Synthesis and Characterization of
Quantum Size Metal Oxide Colloidal Particles.
Photocatalytic Peroxide Formation on ZnO and TiO₂

Thesis by

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Meinen Eltern gewidmet.
Licht!
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ABSTRACT

The syntheses of transparent colloidal solutions of extremely small ZnO (d< 5nm) and TiO₂ (d< 3 nm) particles in water, alcohol, and acetonitrile are presented. Quantum size effects are observed during particle growth and at final stages of synthesis. They are qualitatively and quantitatively (TiO₂) interpreted by using a simple molecular orbital (MO) picture and a quantum mechanical model developed by Brus. The optical absorption and fluorescence properties as well as the surface acid–base properties are characterized in detail. The two materials are shown to be active photocatalysts in the formation and degradation of H₂O₂ and organic peroxides and in the degradation of chlorinated hydrocarbons. Quantum yields and steady state concentrations are given as function of various reaction parameters such as the oxygen concentration, the nature and concentration of electron donor, pH, and charge of the electron donor. Rates of reaction are correlated with surface speciation as calculated by the SURFEQL computer code. Transparent colloidal solutions of Fe₂O₃ (hematite) have also been prepared, however only negligible photocatalytic activity is found when compared to ZnO and TiO₂. Evidence is presented for OH• radical activity when aqueous TiO₂ suspensions are illuminated at high pH.
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OVERVIEW

The main objectives of this thesis are to elucidate the principles of the photocatalytic formation of hydrogen peroxide and to study the transformations of organic molecules in suspensions of metal oxides that are relevant to the environment. For this purpose three metal oxide systems (ZnO, TiO₂, and Fe₂O₃) have been prepared in transparent colloidal form.

Rates of formation and steady-state concentrations of hydrogen peroxide generated via the photocatalytic reduction of molecular oxygen and the concomitant oxidation of organic molecules (such as acetate or 2-propanol) have been obtained for ZnO, TiO₂, Fe₂O₃ and a sample of desert sand.

The fate of photogenerated valence band holes has been explored by studying the photocatalytic oxidation of organic anions (acetate and its chloro derivatives) and cations (chloroethylammonium). The product spectra obtained for surficial photochemical oxidations have been compared with the product spectra from corresponding oxidation studies in homogeneous solution. These experiments have shown that the OH⁻ radical is a likely intermediate in photocatalytic oxidations of suspensions of TiO₂.

Transparent colloids offer several advantages for the study of heterogeneous photocatalysis. In addition to providing a high specific surface area for the adsorption of solutes, the transparency of such suspensions aids in the direct observation of transient and stable absorbent or fluorescent species (i.e., molecules in the homogeneous phase, surface complexes, or colloidal particles). The well defined optical properties of transparent colloidal suspensions allow photochemical quantum yields to be calculated with a high degree of accuracy.
To study the photochemical and photophysical properties of these metal oxide particles turns out to be an interesting subject. In fact, due to the small size of colloidal particles (e.g., \( r \approx 25 \) Å for ZnO colloids, \( r \approx 15 \) Å for TiO\(_2\)), electrostatic perturbations (from such sources as excess charge carriers) have an enhanced effect on absorption and fluorescence spectra of the crystallites.

In the course of the metal oxide synthesis (ZnO, TiO\(_2\)) characteristic spectroscopic changes are observed that accompany the particle growth which starts with molecular species (Zn(CO\(_2\)CH\(_3\))\(_2\), TiCl\(_4\)) and yields measurable (by transmission electron microscopy) crystallites. These effects are due to the "quantum sized" nature of the particles at early growth stages and can be interpreted using quantum mechanical models that were recently described in the literature. In addition, a molecular (MO) model has been proposed to explain the observed spectroscopic properties of extremely small particles.

Recently, it has been shown that ceramics can be made ductile at low temperature, allowing plastic deformations once a polycrystalline material was generated with a crystal size of a few nanometers. The synthetic methods developed during this thesis research for the preparation of large quantities of oxide particles (e.g., TiO\(_2\)) of extremely small sizes appear to be much less costly and energy consuming than previous methods of synthesis.
INTRODUCTION

Photocatalysis on colloidal semiconductor particles has become a recognized research field over the last decade. The main impetus for much of the research has been the potential use of simple semiconductors for solar energy conversion.\[1\] Extremely small colloidal semiconductor particles, that fall into the transition range between molecular and bulk properties (i.e., 20 to 500 Å) have been found to exhibit properties not found in the bulk phase materials.\[2–5\] Colloidal semiconductors have been used as heterogenous catalysts for selected synthetic reactions.\[6\] In environmental systems, the potential importance of photochemically active metal oxides has not been fully recognized. For example, the photochemically induced transformation of small organic molecules and the production of hydrogen peroxide in cloudwater may be mediated by photochemically active particles.

Hydrogen peroxide, \(\text{H}_2\text{O}_2\), appears to be the most effective oxidant in haze aerosols, clouds, and hydrometeors at low pH.\[7–8\] Jacob and Hoffmann have shown that the predominant pathway for the formation of sulfuric acid in humid atmospheres below pH 5 is the oxidation of sulfur dioxide by \(\text{H}_2\text{O}_2\).\[8\]

Hydrogen peroxide in cloudwater has a number of gas–phase sources,\[9\] however, heterogeneous photosynthesis of \(\text{H}_2\text{O}_2\) may prove to be an important source in haze aerosols, fogs, and cloudwater. Various metal oxides, some of which are abundant in natural environments, are known to act as photocatalysts for a variety of reactions.\[1\] The photocatalytic formation of \(\text{H}_2\text{O}_2\) in suspensions of zinc oxide for instance is well established (see Chapter 4), however little is known about the mechanism or the nature of reactive intermediates. The photochemical formation of \(\text{H}_2\text{O}_2\) on \(\text{TiO}_2\) particles has been postulated,\[10–11\] although direct chemical evidence for the photocatalytic \(\text{H}_2\text{O}_2\)
production in colloidal suspensions of TiO$_2$ has not been obtained. The photochemical activity of Fe$_2$O$_3$ sols has also been established.$^{[12-13]}$

Semiconductors such as Fe$_2$O$_3$, TiO$_2$ and ZnO are often found in aerosol samples (e.g., from desert sands $^{[14-15]}$). Rates of the photochemical formation and destruction of H$_2$O$_2$ needed to be established. Furthermore, the potential role of these minerals in the photochemical transformation of organic molecules needed to be explored.

In addition, the mechanism of oxidation by photogenerated holes needed to be established. For example, oxidation of an electron donor may proceed either by direct electron transfer to a hole or via the intermediate formation of OH$^\cdot$ radicals on the surface (cf. Figure 1).

### Proposed Reaction Mechanism

\[
\begin{align*}
\text{CH}_3\text{CO}_2^- + h^+ & \rightarrow \text{CH}_3^+ \rightarrow \text{CH}_3\text{O}^- \\
+ \text{OH}^- & \rightarrow \text{H}_2\text{O} \\
\cdot \text{CH}_2\text{CO}_2^- & \rightarrow \cdot \text{CH}_2\text{O} \\
+ \text{O}_2 & \rightarrow \text{CH}_2\text{OH}^- \\
\cdot \text{O}_2\text{CH}_2\text{CO}_2^- & \rightarrow \text{H}_2\text{O}_2, \cdot \text{O}_2\text{CCH}_2\text{OOCH}_2\text{CO}_2^- \\
\text{CHO}\text{CO}_2^-, \text{CH}_2\text{OHCO}_2^- & \\
\text{CH}_2\text{O}, \text{CO}_2 &
\end{align*}
\]

Figure 1

Oxidation of Acetate
Charge-transfer reactions at the interface between a semiconductor and the aqueous medium may provide a route for the conversion of solar energy through water photolysis. While the reduction process initiated by transfer of conduction band electrons is fairly well understood, the fate of the highly oxidizing valence band holes, generated upon illumination of wide bandgap semiconductors such as TiO₂, ZnO, and Fe₂O₃ is less well known. By determining the photo-oxidation products starting from small organic molecules and by comparing the results obtained with those from γ– and pulse- radiolytic studies performed in homogeneous solutions,¹⁶–¹⁷ evidence will be obtained for likely reaction intermediates (Figure 2).

The synthesis of transparent aqueous ZnO colloids has been reported only recently (Chapter 2), yet there are no reports about detailed mechanistic studies of photochemically induced H₂O₂ formation on semiconductor particles in the literature.

