_2\cdot + H^+ + e^- = H_2O_2$	1.5	1.1
10	$O_2 + H^+ + e^- = HO_2\cdot$	−0.13	−0.54
11	$HO_2\cdot + 3H^+ + 3e^- = 2H_2O$	1.70	
12	$2H^+ + 2e^- = H_2$	0.0	−0.41
13	$H^+ + e^- = H\cdot$	−2.10	
14	$2D^+ + 2e^- = D_2$	−0.003	

no.	reaction	$\Delta G°$, kcal
15	$^1/_2O_2 + H_2 = H_2O$	−56.69
16	$2H_2O_2(aq) = 2H_2O + O_2$	−50.44
17	$2OH\cdot = H_2O_2$	−48.7
18	$2OH\cdot = H_2O + O$	−18.8
19	$2HO_2\cdot = H_2O_2 + O_2$	−37.5
20	$H_2O_2 + OH\cdot = HO_2\cdot + H_2O$	−30.0

[a] Data from Latimer,[49] corrected to IUPAC sign convention. [b] In volts.

$$H(X)C{=}N^+O^-\text{-}t\text{-Bu} + R\cdot \rightarrow H(X)(R)CN\dot{O}\text{-}t\text{-Bu} \qquad (5)$$

$$\text{PBN, X} = \text{Ph}$$

$$\text{4-POBN, X} = 4\text{-}C_5\text{-}H_4N^+O^-$$

These materials are suitable for experiments involving TiO_2 and aqueous solutions, since both the spin trap and the spin adduct are very stable and both traps are quite soluble in water (~0.05–0.1 M). The main disadvantage of these spin traps is the difficulty in identifying the nature of the trapped radical.[15c] In general, the magnitudes of the hyperfine splitting constants (hfsc) of nitrogen (a_N) and the β-hydrogen (a_H^β) in the ESR spectra are used to identify the trapped radicals. The effect of the solvent and solution conditions on the magnitude of the hfsc values has been discussed in the literature[16] and must be considered when comparing a_N and a_H^β values found with different solutions.

Within the past few years the use of the spin trapping technique has been extended to a variety of different systems, in particular, the detection of spin adducts from photoinduced reactions.[17-25] For example, methyl radical was detected with PBN in the photodecarboxylation of

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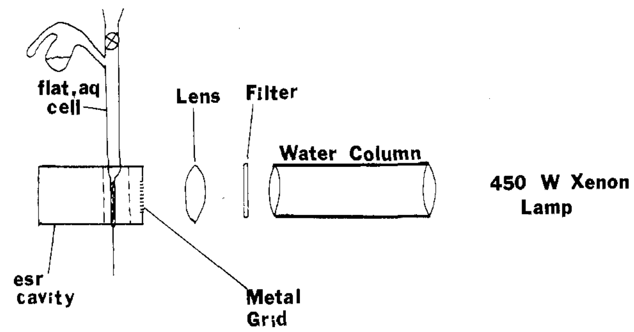

Figure 1. Experimental apparatus for the detection of radical intermediates during the illumination of TiO_2 powder samples.

acetates on platinized TiO_2.[17] Superoxide ions were detected in photolysis with CdS and metal-free phthalocyanine dispersions in nonaqueous media,[22] as well as in aqueous media with CdS[23] and chloroplasts.[24] With ZnO dispersions radical intermediates were also detected.[25] We report here experiments involving spin trapping of intermediates produced during irradiation of TiO_2 and platinized TiO_2 in deaerated aqueous solutions which demonstrate the intermediacy of hydroxyl (·OH) and perhydroxyl (HO_2·) radicals in the photoprocess.

Experimental Section

Materials. The TiO_2 powder and platinized alumina (5% catalysts) were purchased from Matheson Coleman and Bell. The TiO_2 powders used in these experiments were sieved and had a particle size of 125–250 μm. The platinization of the TiO_2 was carried out by the procedure described previously.[26] The powders were reduced by heating at 400 °C either in a flow of H_2 or under vacuum. The degree of reduction depended upon the duration of the treatment (0.5–12 h). TiO_2 treated in this way remained in the anatase form as shown by X-ray diffraction. Conversion to the rutile structure took place upon heating the TiO_2 powder at 900 °C under a flow of prepurified nitrogen for 120 h. Reduction of this powder was then carried out as described for anatase. The α-phenyl *N*-*tert*-butyl nitrone (PBN) was purchased from Eastman and the α-(4-pyridyl *N*-oxide) *N*-*tert*-butyl nitrone (4-POBN) was purchased from Dr. E. G. Janzen (Guelph, Ontario).

Water used in all experiments was distilled first from alkaline $KMnO_4$ and then at least three times in leached glassware. In some experiments, a 0.005 M potassium phosphate buffer solution (pH 7) (Fisher Scientific) was used. The hydrogen peroxide (30% aqueous solution) was obtained from Fisher Scientific. The deuterium oxide (99.8%) was obtained from Clini-Chem.

Apparatus. A schematic diagram of the experimental arrangement is shown in Figure 1. A flat, quartz, aqueous ESR cell with two side-arm compartments was used. Approximately 100 mg of powder and a 0.1 M spin trap solution were placed in one compartment. The other compartment contained the solution which had been degassed at least three times to remove all dissolved gases. The degassed solution and powder were then mixed and this powder suspension was poured into the flat portion of the ESR cell. The cell was then inserted into the cavity of the ESR spectrometer (Varian E-9). The sample was illuminated with a 450-W xenon lamp. Two glass filters, (1) Oriel G-882-4750, 50% transmittance (*T*) at 500 nm and <1% *T* at 465 nm, and (2) Oriel G-772-3900, 50% *T* at 395 nm and <1% *T* at 360 nm, were used in all experiments. In all cases, the light beam passed through a water column and the metal grid of the ESR cavity.

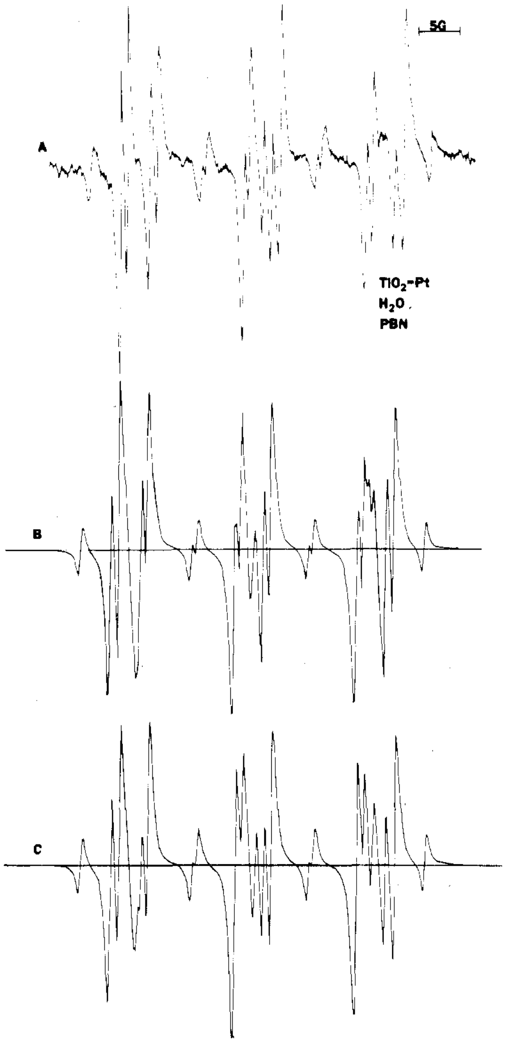

Figure 2. (A) Experimental spectrum consisting of the superposition of four different spin adducts (H_2O, 0.1 M PBN, TiO_2 (anatase)/Pt). The sample was illuminated first through filter 2 and then without any filters. (B) Computer simulation with four species with the following relative intensities (RI): I ($a_N = 15.45$, $a_H{}^\beta = 2.8$, RI = 1.0); II ($a_N = 14.80$, $a_H{}^\beta = 2.50$, RI = 0.32); III ($a_N = 15.55$, $a_H{}^\beta = 4.8$, RI = 1.0); IV ($a_N = 14.7$, $a_{2H}{}^\beta = 7.0$, RI = 0.40). (C) Computer simulation using the spectrum of four spin adducts of a triplet of doublets with the following relative intensities (RI): I ($a_N = 15.4$, $a_H{}^\beta = 2.75$, RI = 0.67); II ($a_N = 14.8$, $a_H{}^\beta = 2.38$, RI = 0.50); III ($a_N = 15.5$, $a_H{}^\beta = 4.78$, RI = 1.0); IV ($a_N = 14.63$, $a_H{}^\beta = 14.0$, RI = 0.30).

Results

Reactions on Platinized TiO_2 Anatase Powders. The experimental spectra observed when platinized/TiO_2 (anatase) powders were illuminated with greater than band-gap light (3.2 eV) in the presence of a spin trap in water are shown in Figures 2–4. In all of the experiments, no ESR signal was observed either in the dark or upon illumination through filter 1. However, immediately upon irradiation of the sample through filter 2, an ESR signal appeared. In all cases, the signal observed was a superposition of spectra from two to four different species. Attempts were made to optimize the experimental conditions so that the best resolution could be obtained. Generally the modulation amplitude was ≤0.1 G and the microwave power was ~20 mW. At these settings, very high receiver gains were required so spectra were recorded with long time constants and slow scan rates. If the illuminated sample was not at a photostationary state when the spectrum was taken, changes in peak intensities were observed during the scan.