General concepts of semiconductor redox-chemistry

In general, the photoinduced redox chemistry of semiconductor surfaces can be represented simply as

$$\text{semiconductor} \xrightarrow{\frac{h\nu}{h\nu/\text{heat}}} e^-(cb) + h^+(vb) \quad (1)$$

Absorption of a photon with an energy equal to or greater than the bandgap energy [¹⁹] (cf. Figure 2) leads to the formation of an electron/hole pair in the semiconductor particle. It should be noted that under steady state illumination with an actinometry on the order of 5×10⁻⁶ Einstein/l·s (assuming 100% absorption) and a particle concentration of about 10⁻⁶ mol/l the average time lag
between two effective hits is on the order of 0.2 s. The lifetime of an electron–hole pair depends on the energetic structure of the semiconductor particle (e.g. the density of states in the bandgap and the density of non–reactive vibrational relaxation channels) and was found to be (30 ± 15) ns in a 120 Å sized TiO$_2$ particle.[20]

It is assumed that the solution surrounding the semiconductor particle contains electron acceptors A (e.g., O$_2$ or methylviologen) and electron donors D (e.g., 2–propanol, acetate) as shown in Figure 2. There are two conceptionally different ways in which an overall redox reaction between a donor D and an acceptor A can be driven by illuminated semiconductor particles.

$$\text{D} + \text{A} \rightarrow \text{D}^\bullet + \text{A}^\bullet$$

(2)

If the overall reaction is endothermic ($\Delta G^0 > 0$) like, for example, the splitting of H$_2$O in H$_2$ and O$_2$, no material will be able to catalyze this process under normal (thermal) conditions (i.e., 25 °C and 1 atm). Under these circumstances, a semiconductor would act as a photosensitizer generating chemical molecules on a higher energy level than the parent compounds (see left side of Fig. 2). Since the back reaction in this case is exothermic it is crucial for continuous photosynthetic activity to separate the products. If reaction (2) is exothermic ($\Delta G^0 < 0$) but kinetically hindered by high activation energies ($E_a$) then semiconductors act as photocatalysts (see right side of Fig. 2) resulting in an overall lowering of $E_a$. Actually, in many systems one encounters two subsequent one–electron transfers, where the first transfer is slightly endothermic and the second step is strongly exothermic, resulting in an overall exothermic redox reaction. This behavior is illustrated in Figure 3 for an idealized photoassisted redox reaction between oxygen and acetate.
**SEMICONDUCORS AS**

**PHOTOSENSITIZERS**

\[
D + A \xrightarrow{h\nu} D^+ + A^- \\
\Delta G^0 > 0
\]

**PHOTOCATALYSTS**

\[
D + A \xrightarrow{h\nu} D^+ + A^- \\
\Delta G^0 < 0
\]

**Figure 2**

**H_2O_2 Formation on colloidal ZnO**

\[
\Delta G_f^0 = -150 \text{ kJ mol}^{-1}
\]

\[
O_2 + 2H_{aq}^+ \xrightarrow{h\nu, \lambda_{ex} \leq 370\text{nm}} HO_2^-
\]

\[
\Delta G_f^0 = +13 \text{ kJ mol}^{-1}
\]

\[
CH_3COO^- + H_2O \xrightarrow{h\nu} CH_3COO^- + CH_3OH + CO_2 + H_{aq}^+
\]

\[
\Delta G_f^0 = +50 \text{ kJ mol}^{-1}
\]

**Figure 3**
On the right side of Fig. 3 the enthalpy change for the first electron transfer is found to be endothermic. The left side of Fig. 3 shows the free enthalpy changes for two--electron transfers. The overall change \((-150+45)\) kJ/mol = \(-105\) kJ/mol indicates that the reaction of O\(_2\) with acetate is exothermic. The majority of reactions studied as a part of this research can be classified as overall exothermic and hence photocatalytic.

**Objectives:** In order to study photocatalytic transformations of molecules, i.e., the formation of hydrogen peroxide by oxygen reduction and the oxidation of organic molecules the oxide catalysts had to be synthesized in a well defined form that also allows fast spectroscopic measurements. The synthesis and characterization of colloidal zinc oxide which exhibits quantum size properties is described in Chapter 2. Titanium dioxide colloids were also shown to exhibit quantum size effects once the synthesis was carried out under tightly controlled conditions (Chapter 3). Special emphasis was laid on the characterization of the surface acid–base chemistry that determines the surface charge of the particles. Photochemical experiments were conducted to obtain quantitative insight into the factors that determine the rates of formation and degradation of H\(_2\)O\(_2\) and organic peroxides in aqueous suspensions of selected metal oxides (Chapter 4).

Chapter 5 which has been published in the ACS symposium series 349 gives a broad overview of the principles that govern the fate of hydrogen peroxide in the atmospheric environment. The objectives of Chapter 6 are to compare the photocatalytic activity of three metal oxide systems: ZnO, TiO\(_2\), and Fe\(_2\)O\(_3\). Chapter 7 is a contribution to the ongoing discussion on how the oxidizing species behaves that is generated after photoexcitation of TiO\(_2\) particles. Does it have the reactivity of a hole or an OH\(^-\) radical? Chapter 8 concludes this thesis with recommendations for future research.
REFERENCES

PREPARATION AND CHARACTERIZATION OF QUANTUM SIZE
ZINC OXIDE: A DETAILED SPECTROSCOPIC STUDY

Preparation and Characterization of Quantum Size Zinc Oxide: A Detailed Spectroscopic Study

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We report the synthesis of transparent colloidal suspensions of small zinc oxide particles in water, 2-propanol, and acetonitrile. Quantum(Q)-size effects are observed during particle growth and qualitatively interpreted by using a simple molecular orbital (MO) picture. The particles at the final stage of growth are approximately spherical in shape and consist of 2000-3000 ZnO molecules. They exhibit many of the photophysical properties of bulk zinc oxide. However, pronounced shifts in the absorption spectrum during the illumination of anoxic suspensions of ZnO reveal a distinctively different behavior of these small particles. Fluorescence spectra of the ZnO sols suggest that adsorbed electron relays are necessary to shuttle electrons from the conduction band into lower lying traps. Two fluorescence maxima are observed at the final growth stage of the ZnO particles. The bandgap fluorescence at 365 nm has an extremely short lifetime (<100 ps), while the visible luminescence at 520 nm exhibits a slower biexponential decay with lifetimes of 0.03 measured in these cases.

Introduction

The photoelectrochemistry of small semiconductor particles has been an area of active research. Recently, there has been a growing interest in ultrasmall particles that fall into the transition range between molecular and bulk properties (i.e., with diameters from 1 to 10 nm). Bulk semiconductors exhibit a pronounced increase in light absorption when photon energies exceed the bandgap energy (Eg); however, the photophysics of ultrasmall semiconductor particles is substantially different. Quantum mechanical calculations and experimental observations suggest that the energy level of the first excited state (E1) of the exciton increases with decreasing particle size thus leading to a blue shift in the absorption spectrum. Particle growth results in spectral shifts from an absorption onset (λ0) in the UV for dimers and oligomers to a λc for the bulk material in the visible or near-IR. In several cases, a concomitant shift in the visible fluorescence (i.e., with λc > λ0) has been noted. Koch et al.21 have reported a shift of the onset of absorption of ZnO colloids from 310 to 360 nm during particle growth in 2-propanol, while at the same time the maximum of the fluorescence peak shifted from 460 to 540 nm. Their paper also describes the preparation of an aqueous colloidal suspension of ZnO which, however, requires the presence of a colloid stabilizer, e.g., hexametaphosphate.21

α-Fe2O3,20-21 WO3,22 and TiO2,23,24 can be synthesized as transparent colloids in water; however, synthesis of ZnO in H2O is not readily achieved (e.g., ΔG° = -0.39 kJ mol-1 for reaction 1 at 25 °C; ΔG° = -2.79 kJ mol-1 at 100 °C; ΔG° = 0 at 13 °C).25

Zn(OH)2 = ZnO + H2O

Further, Schindler et al.27-29 have shown that the dissolution rate of ZnO increases with decreasing particle size. In this respect we report a novel method for the synthesis of transparent ZnO colloids that are stable both in organic and aqueous suspensions in the absence of stabilizers. In addition, we provide an analysis of the dynamic changes in spectral properties of transparent colloidal suspensions of ZnO that take place during particle growth.

Crystalline ZnO exhibits a characteristic fluorescence spectrum with two maxima around 380 and 500 nm.40-51 However, the emission at λ = 380 nm has been attributed to the exciton band; however, no conclusive interpretation for the visible fluorescence has been presented.
peak has been given previously. A detailed study of the fluorescence behavior of the zinc oxide sols thus affords further insight into its mechanism.

**Experimental Section**

Chemicals and solvents were of reagent grade and used without further purification. The water employed in all preparations was purified by a Milli-Q/RO system (Millipore) resulting in a resistivity of $>18\ M\Omega\ cm$. Reflectance spectra of powder samples with BaSO$_4$ as a reference were obtained with a Shimadzu MPS-2000 spectrophotometer equipped with an integrating sphere. The same instrument and a HP 8451A diode array spectrophotometer were used to measure UV/vis absorption spectra. Fluorescence spectra were recorded using a Shimadzu RF 540 spectrofluorometer. Appropriate filters to avoid second-order contributions were installed in the excitation and emission light paths. Fluorescence quantum yields were measured with $6 \times 10^{-5}$ M quinine sulfate in 1 N H$_2$SO$_4$ as a reference standard. All steady-state spectra were measured at 25 °C.

Particle sizes were determined by transmission electron microscopy (TEM). To prepare the TEM samples a drop of the colloidal suspension was applied for 30 s to a copper mesh supported by a carbon film and subsequently removed with a paper tip. Adhesion of the particles was promoted by exposing the carbon film to a glow discharge prior to this procedure.

The irradiation apparatus consisted of an Osram XBO 450-W xenon lamp in a Muller LX 1450-2 lamp housing and a GM 252 (Kratos) monochromator with the appropriate UV filters. Attenuation of the spectral line for wavelengths $>400\ nm$ was achieved by using a liquid light filter. Cutoff filters were used when appropriate.