In Figure 2A, the experimental ESR spectrum from the

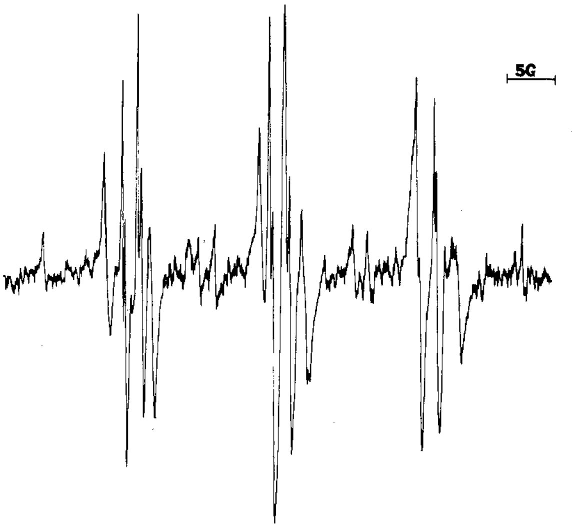

Figure 3. Experimental spectrum of an illuminated sample of H_2O (pH 4), 0.1 M POBN and TiO_2 (anatase)/Pt powder: $a_N = 15.63$, $a_H^\beta = 17.2$; $a_N = 15.75$, $a_H^\beta = 4.38$; $a_N = 15.0$, $a_H^\beta = 1.72$, $a_H^\gamma = 0.35$.

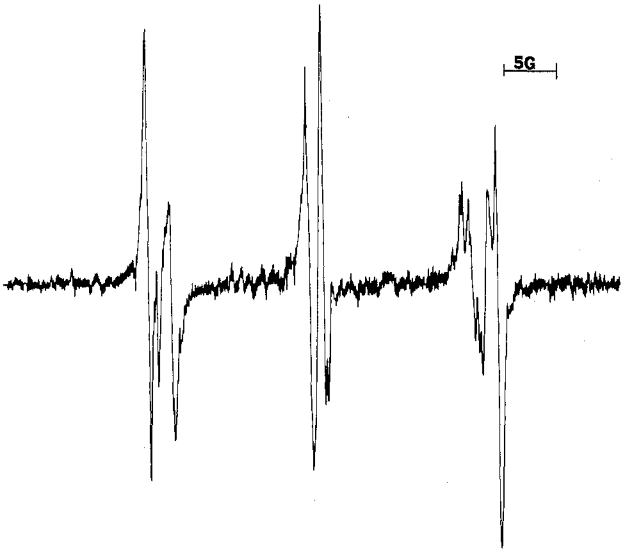

Figure 4. Experimental spectrum of an illuminated sample of H_2O (pH 7), 0.1 M POBN, and TiO_2 (anatase)/Pt powder: $a_N = 15.6$, $a_H^\beta = 1.03$; $a_N = 15.0$, $a_H^\beta = 1.73$, $a_H^\gamma = 0.35$.

$Pt-TiO_2/H_2O/PBN$ at room temperature is shown. This spectrum can be simulated by the superposition of spectra of four different paramagnetic species. The signal arising from two of the species, I and II, can be assigned to PBN spin adducts of the hydroxyl and perhydroxyl radials with hfsc values of $a_N = 15.45$ G and $a_H^\beta = 2.8$ G and $a_N = 14.8$ G and $a_H^\beta = 2.38$ G, respectively. These values correspond reasonably well to previously reported values for these spin adducts (Table II). The exact nature of the other two species is still uncertain. These species, III and IV, were not always observed and generally arose only after prolonged irradiation, especially without filters. The species with values of $a_N = 15.5$ G and $a_H^\beta = 4.78$ G may be the benzoyl spin adduct. The nature of this spin adduct was discussed by Janzen et al.[18] We initially believed that the remaining spin adduct (IV) was due to the trapping of hydrogen atoms. This would result in a spectrum which included a triplet of triplets, $a_N = 14.7$ G and $a_{2H}^\beta = 7.0$ G (±0.1 G), illustrated in the computer simulation in Figure 2B. Although the computer simulation is quite close in appearance to our experimentally observed spectrum, the values of the coupling constants attributed to the H· spin adduct are much lower than previously reported values (Table II). Moreover, when the TiO_2/Pt powder is irradiated with PBN or POBN in D_2O, no spin adducts of D· were observed. When these samples were irradiated for prolonged durations without any filters, a small signal with the same coupling constants as that of species IV appeared. This clearly eliminates the possibility that species IV arises from trapping of H·. The simulation in Figure 2C is based upon a spectrum using for IV a triplet of doublets, $a_N = 14.63$ G and $a_H^\beta = 14.0$ G. These hfsc values are quite close to those observed for *tert*-butyl hydronitroxide.[18] Since this spin adduct and the one attributed to the benzoyl radical generally appear together, it is likely that the observed spectra for species III and IV are due to some decomposition products of the spin traps.

TABLE II: Spin Adducts of PBN and 4-POBN

conditions	splitting constants, G a_N	a_H^β	a_H^γ	trapped radical	ref
	PBN				
photolysis of 1% H_2O_2	15.3	2.75		OH·	20
photolysis of 30% H_2O_2	15.3	2.75		OH·	20
	14.8	2.75		O_2H·	
	15.55	2.95		OH·	18
	14.76	2.95		*a*	
	15.55	4.75		*b*	18
	15.5	2.92		OH·	
	14.8	2.92		*a*	
microwave discharge					
H_2O into benzene	14.63	2.88		OH·	18
	14.98	7.50		H·	18
D_2O into benzene	14.70	2.61		OD·	18
	14.94	7.66		D·	18
α-radiolysis of H_2O	15.98	3.12		OH·	18
	16.57	10.50		H·	18
photolysis of NaOH	15.57	4.03		OH·	18
	16.42	10.34		H·	18
electrolysis of H_2O	16.7	10.6		H·	48
	20.2	28.9		*c*	48
	4-POBN				
$Na_2S_2O_3 \cdot H_2O$	15.03	1.67	0.36	OH·	18
photolysis of 1% H_2O_2	14.95	1.67	0.34	OH·	19
pH 4	15.61	2.63		*a*	19
pH 7	15.0	1.70	0.34	OH·	19
pH 6	14.97	1.68	0.36		
pH 6	15.58	2.62		*a*	19
photolysis of 30% H_2O_2	14.99	1.73	0.33	OH·	19
	15.0	1.70	0.32	OH·	
	15.5	2.55			

[a] The identity of the trapped radical has not been confirmed, although the possibility of O_2H· was considered. [b] Signal observed upon further photolysis. [c] This spin adduct was proposed originally to be due to OH· but recently the possibility of a cyclic nitroxide has been proposed.[43]

The spectrum observed when TiO_2/Pt powder is illuminated in a 0.1 M 4-POBN solution of pH 4 buffer is shown in Figure 3. In this case, the spectrum is composed of signals from three different spin adducts. We assign the species with $a_N = 15.0$ G, $a_H^\beta = 1.73$ G, and $a_H^\gamma = 0.35$ to the hydroxyl spin adduct. In D_2O, this spin adduct did not show the splitting attributed to the γ-hydrogen of the hydroxyl.[18] This smaller splitting would not be expected if OD· had been trapped. The other two spin adducts again may be due to the *tert*-butyl hydronitroxide and the benzoyl spin adduct. It may be that 4-POBN in acidic media is not sufficiently stable to be utilized with any degree of certainty.[18] The spectrum observed with 4-POBN in a pH 7 buffer solution is shown in Figure 4. At this pH, the 4-POBN appears stable with respect to the detection of hydroxyl radicals. The observed spectrum consists of only two spin adducts: $a_N = 15.0$ G, $a_H^\beta = 1.70$ G, and $a_H^\gamma =$

Figure 5. Experimental spectrum of an illuminated sample of H_2O (pH 7), 0.1 M POBN, and TiO_2 (anatase) powder: $a_N = 15.6$, $a_H^\beta = 1.06$; $a_N = 15.0$, $a_H^\beta = 1.8$, $a_H^\gamma = 0.30$.

0.35 G and $a_N = 15.6$ G and $a_H^\beta = 2.55$ G. The first spin adduct is due to the hydroxyl radical and the latter probably to the perhydroxyl radical (see Table II).

Reactions on Unplatinized Anatase Powders. The results reported above were obtained by using platinized TiO_2. Illumination of unplatinized TiO_2 (anatase) powder also results in the formation of spin adducts (Figure 5). This signal is the superposition of signals from two spin adducts, $\cdot OH$ and $HO_2\cdot$. The coupling constants for these two adducts are nearly the same as those for platinized powders except the splitting due to the γ-hydrogen was not observed. The intensity of the signal was generally only slightly smaller than those for the platinized powders.

Reactions on Platinized Al_2O_3 and TiO_2 Rutile Powders. Oxidations of benzene[27] and anthracene[28] by ultraviolet light on both silica and alumina have been reported. When a platinized Al_2O_3 powder (5% Pt) in the presence of both PBN and 4-POBN aqueous solutions was used, no ESR signal was observed in the dark. Illumination through filters 1 and then 2 still gave no ESR signal. Even illumination without any filters resulted in only a very small signal after approximately 10 min.