In order to assess the fluorescence yield of the colloidal suspensions under various oxygen partial pressures 3-nl aliquots of the isopropanolic suspensions were subjected to at least three freeze-pump-thaw cycles ($p \approx 10^{-7}\ Torr$) before the measurement. In order to determine the dependency of the fluorescence yield on the H$_2$O$_2$ concentration for oxygen free suspensions, 3-nl aliquots containing calibrated amounts of H$_2$O$_2$ were subjected to at least three freeze-pump-thaw cycles ($p \approx 10^{-7}\ Torr$) before the measurement.

Fluorescence decay times were measured in collaboration with Douglas Magde at the University of California, San Diego.

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For a typical preparation 1 mmol of Zn(OAc)$_2$ (zinc acetate) was dissolved in 80–90 mL of 2-propanol under vigorous stirring at $\approx 50\ °C$ and subsequently diluted to a total volume of 920 mL. 80 mL of a 2 $\times$ 10$^{-3}$ M NaOH solution in 2-propanol (pellets of sodium hydroxide dissolved in 2-propanol at $\approx 50\ °C$) was then added at 0 °C within 1 min under continuous stirring. The mixture was then immersed for 2 h into a water bath preheated to 65 °C. After 3 days of further aging at room temperature the solvent was removed by rotary evaporation (conditions: 30 °C, 1 Torr) of 10–50-M aliquots of the isopropanolic ZnO colloid. The remaining hygroscopic white film was immediately resuspended in water to yield a transparent aqueous colloid (pH 7.7). Acetonitrile also dissolved the film yielding colloidal ZnO in an organic solvent.

A flow system consisting of a 250-ML thermostatted reactor connected through short silicon and Tygon tubes with a Masterflex peristaltic pump (flow rate ca. 100 mL/min) and a flow cell (Hellma No. 176.50, light path 10 mm, height 11 mm, width 4 mm) was used for investigations of the time evolution of the absorption spectra. Mixtures of the zinc salt and the NaOH solutions in 2-propanol were prepared at the desired temperature and immediately introduced into the flow system. Spectra were recorded for 1 s at regular intervals with the HP 8451A diode array spectrophotometer and stored for further treatment. UV cutoff filters were used when appropriate.

Characterization of the Surface of the Colloidal Particles. Titrations of 40-nl samples of 1 $\times$ 10$^{-3}$ M aqueous colloidal ZnO, thermostatted to 25 °C, were carried out with a Radiometer automatic titrator system consisting of a PHM84 pH meter, a TTT80 titrator, and a ABU80 autoburette. A vigorously stirred suspension of ZnO colloid was titrated with freshly prepared 1 $\times$ 10$^{-2}$ M stock solutions of NaOH (N$_2$ bubbled) or HCl at a rate of 10 µmol min$^{-1}$.

Coagulation studies were performed using the above-described flow system at 25 °C and monitoring the absorption changes in the visible ($\lambda_{	ext{max}} = 500\ nm$). The lack of any absorption of zinc oxide at this wavelength due to electronic transitions allows the observation of particle coagulation that results in an increase in absorbance. In typical experiments, 40 mL of 1 $\times$ 10$^{-3}$ M aqueous colloidal ZnO solutions was titrated at a rate of 5 $\times$ 10$^{-1}$ mol min$^{-1}$ starting at pH 7.6 with a 1 $\times$ 10$^{-2}$ M solution of NaOH, while the absorbance was recorded. The first derivative of the absorption vs. time profile yielded the coagulation rate as a function of pH.

**Results**

The UV/vis absorption spectra recorded at various times during the preparation of a stable transparent suspension of ZnO colloid in 2-propanol are shown in Figure 1a. Sixteen seconds after mixing the zinc acetate with the base solution at 0 °C an onset of absorption (determined by the linear extrapolation of the steep part of the UV absorption toward the base line) $\lambda_{	ext{max}} = 306\ nm$ is observed. The absence of any detectable particles in the electron

Characterization of Quantum Size Zinc Oxide

![Graph](image)

micrographs taken with a freshly prepared sample indicates that only extremely small ZnO particles are present at this stage (species with diameters ≤ 5 Å fall below the detection limit of the TEM). Upon continuous heating for 2 h at 65 °C λ₈₈₆ steadily shifts toward 365 nm. Electron microscopy reveals that the reaction mixture now contains almost spherical particles with a mean diameter of 50 Å and a relatively narrow size distribution (Δ5 Å) as shown in Figure 2a. Plots of λ₈₈₆ vs. the logarithm of the reaction time are given in Figure 1b for the results shown in Figure 1a as well as for various isothermal preparations. Data of analogous experiments using zinc perchlorate instead of zinc acetate are also presented in this diagram. Despite a rather similar dynamic behavior the formation of turbid suspensions is indicated with perchlorate as the anion; i.e., coagulation of the particles takes place. The linearity of this semilogarithmic presentation in the case of isothermal syntheses at 25 and 50 °C reveals that the spectral shift is strongly retarded toward the end of the preparation.

Some other features should be noted from the growth curves shown in Figure 1b:

The pronounced temperature dependence of the particle growth suggests that activation and not diffusion-controlled processes occur. A reaction mixture of acetate and base kept at 25 °C, for instance, needs 50 h to reach the same onset of absorption (363 nm) as an identical mixture at 50 °C after 1 h.

The choice of the anion is critical for the preparation of transparent, stable ZnO colloids. It has already been mentioned that the use of zinc perchlorate instead of zinc acetate yields a turbid suspension, λ₈₈₆ initially changes more slowly in the case of zinc perchlorate. However, after a few minutes at 65 °C, when λ₈₆ = 360 nm is reached, the colloid coagulates. A preparation made up of zinc acetate and base remains transparent for more than 2 h at 65 °C before precipitation. Experiments with ZnCl₂ or Zn(NO₃)₂ and otherwise similar reaction conditions reveal an even faster coagulation than in the case of Zn(ClO₄)₂ following the initial formation of a clear colloidal suspension.

A strong visible fluorescence is noted for all colloidal suspensions of ZnO. Figure 3 shows absorption and fluorescence spectra of isopropanolic suspensions of ZnO colloid at various growth stages. Excitation wavelengths for the fluorescence spectra were chosen to ensure identical absorbancies of the suspensions. As illustrated in Figure 3, the absorption spectra of freshly prepared colloidal suspensions of ZnO are characterized by blue-shifted onsets of absorption. Furthermore, pronounced absorption maxima ≥ 25 nm below λ₈₆ are noted for the young preparations. Their fluorescence spectra (shown on the right-hand side of Figure 3) exhibit a single broad fluorescence band with an initial maximum located around 460 nm. Concomitant to the changes of λ₈₆ a bathochromic shift of this visible emission is perceived upon aging of the colloid. In fact the visible fluorescence appears to be consistently redshifted by 155 ± 5 nm compared to λ₈₆. While the former peak changes from 460 to 516 nm, its intensity passes through a maximum with the highest fluorescence quantum yield of φ = 0.16 measured for a sample that had been reacting at 25 °C for 2 min. After the colloidal suspension has been aged either by heat treatment or long reaction times (i.e., the ZnO colloids have reached their final growth stage as defined by a value of 365 nm for λ₈₆), a second fluorescence is encountered at 365 nm coinciding with the onset of the absorption spectrum. However, young ZnO colloids do not exhibit this fluorescence band.

Absorption and fluorescence spectra of an aqueous colloidal suspension containing 1 × 10⁻² M zinc oxide at pH 7.7 are shown in Figure 4. The absence of absorption above 370 nm indicates that this suspension does not scatter light to any appreciable extent in the visible part of the spectrum. This is consistent with the observation (see TEM in Figure 2b) that particle sizes and size distribution have not changed during the preparation of the aqueous sample. However, upon comparison of parts a and b of Figure 2, the formation of chains of ZnO particles is obvious in the latter. Similar observations have been made before during the electron microscopy of aqueous TiO₂ colloids. It is not yet clear whether these chains were already present in solution or were formed upon preparation of the samples for TEM. Recent investigations in this laboratory show the absence of comparable aggregation effects during the electron microscopy of aqueous α-Fe₂O₃ colloids.

The onset of the absorption spectrum for the aqueous suspension, which is shown in Figure 4 is located also at 365 nm. Two maxima are again observed in the fluorescence spectrum, one coinciding with λ₈₆ and a green emission at 520 nm. Fast titration to pH 12 likewise yields a transparent sol with similar spectral features.

The reflection and fluorescence spectra of zinc oxide powder (Baker, U.S.P.) are given in parts a and b of Figure 5, respectively. The white powder absorbs practically all UV light below 370 nm (i.e., with energies greater than 3.35 eV). Two fluorescence maxima are noted in the emission spectrum when the powder sample is irradiated with UV light (λ₈₆ ≤ 370 nm). A first sharp fluorescence peak (fwhm = 15 nm) is observed at 380 nm, coinciding with the onset of the reflectance drop (Figure 5a). The second

---

ZnO, 2-PROPANOL

Figure 2. Transmission electron micrographs of ZnO colloid in (a, left) 2-propanol and (b, right) water.