Because the photoinduced decomposition of water in a TiO_2/Pt PEC with an external bias as discussed earlier utilizes a TiO_2 electrode of rutile (r) structure, we investigated spin trapping with platinized TiO_2 (rutile) powder. A sample prepared with this powder, water, and either PBN or 4-POBN gave no ESR signal in the dark. Illumination through filter 1 and then filter 2 still resulted in no ESR signal being observed. Although it is possible that this lack of signal can be ascribed to changes in the nature of the catalyst surface during the transformation to rutile, we feel they rather point to a lower efficiency for rutile compared to anatase. These results are consistent with the observations that (1) a small bias is required in a TiO_2 (r)/Pt PEC for photoinduced decomposition of water to occur and (2) experiments using platinized TiO_2 in the photodecarboxylation of carboxylic acids[9] and the photocatalytic oxidation of CN^- on TiO_2 powder[10] showed that rutile powders were less efficient than anatase.

ESR Signals Due to TiO_2 Powder in the Absence of Spin Trap. The ESR spectra observed for reduced and unreduced TiO_2 platinized powders in aqueous media are shown in Figure 6. Such signals are observed at room temperature and are present as background signals. Generally the TiO_2 powders used in the spin trapping experiments were reduced and as a result a very broad structureless signal was seen initially. The magnitude of these signals varied for different reduced powders, but they were so broad and small compared to the signals found by trapping that they did not interfere. Unplatinized powders gave similar signals. There have been many studies of the interaction of oxygen and metal oxides.[29] The nature of the adsorbed oxygen species has generally been attributed to O_2^- and O^-; Ti^{3+} has also been observed.

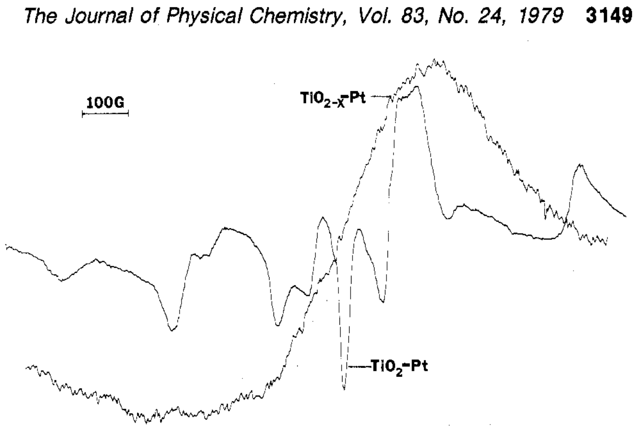

Figure 6. Experimental spectra of reduced and unreduced platinized TiO_2 (anatase) powders in aqueous media.

Reactions in the Absence of Powder. To ensure that the observed signals did not arise from photolysis or oxidation products of the spin traps themselves, several control experiments were carried out. A degassed 0.1 M PBN solution in water (unbuffered and with pH 7 buffer) showed no ESR signal in the dark. Irradiation through filter 1 and then filter 2 still gave no signal even at the maximum receiver gain of the spectrometer. Irradiation through only a piece of Pyrex glass (T <1% at λ's <270 nm) produced a very small signal in a few experiments after several minutes of irradiation. Degassed 0.1 M solutions of 4-POBN in unbuffered or pH 4 and pH 7 buffer solutions produced no ESR signal in the dark or upon irradiation through filters 1 or 2. Upon irradiation through only Pyrex glass, a very small signal was observed in the unbuffered and pH 7 solutions after approximately 10 min of irradiation. However, in the pH 4 solution, an ESR spectrum consisting of a triplet of doublets appeared within a few minutes. This spin adduct may be due to the hydrolysis addition product.[18] The photochemical oxidation of nitrones has been reported by several groups.[30] We did not observe this product in our experiments with water. These experiments suggest that both PBN and 4-POBN are stable in aqueous media, if short-wavelength light is eliminated, especially if the solutions are not acidic; the signals observed with TiO_2 did not arise from photodecomposition of the spin traps. Another possibility that must be considered is the occurrence of signals arising from oxidation or reduction of the traps or the product nitroxides at the particle surface. A previous study reported that within the potential limits of −2.0 to +1.5 V (vs. SCE) in acetonitrle, PBN was electroinactive.[31] Thus with respect to reduction, the spin traps should be inactive. To evaluate the ease at which the spin traps are oxidized, solutions were prepared in 30% H_2O_2 and 0.1 M $Ce(NH_4)_4(SO_4)_4$. In both solutions, no ESR signal was observed in the dark.

A sample containing PBN platinized TiO_2 (anatase) in water-free acetonitrile upon irradiation with light greater than the band gap energy of TiO_2 (3.32 eV) produced no ESR signal. In addition a 0.05 M POBN solution in pH

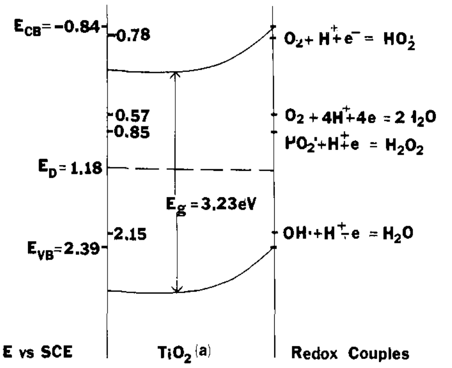

Figure 7. Energy levels for TiO_2 (anatase) and the redox potentials of selected water couples (pH 7). The energy levels for the anatase were estimated by assuming that the valence band edge is the same as that for a rutile electrode with the E_g value of 3.23 eV used to locate the conduction band edge.