Figure 3. Superposition of absorption and fluorescence spectra measured in 2-propanol at various times after mixing 1.0 x 10^{-3} M Zn(OAc)₂ with 1.6 x 10^{-2} M NaOH: ---, 30 s at 25 °C, after mixing at 0 °C (λ₁ = 280 nm); ----, 15 min at 25 °C (λ₁ = 310 nm); -----, 2 h at 50 °C, 15 h at 25 °C (λ₁ = 340 nm); -----, 2 h at 65 °C, 70 h at 25 °C (λ₁ = 340 nm).

rather wide (fwhm ~ 90 nm) green fluorescence band has its maximum around 510 nm.

Titration experiments have been conducted to determine the acid–base properties of colloidal ZnO. The initial pH of a 1 x 10^{-3} M aqueous suspension of ZnO colloid containing 2 x 10^{-3} M acetate (this anion is inherently present in all samples from their preparation) is 7.7 as shown in Figure 6. Titration with base promotes coagulation, while titration with acid leads to the dissolution of the colloid below pH 7.4. Figure 6 clearly shows that the pH increases upon addition of aqueous NaOH and eventually passes through an inflection point at pH 9.3 (after 45 µmol of base, i.e., 4.5 mL of a 1 x 10^{-2} M NaOH solution, have been added to 40 mL of 1 x 10^{-3} M ZnO). On the other hand, 100 µmol of HCl can be added with no pronounced change in pH, indicating a significant buffering capacity of the oxide system. Another inflection point is noted at pH 6.4. The slow drop of pH below pH 5.5 is well explained by the buffering capacity of the acetate.

Plots of the intensities of the UV (λₘₐₓ = 365 nm) and the green (λₘₐₓ = 516 or 520 nm) fluorescence as a function of the O₂ partial pressure are shown in parts a and b of Figure 7 for 3.3 x 10^{-4} M colloidal suspensions of ZnO in 2-propanol and water, respectively. While a similar qualitative behavior is observed in both cases, the fluorescence intensities of the isopropanolic arc almost 1 order of magnitude larger than those of the aqueous colloid. Only 20% of this difference is due to the higher extinction coefficient of the isopropanolic sol at the excitation wavelength.

Both fluorescence peaks are initially present in carefully evacuated samples of ZnO. Upon exposure to the weak monochromatic light of the spectrofluorometer (λₘₐₓ = 330 nm) a noticeable dynamic behavior is observed. The green emission is
Characterization of Quantum Size Zinc Oxide

Figure 5. Powder spectra of ZnO crystals: (a, upper) reflectance and (b, lower) fluorescence, λexc = 320 nm.

Figure 6. Titration curve obtained upon addition of 10⁻⁵ M HCl or 10⁻⁵ M NaOH to 40 mL of an aqueous ZnO colloid (1 × 10⁻⁵ M ZnO, 2 × 10⁻⁵ M acetate, 25 °C, air).

Figure 7. Fluorescence intensity (at equilibrium, see Results section) as a function of O₂ content: -O-, O₂/N₂ gas mixtures; X, evacuated samples. (a, upper) 3.3 × 10⁻⁴ M ZnO in 2-propanol and (b, lower) 3.3 × 10⁻⁴ M ZnO in water.

Figure 8. Fluorescence intensity as a function of the H₂O₂ concentration (3.3 × 10⁻⁴ M ZnO, evacuated samples).

The suspension remained virtually unchanged during all the experiment described in Figures 7 and 8. Even though only an estimate of the initial magnitude of the two luminescence peaks can be given due to the instrument’s limited time resolution (≈ 1 s), we are confident that they do not differ by more than 20% from the values measured in aerated samples.

Following this short preirradiation period evacuated suspensions of ZnO fluoresce predominantly at 365 nm (cf. Figure 7, X) with the intensity of this emission a factor of 3 or 7 higher than in oxygenated isopropanolic or aqueous colloids, respectively. All points given in Figure 7 represent equilibrium values measured subsequent to the initial dynamic behavior. Apparent differences between the results obtained for samples under vacuum and under N₂ can thus be explained by traces of O₂ still present in the nitrogen stream. The magnitude of the green fluorescence peak increases significantly with increasing content of molecular oxygen. In both suspensions, an O₂ concentration of 2.5% by volume is sufficient to promote 50% of the maximum intensity of the visible
emission, while at the same time the UV fluorescence intensity decreases (cf. Figure 7). In isopropanolic suspensions this decay closely matches the observed increase at \( \lambda_{em} = 516 \text{ nm} \). Air-saturated sols of ZnO in water exhibit a very weak UV emission but their 365-nm fluorescence in 2-propanol is more than 1 order of magnitude higher. Minor changes in the emission intensities are encountered between aerated and 100% oxygenated colloids of ZnO.

Addition of hydrogen peroxide also results in a green fluorescence and a lower UV emission as shown in Figure 8. However, a substantial difference in the response of the aqueous and the isopropanolic sols in the presence of H\(_2\)O\(_2\) is apparent. In the former case, addition of 5 \( \times \) 10\(^{-3}\) M H\(_2\)O\(_2\) yields 50% of the maximum intensity of the visible and suppresses half of the initial UV emission. For H\(_2\)O\(_2\) concentrations above 10\(^{-2}\) M the green fluorescence is depressed. In the case of the isopropanolic colloids, higher concentrations of H\(_2\)O\(_2\) (100-fold) are required to suppress 50% of the UV fluorescence, whereas the green emission increases slightly without reaching a limiting value.

Figure 9 shows the time-resolved decay curves of the visible emission of colloidal suspensions of ZnO where the solid lines represent a double-exponential decay according to the following formula:

\[
\frac{I(t)}{I(0)} = \frac{I_1(t)}{I_1(0)} + \frac{I_2(t)}{I_2(0)}
\]

This fit accounts for the fate of \( \approx 90\% \) of the observed emission. For a 10\(^{-3}\) M suspension of ZnO colloid in 2-propanol, 80% of the intensity decays with a characteristic time \( \tau_1 \) of 17 ns, while the remainder decays with \( \tau_2 = 190 \text{ ns} \). The aqueous suspension shows that 48% of the intensity decays with a characteristic time of 14 ns and the remainder with \( r = 140 \text{ ns} \). The data for the decay of the UV emission suggest, on the other hand, that its lifetime is less than 100 ps and probably even less than 50 ps (rise time of the photomultiplier employed in this study) in both sols. Experiments with a higher time resolution are thus required to resolve differences between the two colloidal preparations.

Table I summarizes rate constants obtained from the Stern–Volmer analysis of fluorescence quenching studies at \( \lambda_{em} = 520 \text{ nm} \) using aqueous colloidal suspensions of ZnO. Plotting \( \phi_0/\phi \) vs. the concentration of the quencher (Q) yields straight lines with slopes denoted conventionally as \( k_q \) (see second column of Table I):

\[
\phi_0/\phi = 1 + k_q c Q
\]

Taking a lifetime \( \tau \) of the visible fluorescent center of 14 ns, as obtained by the kinetic decay measurements, the bimolecular quenching constant \( k_q \) can be calculated (third column). Values between 10\(^{12}\) and 10\(^{15}\) M\(^{-1}\) s\(^{-1}\) indicate that at pH 7.7 oxidizing molecules like MnO\(_4^-\) or Cr\(_2\)O\(_7^2-\) but also nonoxidizing cations, e.g., Fe\(^{3+}\), are extremely efficient quenchers. Other cations such as Ni\(^{2+}\) or Co\(^{3+}\) also quench the green fluorescence yielding straight Stern–Volmer plots with lower bimolecular rate constants. Methylviologen (1,1'–dimethyl-4,4’-bipyridinium chloride, MV\(^{2+}\)) and Ag\(^+\) are inefficient quenchers at pH 7.7. At pH 12, quenchers which are ineffective at pH 7.7 such as MV\(^{2+}\) and Ag\(^+\) are more efficient by a factor of about 10\(^2\). Anions such as Cr\(_2\)O\(_7^2-\) and MnO\(_4^-\) which are most effective at pH 7.7 are less effective at pH 12.

When permanganate or dichromate is used as quencher a time-dependent relationship is noted. For example, 1 \( \times \) 10\(^{-4}\) M MnO\(_4^-\) is sufficient to reduce the emission intensity at 520 nm by a factor of 9 \( (1 \times \) 10\(^{-3}\) M ZnO, pH 7.7, air, \( \lambda_{em} = 330 \text{ nm} \)). Continuous illumination with a weak light source (e.g., 8 \( \times \) 10\(^{-8}\) M photons absorbed per second by the colloidal suspensions) results in a subsequent increase of the fluorescence intensity over a period of 1 min until it reaches about 75% of the intensity value it had without absorbates. Similar phenomena are observed at pH 12 or when Cr\(_2\)O\(_7^2-\) is employed instead of MnO\(_4^-\). All values reported in Table I refer to the initial emission intensities.

The optical properties of an evacuated sample of ZnO colloid are changed upon prolonged ultraviolet illumination as shown in Figure 10. The absorption and fluorescence spectra of an aerated solution of 1 \( \times \) 10\(^{-3}\) M ZnO in 2-propanol containing 2 \( \times \) 10\(^{-3}\) M acetate and 6 \( \times \) 10\(^{-6}\) M methylviologen are given as a reference (full line). The absorption spectrum of an evacuated solution which has been irradiated with 60 \( \mu\)M photons (\( \lambda_{em} = 330 \text{ nm} \)) shows the characteristic pattern of reduced methylviologen, MV\(^{2+}\),\(^{37}\) at 396 nm. However, no change is noted in the UV portion of the absorption spectrum which is characteristic for ZnO. Concurrently, the UV emission increases in intensity while the green fluorescence decreases by about 1 order of magnitude. This effect has already been described when the O\(_2\) dependence of the fluorescence was studied (Figure 7a). Further irradiation with 10 mM photons results in a shift in the absorption spectrum of \( \lambda_{em} \) from 365 to 345 nm. In addition, the blue color of MV\(^{2+}\) disappears. The new absorption pattern near 396 nm is characteristic of doubly reduced methylviologen, MV\(^{2+}\).\(^{37}\) The fluorescence spectrum of this extensively irradiated solution features only the UV emission redshifted to 368 nm. When the colloidal suspension is exposed to air the blue color of MV\(^{2+}\) reappears. After 30 s of exposure, the absorption and fluorescence spectra return to the original reference spectra with slight variations in the intensities.

**Discussion**

**Synthesis.** The results clearly show that we have been able to synthesize stable transparent solutions of colloidal ZnO suspended in either water, 2-propanol, or acetonitrile. Since the formation of zinc oxide in water is not favorable compared to the formation of Zn(OH)/\(_6\)\(^{-3}\) (vide supra) synthesis in a nonaqueous solvent was found to be necessary. Zinc acetate in the presence of 80% of the stoichiometric amount of NaOH yields the most stable

---

**Table I: Quenching of the Visible Emission of Aqueous ZnO Sols**

<table>
<thead>
<tr>
<th>Quencher</th>
<th>( k_q \times 10^{15} \text{ M}^{-1}\text{ s}^{-1} )</th>
<th>( k_q \times 10^{14} \text{ M}^{-1}\text{ s}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnO(_4^-)</td>
<td>8 ( \times ) 10(^{-3})</td>
<td>6 ( \times ) 10(^{-4})</td>
</tr>
<tr>
<td>Cr(_2)O(_7^2-)</td>
<td>3 ( \times ) 10(^{-4})</td>
<td>2 ( \times ) 10(^{-4})</td>
</tr>
<tr>
<td>Fe(^{3+})</td>
<td>2.0 ( \times ) 10(^{-4})</td>
<td>1.4 ( \times ) 10(^{-4})</td>
</tr>
<tr>
<td>Co(^{3+})</td>
<td>6.4 ( \times ) 10(^{-4})</td>
<td>4.6 ( \times ) 10(^{-4})</td>
</tr>
<tr>
<td>Fe(^{2+})</td>
<td>3.5 ( \times ) 10(^{-4})</td>
<td>2.5 ( \times ) 10(^{-4})</td>
</tr>
<tr>
<td>Zn(^{2+})</td>
<td>1.6 ( \times ) 10(^{-4})</td>
<td>1.1 ( \times ) 10(^{-4})</td>
</tr>
<tr>
<td>Ni(^{2+})</td>
<td>1.6 ( \times ) 10(^{-4})</td>
<td>1.1 ( \times ) 10(^{-4})</td>
</tr>
<tr>
<td>Cr(^{2+})</td>
<td>5.9 ( \times ) 10(^{-4})</td>
<td>4.2 ( \times ) 10(^{-4})</td>
</tr>
<tr>
<td>Mn(^{2+})</td>
<td>1.7 ( \times ) 10(^{-4})</td>
<td>1.2 ( \times ) 10(^{-4})</td>
</tr>
<tr>
<td>Mg(^{2+})</td>
<td>1 ( \times ) 10(^{-10})</td>
<td>7 ( \times ) 10(^{-10})</td>
</tr>
<tr>
<td>Mg(^{2+})</td>
<td>5 ( \times ) 10(^{-10})</td>
<td>4 ( \times ) 10(^{-10})</td>
</tr>
</tbody>
</table>

*Assuming \( r = 14 \times 10^{-9} \) s from the fluorescence decay time measurement.*
Characterization of Quantum Size Zinc Oxide


Figure 10. Effect of illumination on the spectroscopic properties of colloidal ZnO, 1 × 10^{-3} M ZnO, 2 × 10^{-4} M acetate, 6 × 10^{-4} M methylviologen, in 2-propanol, λ_{ex} = 330 nm, --, aerated, no air, ---, evacuated, 6 × 10^{-4} M H_{2}SO_{4}, ---, evacuated, 1 × 10^{-5} M H_{2}SO_{4}, 30 s air.

Figure 11. MO model for the particle growth.

where \( E_{g} \) is the bulk bandgap energy and \( m_{e} \) and \( m_{h} \) are the effective masses of the electron and hole, respectively. This equation predicts that the energy level of the first excited state increases as the cluster size \( R \) decreases. Henglein and coworkers, on the other hand, have used a semiclassical treatment\(^{16}\) and subsequently various quantum-mechanical approaches\(^{22,23}\) to predict the dependence of the onset of absorption upon particle size. They observed good qualitative agreement with experimental data in the case of CdS.\(^{22}\)

Throughout the following discussion we shall use an alternative qualitative molecular orbital (MO) picture\(^{50}\) to account for the bathochromic spectroscopic shift observed during the early growth stages of ZnO (Figure 11). It is obvious from this figure how the splitting of energetic levels into a filled and an empty region proceeds as the number of contributing MO's increases. In large particles the ensemble of energetic levels becomes dense yielding the valence and the conduction band, respectively. Since electronic transitions from the highest occupied molecular orbitals (HOMO's) to the lowest unoccupied molecular orbitals (LUMO's) yield the observed absorption spectrum the blue-shifted \( \lambda_{ex} \) is readily explained for the Q-size particles.

It is interesting to note that ZnO particles must be smaller than 50 Å before a bandgap shift becomes obvious. In a recent in-
vestigation Spanhel12 showed that TiO₂ crystallites of only 36 Å diameter still show the same αₚ as the bulk material. On the other hand, CdS particles exhibit Q-size effects until particle sizes with diameters around 80 Å are reached.22 Properties of the respective anions such as size and polarizability seem to be important factors determining the quantum size regime of a material.

Transition probabilities between the MO’s are also governed by symmetry selection rules, which become more important as the total number of orbitals decreases. This might explain the pronounced maximum structure observed in the absorption spectra of very small ZnO clusters, indicating that transitions of narrow energy distribution and high probability occur (cf. Figure 3).

**Surface Properties.** A more detailed description of the surface structure of metal oxides is useful for the better understanding of surface phenomena and for the discussion of the fluorescence behavior of our colloidal particles. In water, metal oxide surface chemistry is controlled by surface hydroxyl groups.61 The following equilibria must be considered:

\[
\begin{align*}
&\text{MOH}^+ + \text{H}^+ \rightleftharpoons \text{MOH}^2+ + \text{H}_2\text{O} \quad \text{pK}_1 \\
&\text{MOH}^+ + \text{H}^+ \rightleftharpoons \text{MO}^2+ + \text{H}_2\text{O} \quad \text{pK}_2
\end{align*}
\]

In some cases pK₁ and pK₂ values may be determined by titration. The surface chemical properties of an oxide surface are sensitive to the composition of the aqueous phase because specific adsorption or binding of molecules to the surface can occur. The surface charge together with the pH of zero point of charge (pHₚ₀ = \frac{1}{2}(pK_1 + pK_2)) are important properties of oxide particles. Besides the above-mentioned charges due to ionizable hydroxy groups, lattice imperfections and the adsorption of surface-actant ions are responsible for surface charges. Titration studies as well as experiments aimed at determining the rate of coagulation of the colloidal particles allow the determination of pHₚ₀.

The acid titration of aqueous colloidal ZnO (Figure 6) results in an estimated value for pK₁ of 7.6 ± 0.1 (flat part of the curve, reflecting the buffering capacity of the surface with similar concentrations of protonated and neutral surface groups). Under the assumption that the surface charge is due to ionized hydroxy groups (equilibria 2 and 3) a pHₚ₀ of 9.3 ± 0.2 can be derived from the inflection point indicated in Figure 6. Since specific adsorption of carbonate or acetate could have lowered the pHₚ₀—in fact, specific adsorption of impurities such as fatty acids can provoke a shift in the pHₚ₀ of more than two pH units—additional titration-coagulation experiments were performed. The coagulation rate (as determined by the rate of the sol’s turbidity increase) is expected to be a maximum at the pHₚ₀ due to surface electroneutrality. Titration studies with our aqueous ZnO sols showed that starting at pH 7.6 and titrating toward pH 11 the coagulation rate peaked at pH 9.2. These results for pHₚ₀ can be favorably compared with literature values for macrocrystalline ZnO that give a mean pHₚ₀ of 9.0 ± 0.3.32

**Fluorescence Spectra.** The luminescence maximum at 365 nm which closely coincides with the onset of absorption can be assigned as "bandgap" fluorescence caused by a transition from the lower edge of the conduction to the upper edge of the valence band. Temperature studies with bulk crystals are consistent with this interpretation.44 The name “exciton” emission has been alternatively used.44 To describe the UV band of the luminescence spectrum in terms of a quantum-mechanical picture. Similar to earlier observations for CdS 16 small (ZnO), clusters prepared in the absence of excess electrons and/or Zn⁺ centers on the particles should be minimal. Several millimoles of photons are in fact necessary to provoke such spectral shifts (cf. later part of Discussion and Figure 10).