7 buffer was oxidized electrochemically (+1.6 vs. Ag wire) on a Pt-foil electrode inside the ESR cavity. No ESR signal was observed. This reinforces our belief that the spin trap is not oxidized or reduced by the TiO_2 powder, although for acetonitrile, solvolysis of the PBN may not occur to the extent that it does in water.

Discussion

The experimental results provide clear evidence for the formation of ·OH and HO_2· during the irradiation of Pt/TiO_2 in deaerated aqueous solutions. We can speculate about their origin based on the energy level diagram of TiO_2 and the redox levels for different possible elementary steps (Table I) shown in Figure 7, as well as the results of past experiments on the irradiation of TiO_2 powders and single crystal electrodes. The potential for oxidation of H_2O or OH^- to free ·OH lies above the valence band edge of TiO_2, so that a photogenerated hole there would be sufficiently energetic to produce this species. If the hydroxyl radical formed is adsorbed at the TiO_2 surface, it would be stabilized and require an even less positive potential for its production. The intermediacy of ·OH can also account for the very energetic photoprocesses that can occur at irradiated TiO_2, such as the oxidation of acetate ion[9] and the formation of amino acids.[32] The potential for formation of ·OH is more positive than the decomposition half-reaction of TiO_2 (to TiO^{2+} and O_2), +1.18 V vs. SCE.[33] Extensive decomposition of the TiO_2 material probably does not occur because of the rapid disappearance of the hydroxyl radicals and perhaps some reprecipitation of Ti(IV) at the surface. Some decomposition of TiO_2 has been observed in sulfuric acid solutions.[34] While some models for the photoassisted evolution of oxygen at TiO_2 have invoked transfer to surface states at energies near the O_2/H_2O level,[35] it appears unlikely that the elementary step in the evolution of O_2 occurs at such potentials. The requirement of free or adsorbed ·OH as an intermediate in the production of oxygen places rather severe requirements on the choice of a semiconductor for carrying out the photodecomposition of water in terms of the location of the valence band and stability. H_2O_2 production probably occurs by combination of ·OH (reaction 17) with O_2 produced by its decomposition (reaction 16) or further oxidation (reaction 9). Indeed the following test-tube experiments involving mixing different forms of TiO_2 and 30% H_2O_2 are relevant. Platinized TiO_2 causes very rapid evolution of gas when added to H_2O_2. Unreduced anatase upon exposure to H_2O_2 turns bright yellow (presumably because of formation of the known Ti(IV) peroxide) and causes rapid evolution of gas. However, reduced anatase does not change color and does not cause appreciable decomposition of H_2O_2. It is worth noting that previous studies of the photoassisted decomposition of water in cells with rutile electrodes showed appreciable formation of H_2O_2.[36]

The source of HO_2· is less clear. It could arise from oxidation of H_2O_2 at the TiO_2 (reaction 9) or by reaction with ·OH (reaction 20). Another possible route is via reduction of the O_2 produced during irradiation. Thus reaction of O_2 with an adsorbed H atom or directly (reaction 10) would also produce this species. Evidence for this reductive route to HO_2· was provided by the following experiments. A solution of the superoxide ion, O_2^-·, was produced by reducing dry oxygen electrolytically at a platinum-gauze electrode in a 0.2 M tetra-*n*-butylammonium perchlorate (TBAP) in dry acetonitrile.[39] After about 2 h the solution had turned yellowish and the equivalent of (2–3) × 10^{-4} M O_2^-· had been produced. Two milliliters of the solution was injected with a syringe into a dry, oxygen-free (nitrogen atmosphere) flat quartz aqueous ESR cell. At room temperature, no ESR signal was observed. The solution was then poured into a side arm containing sufficient PBN to produce a 0.5 M solution upon mixing. After all of the PBN had dissolved, the solution was poured back into the main cell compartment. Only a very small ESR signal (a triplet of doublets with a_N = 14.65 G and a_H = 2.87 G) was observed. When 0.25 mL of water was injected to this solution in the cell, the magnitude of this very small ESR signal immediately increased. As more water was added, the signal first gradually increased and then slowly decreased. The results demonstrate that protonation of O_2^-· can produce trappable HO_2·. The very small signal observed initially was probably due to the presence of a small amount of residual water, since it is known that PBN should not trap O_2^-·.[15c]

Recently, the formation of H_2O_2 has been shown to take place on TiO_2 electrodes in O_2 containing solutions.[40] The H_2O_2 is formed via the reduction of O_2 in the dark while the photooxidation of water occurs at the illuminated surfaces. This H_2O_2 produced via reduction could provide a possible source of ·OH. Several experiments were conducted to evaluate the extent to which the dark reduction of O_2 contributes to the ESR signal of ·OH observed in the photodecomposition of water in deaerated solutions.