The intensity of the UV emission increases by a factor of 3 or 7 in the absence of molecular oxygen with 2-propanol or water being the solvent, respectively. This observation cannot be explained by the proposed mechanism which would most probably invoke the quenching of both fluorescence bands by the excess e⁻ but should at least not result in an increase of the UV emission.

While a possible explanation for the influence of molecular oxygen and methylviologen on the relative fluorescence intensities could be their electron-accepting ability, this simple picture cannot be applied to explain the marked differences in sensitivity toward H₂O₂ which are observed when either water or 2-propanol is the
solvent (cf. Figure 8). A polar molecule such as hydrogen peroxide should be more strongly adsorbed to the hydrophilic ZnO surface in 2-propanol (dielectric constant $\epsilon_{2-} = 18.3$) than in $H_2O$ ($\epsilon_{2-} = 78.5$) where it nevertheless exhibits a much higher activity in promoting the visible fluorescence.

In the following we propose a mechanism to explain our observations. The main pathway of energy dissipation is a radiationless relaxation as deduced from the overall low fluorescence yield for fully developed ZnO colloids ($\phi \approx 0.03$). In the absence of electron acceptors, part of the photogenerated conduction band electrons ($e_{\text{CB}}$) can also radiatively combine with valence band holes ($h_{\text{VB}}$) giving rise to the bandgap fluorescence. However, following the careful evacuation of our samples both fluorescence bands are initially still apparent with their relative intensities being similar to those observed in the absence of air. Absorption of a few micromoles of photons ($\lambda_p \leq 365$ nm) results in the effective bleaching of the visible emission while there is a significant simultaneous increase of the UV emission (cf. Figure 7). This observation can be explained by a photodesorption of trace amounts of molecular oxygen (reaction 4). $O_2$ is known to be strongly chemisorbed to the surface of zinc oxide (probably in the form of superoxide, $O_2^-$, since an electronegative molecule such as $O_2$ readily accepts an excess electron from ZnO which is a typical n-type semiconductor) and thus cannot be removed under reduced pressure at room temperature. The concentrations of hydrogen peroxide resulting from this reaction are too small ($\leq 1 \mu M$) assuming the adsorption of one molecule of O$_2$ per ZnO particle to have a noticeable influence on the fluorescence yields (cf. Figure 8).

The significant influence of adsorbed molecular oxygen and methylviologen can then be explained by a relay action of these compounds resulting in the formation of the respective radical valence band holes (reaction 5) having giving rise to the bandgap fluorescence. However, the reaction mixture. Upon exposure to air the UV emission immediately disappeared giving rise to the broad visible fluorescence that had been observed during the original preparations (cf. Figure 3). This observation clearly supports the proposed electron relay mechanism. This is, to the very best of our knowledge, the first time that a blue-shifted bandgap fluorescence has been observed at these very early growth stages during the preparation of Q-size particles. Fojtik et al. also observed a UV emission shifted to shorter wavelengths as compared with the absorption onset of bulk crystals when they prepared small CdS particles. However, this band only appeared with an onset of the concurrent absorption spectrum of $\lambda_{\text{abs}} \geq 430$ nm; i.e., particle diameters above 25 Å had been reached. While this value corresponds to almost 200 molecules of CdS per particle, an upper limit of $d = 10$ Å (estimated from the absorption of any image in the TEM) suggests that each zinc oxide cluster contains only about 20 ZnO molecules as the UV fluorescence is observed.

Species of the bimolecular fluorescence quenching constants $k_q$ (listed in Table I) exceed the limit of diffusion-controlled reactions. We conclude that the quenching molecules are adsorbed onto the surface of the colloidal particles at the moment of excitation. This is clearly indicated by the different behavior noted at pH 7.7 and pH 12. At pH 7.7 the cations Ag$^+$, Mn$^{2+}$, and MV$^{2+}$ are poor quenchers (i.e., the ZnO surface is positively charged) whereas at pH 12 very steep Stern-Volmer plots are obtained. Anions such as MnO$_4^-$ and CrO$_7^{2-}$ are not accommodated readily on negatively charged surfaces but exhibit the highest quenching constants when positive sites are available at pH 7.7. We have in fact used this behavior as a third alternative to estimate the $k_q$ values of our aqueous colloids by performing titrations in the presence of minute amounts of the appropriate quenchers and measuring the variations in the emission intensity at 520 nm. This method yields pH-dependent $k_q$ values in agreement with the results presented above. Some cations are very efficient quenchers even at pH 7.7, e.g., Ca$^{2+}$, Cu$^{2+}$, Fe$^{3+}$, and Fe$^{2+}$, suggesting that the electrostatic interaction is not the only force governing surface adsorption. We propose an electron-transfer mechanism to account for the fluorescence quenching. Strongly oxidizing adsorbates such as MnO$_4^-$, CrO$_7^{2-}$, Fe$^{3+}$, and Ag$^+$ irreversibly accept photogenerated electrons without back donation to electron traps, whereas Fe$^{2+}$ appears to act as a hole scavenger.

A limited number of quenching experiments have also been performed with 2-propanol as the solvent resulting in $k_q$ values for the suppression of the visible emission similar to those given in Table I for the aqueous sol. However, since an aerated isopropanolic suspension of ZnO still exhibits a considerable bandgap fluorescence (cf. Figure 7a) its quenching was also studied. We noted a complete quenching of the UV emission with $k_q \approx 4 \times 10^{13}$ M$^{-1}$ s$^{-1}$ (e.g., Cu$^{2+}$) before the visible fluorescence appeared.
electrostatic model. While it describes the pronounced UV shift because the energy of the excitonic state thus leading to a blue-conductor particle suffices to create a polarizing field which in-shifted absorption spectrum.

Finally, no spectral change is observed in alkaline sus-

cceptibility. 23 These authors suggested that the finding that the bandgap emission of the illu-

duced. A blue shift of the absorption spectrum that was observed by Koch et al. when they illuminated colloidal ZnO in the absence of oxygen was originally explained on the basis of a reversible model. However, our observations cannot readily be explained by this electrostatic model. While it describes the pronounced UV shift in the absorption spectrum very well, this theory is unable to account for the finding that the bandgap emission of the illuminated solution is not blue-shifted but rather slightly red-shifted (cf. Figure 10). Furthermore, a large number of photons have to be absorbed by the sol before a shift in the absorption spectrum is observed suggesting that a considerable number of electrons, rather than only one, have to be stored per particle to yield this effect. Finally, no spectral change is observed in alkaline suspensions where a negatively charged surface should result in overall negatively charged particles, evincing that the mechanism proposed in the case of CdS cannot simply be applied to ZnO. We prefer to use the MO picture introduced above to explain the data shown in Figure 10 (analogous results were also obtained in the absence of MV^2+). Illumination of the ZnO particles results in the oxidation of acetate and/or 2-propanol. Concurrently, the e^- reduce all available electron acceptors such as chemisorbed dioxygen and methylviologen. Only a few micromoles of photons are necessary to deplete all relay compounds which originally promoted the visible emission, while the absorption band due to ZnO remained unchanged (curve --- in Figure 10). Subsequently, i.e., after the sol had been illuminated with 10 mM h_0 (curve --- in Figure 10), excess electrons start to fill the lower MO's of the conduction band as indicated schematically in Figure 12. Hence, succeeding photogenerated electrons have to reach molecular orbitals of higher energy. Since in these small colloidal particles the density of MO's in the conduction band is relatively low, a net blue shift of the absorption spectrum is the expected result. The emission, on the other hand, occurs through transitions from the lower edge of the conduction band to the upper edge of the valence band in agreement with the absence of any blue shift of the UV fluorescence. Eventually, MV^2+ is reduced to MV^0 via an intermediate MV^** as indicated by the changes in the absorption spectra. However, it is not possible to decide whether the e^- from the ZnO or the α-hydroxyalkyl radicals formed during the one-electron oxidation of 2-propanol lead to the observed formation of doubly reduced methylviologen.

Once O_2 is admitted to the system it reacts with the stored electrons and thereby restores the original spectral characteristics. Chemical reactions such as the oxidation of acetate and 2-propanol and the reduction of molecular oxygen resulted in a net chemical change in the colloidal suspension. We envisage that no spectral change would be observable under the given experimental conditions if we were able to produce zinc oxide colloids in the absence of electron donors since e^-/h^+ recombination should then be the main reaction pathway.

Even though the phrase "nonlinear optical effects" has been used to describe similar phenomena 21 a word of caution should be added at this point. Solid-state physics employs this term for completely reversible transient effects which, for example, occur in semiconductors that are irradiated with short light pulses of high intensity (e.g., laser pulses) the energy of which exceeds the bandgap energy. Hence a large number of e^-/h^+ pairs are generated which during their lifetime alter the optical absorption characteristics of the material in a nonlinear fashion. 25 However, as pointed out above, the observed spectral changes are, at least in our case, accompanied by permanent chemical changes within the illuminated system and can therefore not strictly be described by such a reversible model.

Acknowledgment. We gratefully acknowledge the financial support by the U.S. EPA (CR812356-01-0) and in particular we want to thank Dr. Marcia Dodge for her support. We appreciate extensive scientific discussions with Prof. Armin Henglein (Hahn-Meitner Institute Berlin) who also supplied a preprint of his recent work 23 thereby stimulating our ideas concerning the nonlinear optical effects. We enjoyed a very pleasant collaboration with Prof. Douglas Magde (University of California, San Diego) during the fluorescence decay studies and like to thank him and Ms. Gale Rojas for their help. D.W.B. thanks the Hahn-Meitner Instiut for granting him a leave of absence.