As we have discussed previously, H_2O_2 will rapidly decompose on platinized TiO_2. To determine if this reaction is a possible source of radical species, the following experiment was conducted. A 1% H_2O_2 aqueous solution containing 0.05 M 4-POBN was placed in the ESR cavity in the dark. No ESR signal was observed. Then platinized TiO_2 was added to the solution; immediately the H_2O_2 began to decompose, but no ESR signal was observed. When the sample was then irradiated without any filters, an ESR signal appeared. Thus, as has been shown previously, spin adducts due to H_2O_2 are not formed by the dark decomposition of H_2O_2 but only from the homolytic cleavage of H_2O_2 by ultraviolet light.

Several experiments were performed with solutions containing some additive [e.g., $Na_2C_2O_4$, NaI, and hydroquinone (HQ)]. In these cases, the additive competes very efficiently with the water for the photogenerated holes.[41] Thus, the contribution from the photooxidation of water to any observed ESR signal (spin adducts of OH·) should be diminished. When O_2 is present in these solutions, the degree to which O_2 reduction contributes to the ·OH ESR signal might then be evaluated.

A sample was prepared containing a saturated solution of $Na_2C_2O_4$, 0.1 M 4-POBN, and platinized TiO_2. Oxygen was bubbled through the cell and the solution for approximately 10 min. No ESR signal was observed in the dark or under illumination using filter 1. Upon irradiation for a prolonged duration using filter 2, a small signal composed of two sets of triplets of doublets were observed [$a_N = 15.7$ G (±0.1 G) and $a_H = 3.3$ G (±0.1 G); $a_N = 15.7$ G (±0.1 G) and $a_H^\beta = 2.3$ G (±0.1 G)]. However, because $\cdot CO_2^-$ can be formed either by the reaction of oxalate with OH·[42,43] or by the photooxidation of oxalate,[25] only a small ESR signal due to trapped OH· would be expected, i.e., oxalate competes with the spin trap for any OH·. However, the spin adduct which has been attributed to $O_2H\cdot$ had a slightly more intense signal than the other spin adducts.

Photooxidation of iodide forms the free halogen and does not have the other complications as the case of oxalate. Two samples were prepared containing platinized TiO_2, NaI, and a spin trap (one contained 100 mM NaI and 0.1 M PBN and the other contained 10 mM NaI and 0.05 M 4-POBN). Both samples had O_2 bubbled through them for 10 min. Oxidation of the iodide in this neutral solution was not observed. In the dark and under illumination using filter 1, no ESR signal was observed. Irradiation through filter 2 produced a very small signal which was almost completely masked by the background. In this case, radical species produced in the reduction of O_2 appear negligible. After illumination, the solution had darkened and I_2 was present. It was produced by either the direct photooxidation of iodide at the TiO_2 or by intermediates.

A sample containing 10 mM HQ, 0.1 M POBN, and platinized TiO_2 was prepared. The sample was degassed in the same manner as described earlier. In the dark and under illumination using filters 1 and 2, no ESR signal was observed. Oxygen was then bubbled into the cell and the solution. In the dark and under illumination using filter 1 again no ESR signal was observed. Upon irradiation through filter 2 an ESR signal appeared and gradually increased in size until it reached a photostationary state after ~40 min. The spectrum consists of the superposition of three sets of triplets of doublets [hfsc values: I, $a_N = 1.56$ G, $a_H^\beta = 3.1$ G, $a_H^\gamma = 0.25$ G (±0.1 G); II, $a_N = 15.7$ G, $a_H^\beta = 3.2$ G (±0.1 G); III, $a_N = 15.7$ G, $a_H^\beta = 3.17$ G (±0.1 G)]. The exact nature of these spin adducts is unknown at this time, although species I, because of the presence of the extra splitting, may be due to OH·. However, the values for the coupling constants for species I are slightly larger than those found in other experiments and the values presented in Table II. The oxidation products of HQ do undergo further reactions under prolonged illumination,[35] as well as 1.4-addition and cycloaddition reactions.[44,45] Thus there may be a number of species formed under these conditions.

The experiments involving additives show how complex the photoreactions on semiconductor particulates can be because of the presence of both reducing and oxidizing states and the difficulty of providing unequivocal evidence of the oxidative origin of ·OH. However, on the basis of these results and previous studies, we feel that the OH· spin adduct observed in the photodecomposition of water in deaerated solutions comes primarily from the photooxidation process. The fact that the growth of the ESR signal is much faster in the deaerated solution than for samples with an additive and O_2 suggests a lesser importance of a reductive path to ·OH. In the deaerated solution the reductive reaction, at least initially, must involve either proton or Ti(IV) reduction.