Registry No. MV^2+, 4685-14-7; MnO_4^-, 13333-13-2; Cr_2O_3, 11907-47-6; Fe^3+, 15438-31-0; Cu^2+, 15158-11-9; Fe^2+, 20074-52-6; Cr^3+, 16065-83-1; Zn^2+, 23713-49-7; Co^2+, 22541-53-3; Ni^2+, 14701-22-5; Mn^3+, 16397-91-4; Ag^+, 14701-21-4; Li^+, 17341-24-1; ZnO, 1314-13-2.


PREPARATION AND CHARACTERIZATION OF QUANTUM SIZE TITANIUM DIOXIDE

Preparation and Characterization of Quantum-Size Titanium Dioxide

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The syntheses of transparent colloidal solutions of extremely small titanium dioxide particles (d < 3 nm) in water, ethanol, 2-propanol, and acetonitrile are presented. Quantum-size effects are observed during particle growth and at the final stages of synthesis. They are quantitatively interpreted by using a quantum mechanical model developed by Brus. The particles prepared in aqueous solution possess the anatase structure and consist of about 200 TiO$_2$ molecules at their final growth stage. The colloidal particles can be isolated from solution as white powders that are soluble in water and ethanol with no apparent change in their properties. In organic solvents the quantum-size TiO$_2$ particles appear to form with rutile structure. Excess negative charge on the particles resulting either from deprotonated surface hydroxyl groups or from photogenerated and/or externally injected charge carriers causes a blue shift in the electronic absorption spectrum, which is explained by an electrostatic model. Electrons can be trapped in the solid as a Ti$^{2+}$ species, which has a characteristic visible absorption spectrum. As much as 10% of the available Ti$^{4+}$ ions can be reduced photochemically in the solid with a quantum yield of 3%. Molecular oxygen reoxidizes the Ti$^{2+}$ centers, leading to detectable amounts of surface-bound peroxides. The pH of zero point of charge (pH$_{ZPC}$) of the aqueous colloidal suspension has been determined to be 5.1 ± 0.2. The acid-catalyzed dissolution of the aqueous colloid yielding Ti(IV) oligomers has been studied, and an activation energy, $E_a$ = 58 ± 4 kJ/mol has been measured for this reaction. The photocatalytic activity of the small TiO$_2$ particles is demonstrated.

Introduction

Following the observations by Papavassiliou and Ekimov et al., research in the area of quantum-size semiconductor particles has intensified. Most of the quantum-size semiconductors are chalcogenides. However, zinc oxide (ZnO) has been synthesized recently in the quantum-size domain (i.e., particle diameters of d ≤ 5 nm). On the other hand, preparation of colloidal TiO$_2$ normally results in panicles exhibiting bandgap energies of the bulk solid (5 nm ≤ d ≤ 20 nm). Although Anpo et al. have prepared TiO$_2$ powders with particle diameters as small as 3.8 nm that have shown quantum-size effects, this paper describes the synthesis of titanium dioxide colloids with particle diameters d < 3 nm that exhibit typical quantum-size properties such as increasing bandgap energies with decreasing particle size and blue-shifts in the UV–vis spectrum upon charge injection. The photophysical, photochemical, and surficial properties of these TiO$_2$ quantum-size particles have been investigated and reported herein.

Experimental Procedures

Chemicals and solvents were of reagent grade and used without further purification. The water content of the organic solvents was as follows: 2-propanol (Merck, 0.05%); acetonitrile (Merck, 0.3%); ethanol (USI Chemicals, 0.1%). The water employed in all preparations was purified by a Milli-Q/RO system (Millipore) resulting in a resistivity > 18 MO cm. TiCl$_4$ (Merck) was freshly distilled prior use. P25 TiO$_2$ powder was a generous gift by the Degussa Corp.

UV–vis absorption spectra were recorded on a HP8451A diode array spectrometer and on a Shimadzu MPS-2000 instrument.

Particle sizes were determined by transmission electron microscopy (TEM). The time evolution of the absorption spectra was followed by measurement of the absorbance at 400 nm. The quantum yield of photoreduction was measured in comparison with the standard rhodamine 6G, which has a quantum yield of 1.

Quantum-Size Titanium Dioxide

measured as described previously.\(^5\)

The photocatalytic oxidation of iodide was studied by using a 450-W Xe illumination system that has been described elsewhere, but some experiments were performed with a 500-W Xe lamp. The output of this lamp was guided through a water-cooled (Pyrex window) quartz 11 band-pass filter onto 3-ml aliquots of colloid. Excitation thus occurred with light between 300 and 400 nm without heating the sample.

For the photocatalytic oxidation of iodide 2-mL samples of 5 mM TiO\(_2\) colloid containing 1 mM iodide were illuminated with 5 mM H\(_2\) at 330 nm. Iodide was determined spectrophotometrically as I\(_2\) by using (255 nm) as a reference.

The formation of I\(_2\) was monitored by adding 10 mM H\(_2\) and by maintaining the solution at pH 3-4 for the absorption measurement.

Titrations of aqueous colloidal TiO\(_2\) thermostated to 25 °C were carried out with a Radiometer autotitrator system consisting of a pH 684 pH meter, a TTT80 titrator, and a ABU80 autoburette. A vigorously stirred N\(_2\)-bubbled suspension of TiO\(_2\) colloid was titrated with freshly prepared stock solutions of NaOH (N\(_2\) bubbled) or HCl. pH readings were taken after thermodynamic equilibration of between 10 min and up to 1 h (at high pH).

The acid-catalyzed dissolution of TiO\(_2\) colloidal solution of TiO\(_2\) colloid was studied by using the flow system. At t = 0 a small amount of concentrated HCl was added to the thermostated colloid, and the decay of the absorption spectrum was recorded.

Preparation of Colloidal TiO\(_2\) in Water, 2-Propanol, Ethanol, and Acetonitrile. In a typical preparation, 1 mmol (0.11 mL) of TiCl\(_4\) (titanium tetrachloride), cooled to -20 °C, was slowly added to 200 mL of solvent (1°C) under vigorous stirring and then kept at this temperature for 3 h. This colloidal preparation was stable for days at room temperature. Powders of TiO\(_2\), colloid, which are soluble in water or ethanol, were obtained by adding 32 mmol (3.5 mL) of TiCl\(_4\) slowly to 900 mL of cold (1°C) water under vigorous stirring. The resulting colloidal suspension was stable for several hours at 5°C; however, at room temperature, precipitation of TiO\(_2\) occurred within a few hours due to high concentration and ion strength. To increase the stability of the colloid and to facilitate powder formation upon evaporation of the solvent, we reduced the ionic strength by dialyzing twice (Spectrapor membrane) against water (4 L, at room temperature) for a total of about 2 h; the final pH was 2.5. After being stored


Figure 1. Absorption spectra of TiO\(_2\) colloids at various growth stages. Obtained by hydrolysis of 5 mM TiCl\(_4\). Inset: hydrolysis of 10\(^-4\) M TiCl\(_4\) overnight at 5°C, 200-mL aliquots were dried with the aid of a rotary evaporator (ca. 25 mbar, 30°C). The residue was further dried by applying a vacuum of ca. 1 mbar for 30 s, which led to the formation of a white shiny powder (P1). Evaporation and drying also removed HCl, which could be found in a cooling trap. A transparent suspension of 0.5 g/L of this powder in water resulted in a solution with a pH of 3; the transparent colloid was stable for several days at room temperature. Rapid titration with base yielded transparent TiO\(_2\) colloids at pH 9.5-12 without any added stabilizers. TiO\(_2\) colloids at pH 7 required the addition of 2 mM phosphate for stability. Throughout this study colloids obtained by controlled hydrolysis of TiCl\(_4\) (5 mM concentration) and from dissolution of P1 powder behaved analogously.

The results of autoradiography carried out with a \(^{60}Co\) source at the Hahn-Meitner Institute.

Results and Discussion

Synthesis and Spectral Properties. Figure 1 shows the UV-vis spectra obtained during the controlled hydrolysis of titanium tetrachloride. Immediately after TiCl\(_4\) was mixed with water at 1°C the onset of absorption appears at \(\lambda_{\text{onset}} \approx 340\) nm. Upon being aged at 1°C for 3 h the absorption profile flattens slightly. No change in the spectral response of the solution was noted upon storage at 1°C for several days. Warming the suspension to 25°C results in a pronounced steepening of the absorption spectrum and a concomitant red-shift of its onset to approximately 370 nm (Figure 1). No further spectral changes are observed after 75 min at room temperature or 2 min at 75°C. Similar observations have been made during the growth of zinc oxide particles in colloidal solution and are interpreted in terms of the quantum-size effect.\(^6\) The formation of TiO\(_2\) colloids at pH 9.5-12 without any added stabilizers. TiO\(_2\) colloids at pH 7 required the addition of 2 mM phosphate for stability. Throughout this study colloids obtained by controlled hydrolysis of TiCl\(_4\) (5 mM concentration) and from dissolution of P1 powder behaved analogously.