The absence of any spin adduct for H· or D· can be attributed to their rapid reaction with oxygen or intermediates produced via the oxidation process on the TiO_2. Once O_2 is formed, it would be more readily reduced than the proton, leading to the observed adducts of $HO_2\cdot$.

Although the anatase form of TiO_2 has a slightly larger band gap than the rutile form (E_g = 3.23 vs. 3.02 eV), it was the only form which, when irradiated, produced spin adducts due to water decomposition species. This, as was discussed in the case of the decarboxylation reactions, is due to the more negative flat-band potential of the anatase form.[8] Thus a PEC utilizing a TiO_2 anatase photoanode and a Pt cathode may possibly photodecompose water under short-circuited conditions. With $SrTiO_3$, which has a very similar flat-band potential, this is the case.

Conclusions

On the basis of our findings the photodecomposition of water on platinized TiO_2 anatase powders does occur. Spin adducts of OH· and $O_2H\cdot$ indicate the existence of radical intermediates during this process. The presence of the $O_2H\cdot$ spin adduct leads to speculation that molecular oxygen may be preferentially reduced on these semiconducting powders. The origin of the oxygen is believed to be from the oxidation of water, although the presence of strongly adsorbed oxygen on the TiO_2 powder has not been ruled out. Direct observation of these radical species on TiO_2 has not previously been observed, although OH· has been proposed as an intermediate. Other relevant experiments include the detection of hydroxyl radicals by hydroxylation of benzene[45] and the formation of O_2 and H_2 during the illumination of platinized TiO_2 on H_2O.[46] From this laboratory[47] recent experiments have also shown the intermediacy of ·OH in the photo-Kolbe reaction of benzoic acid, where salicylic acid was detected by fluorescence measurements.

The use of the spin trapping technique can serve as a very valuable tool in gaining a better understanding of the reaction mechanisms on semiconducting materials. Certainly our studies and those of several other groups, notably Janzen, and Hair and Harbour, suggest that experiments with other photosynthetic and photocatalytic reactions and the use of more diagnostic spin traps, e.g., di-*tert*-butyl peroxyoxalate (DMPO), would be valuable.

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Electron Spin Resonance Study of Fluoroalkyl Nitroxide Radicals Using the Spin-Trapping Technique

Yosuke Katsumura, Kenkichi Ishigure, and Yoneho Tabata*

Nuclear Engineering Research Laboratory, Faculty of Engineering, University of Tokyo, Ibaraki, Japan 319-11 *(Received April 24, 1979)*

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Many types of spin adducts produced by the photolysis of a mixture of fluoroalkyl iodides and spin-trapping agents in solution were investigated by means of ESR spectroscopy. It was found that not only ESR patterns but also A_F^{β} values depend significantly on temperature. INDO calculations were carried out to obtain information about the structure of the spin adducts, the magnitudes of A_F and A_N, and internal rotations of the fluoroalkyl groups. The temperature dependencies of both the ESR pattern and the A_F^{β} value were attributed to the restricted rotation or torsional oscillation of the fluoroalkyl groups about the nitrogen–carbon bond. The structure of the nitroxide radicals, the magnitudes of A_F^{β} and A_N, and the stable conformations of these spin adducts are discussed.

Introduction

Recently, the spin-trapping technique has been found to be useful to detect and identify short-lived intermediate radical species.[1,2] It is expected that fluoroalkyl radicals may be easily identified by their ESR spectra since spin adducts of the fluoroalkyl radicals are characterized by large fluorine coupling constants, in contrast with the adducts of alkyl radicals. Perfluoroalkyl nitroxide radicals have been investigated by Klabunde[3] and Konaka and Terabe.[4] They found that the β-fluorine coupling constant changes with temperature. We have applied the spin-trapping technique to identify the fluoroalkyl radicals produced from fluorocarbons by γ-irradiation. Both coupling constants and the ESR spectra themselves of the spin adducts of fluoroalkyl radicals were temperature dependent. Therefore, it was necessary to investigate those temperature dependencies as the first step of our studies. Various types of fluoroalkyl spin adducts have been investigated systematically. They were produced by the photolysis of fluoro iodides in the presence of trapping agents; the three different nitroso compounds nitrosobenzene, 2-methyl-2-nitrosopropane, and 2-methyl-2-nitrosobutanone-3 were used. The main advantage of nitroso compounds is that the information concerning the structure of the trapped radical is more easily obtained from the spectrum of the nitroso adducts than in the case of nitrone compounds. It is also interesting to investigate the structure of nitroxide radicals, especially concerning

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* To whom correspondence should be addressed at the Department of Nuclear Engineering, Faculty of Engineering, University of Tokyo, Tokyo, Japan 113.

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