The quantum-size effect is described by the equation

\[ \text{TiCl}_4 + 2\text{H}_2\text{O} \rightarrow \text{TiO}_2 + 4\text{H}^+ + 4\text{Cl}^- \]

(1)

(22) Bahmann, D. W.; Hoffmann, M. R. to be submitted for publication in Langmuir.
will be shown in detail, titanium dioxide surfaces exhibit analogous properties.

Further evidence that the spectral changes occurring during the aging of an aqueous TiCl₄ solution are indeed due to particle growth rather than to concentration effects stems from detailed spectral studies of dilute preparations. As shown in the inset in Figure 1, the absorption spectrum of an aqueous solution containing 10⁴ M TiCl₄ does not exhibit Lambert-Beer behavior during the aging process as would be expected for a concentration increase of the absorbing species. In this case the absorption increases considerably at longer wavelengths, while it simultaneously decreases at wavelengths below 240 nm. Thus, the resulting red-shifted spectrum suggests particle growth in the colloidal solution. Absolute particle sizes of the TiO₂ colloids have been determined at various stages of growth by using TEM. The mean diameter of the fully grown colloid (right curve of Figure 1) was found to be 2.4 nm, while the particles aged for 12 min at 25 °C were 2.0 nm in diameter. This change in size corresponds to agglomeration numbers of about 100, and 120, respectively, that were determined by assuming spherical geometry and a density corresponding to that of anatase (ρ = 3.9 g cm⁻³). Experimental limitations (i.e., the resolution of the electron microscope and the rather low contrast of TiO₂) did not allow unambiguous determination of particle sizes from samples exhibiting even larger spectral blue-shifts. The ΔEₐ of approximately 30 nm corresponds to a bandgap shift of 250 meV. Under the experimental conditions of this study TiO₂ particle growth stops with cluster sizes of close to 200 molecules, whereas bandgap shifts to 1 eV and quantum-size effects up to agglomeration numbers of ~3000 have recently been observed for ZnO colloids. Hence, it is apparent that titanium dioxide particles consisting of a few hundred TiO₂ molecules should exhibit quantum-size effects.

It has recently been shown that lattice planes in small semiconductor particles can be visualized when electron microscopy is coupled with an opalization technique. Indeed, we observe well-resolved lattice planes in TEM pictures even when particle diameters of only 2 nm are measured. Lattice plane distances of 3.7 ± 0.4 Å show that our synthesis has resulted in the formation of anatase titanium dioxide.

Water-soluble white powders, P₃, can be obtained from those TiO₂ preparations with a fully developed spectrum, i.e., maximum particle size under the conditions of hydrolysis as described in the Experimental Section. TEM data show that analyzing the colloid does not change the particle diameters appreciably. Figure 2 shows a plot of ln α versus the photon energy, E = hν⁻¹, for a colloidal solution of P₁ in comparison with a solution of the powder (P₃) obtained by hydrolysis of titanium tetrakisopropoxide. The absorption coefficient α has been calculated from the measured absorbance (A) via

\[
α = \frac{2.303Aλ}{εcMλ}
\]

where ε = 3.9 g cm⁻³ is the density, M = 79.9 g mol⁻¹ is the molecular weight, c is the molar concentration of TiO₂, and λ is the optical path length.

Taking the linear portion of both curves between ln α = 7 and ln α = 10 and assuming that P₃ possesses the bandgap of bulk anatase (Eₐ = 3.2 eV at ln α = 6.5), a 150-meV shift of the bandgap of P₁ to Eₐ = 3.35 eV is evident. Urbach's rule suggests using values between ln α = 6 and 10 for the determination of semiconductor bandgaps. While this method of data analysis is common practice in solid-state sciences, bandgap positions of colloidal semiconductors have mostly been determined from UV-vis spectra at arbitrarily chosen concentrations. Taking the spectrum of the aged colloid at 5 mM concentration (Figure 1, 75-120 min), an absorption onset of 370 nm or 3.35 eV is noted, in good agreement with P₁ in Figure 2. However, if the spectrum of the diluted colloid (10⁻⁴ M, inset of Figure 1, 4 min, 75 °C) were inspected accordingly, λₐ = 350 nm or Eₐ = 3.5 eV would follow. Neither variation of the concentration nor replacement of P₁ by the aged nondialyzed colloid has any effect on the curve shown in Figure 2 for P₁. Therefore, we can conclude that the described synthesis yields a TiO₂ colloid with particle sizes small enough to result in a bandgap shift of 0.15 eV relative to bulk anatase TiO₂.

Reversible Spectral Shifts. It has recently been observed that the absorption spectrum of quantum-size semiconductor particles,
e.g., ZnO and CdS, can be shifted toward shorter wavelengths by the injection of excess negative charges and molecular orbital models have been proposed to explain this so-called nonlinear optical behavior. Since the overall charge of an oxide particle in aqueous solution can also be changed by a variation of pH, i.e., a change of the relative amount of protonated and deprotonated surface hydroxyl groups (vide infra), it was interesting to study the effect of pH on the absorption spectra of the TiO$_2$ solutions. As shown in Figure 3, a reversible blue-shift of the spectrum of P1 by almost 50 meV is observed upon titration from pH 2 to 12. Similar experiments with a solution prepared from P2 (identical concentration: 1 mM) show qualitatively analogous results, but the shift amounts to less than 15 meV (cf. Figure 3). Note again the blue-shifted spectrum of P1. The spectral shifts shown in Figure 3 are explained by using the electrostatic model proposed by Henglein et al. Excess negative charges introduced by an increasingly higher concentration of surface O" groups as the pH of the solution changes from 2 to 12 (cf. eq 12 and 13) create a polarizing field within the particle. This in turn results in an energy increase of the excitonic state and thus a blue-shift in the absorption spectrum.

Figure 4 shows the spectral response of two different titanium dioxide colloids in ethanolic solution upon bandgap illumination. It is obvious from Figure 4a that an intense blue color develops when a 10 mM solution of P1 is illuminated in the absence of oxygen. Simultaneously, a blue-shift of the electronic spectrum of the semiconductor is noted. Both effects are completely reversible when air is admitted into the sample. No change in the absorption spectrum is noted when anoxic solutions of P1 are illuminated in the absence of added hole scavengers. The formation of blue color in TiO$_2$ colloids has already been reported in photochemical and radiation chemical studies, while no spectral blue-shifts were observed. The former was attributed to the generation of Ti$^{3+}$ species within the colloidal particle via

$$\text{TiO}_2 \rightarrow \text{TiO}_2(\text{h}_\text{a}^-, \text{e}_\text{a}^-)$$

(5)

$$\text{C}_3\text{H}_7\text{OH} + \text{h}_\text{a}^+ \rightarrow \text{CH}_3\text{CHOH} + \text{H}^+$$

(6)

$$\text{TiO}_2(\text{e}_\text{a}^-) \rightarrow \text{TiO}_2(\text{Ti}^{3+})$$

(7)

Alternatively, reducing radicals, e.g., $\alpha$-hydroxalkyl radicals, generated by $\gamma$-radiolysis of the ethanolic solution can also react with the colloid:

$$\text{C}_3\text{H}_7\text{OH} \rightarrow \text{CH}_3\text{CHOH}$$

(8)

$$\text{TiO}_2 + \text{CH}_3\text{CHOH} \rightarrow \text{TiO}_2(\text{Ti}^{3+}) + \text{CH}_4\text{CHO} + \text{H}^+$$

(9)

Reaction (9) can also occur in the photochemical system following (6) and thus leads to a current-doubling effect. We also observe the formation of a blue color and a concomitant blue-shift of the absorption edge in the UV upon $\gamma$-radiolysis of ethanolic P1 solutions (10 mM P1 in ethanol, anoxic, 2 $\times$ 10$^5$ rad). Two different extinction coefficients have been reported for the blue

$$\phi \approx 6 \times 10^{-4} \text{ M}^{-1} \text{ cm}^{-1}$$

$$\phi \approx 8 \times 10^{-4} \text{ M}^{-1} \text{ cm}^{-1}$$

(10)

(11)

(12)

(13)

(14)

(15)

(16)

(17)

(18)

(19)

(20)

(21)

(22)

(23)

(24)

(25)

(26)

(27)

(28)

(29)

(30)

(31)

(32)
electrons, $e_{cb-\cdot}$ with oxygen as follows:

$$\text{TiO}_2(\text{Ti}^3+) + O_2 \rightarrow \text{TiO}_2\text{-O}_2^{-}$$  \hspace{1cm} (10)

$$\text{TiO}_2(\text{e}_{cb-\cdot}) + O_2 \rightarrow \text{TiO}_2\text{-O}_2^{-}$$  \hspace{1cm} (11)

In the case of P1 particles, the superoxide radicals subsequently undergo rapid decay reactions, while the yellow color of the illuminated P2 particles is indicative of surface-adsorbed peroxide species on the colloid made in ethanol. The titanyl-peroxide reaction yielding a yellow complex is a well-established method for the quantitative analysis of $\text{H}_2\text{O}_2$, and it has been shown that $\mu$-peroxo complexes on $\text{TiO}_2$ surfaces are formed upon light adsorption of $\text{O}_2$. In our case, reducing equivalents are stored on the semiconductor particles and enable a subsequent thermal reaction to form such peroxy complexes.

The colloid resulting from hydrolyzing $\text{TiCl}_4$ in ethanol is characterized by an absorption edge in the UV that starts already at 400 nm (cf. Figure 4B); on TEM images no particles could be detected. The hydrolysis of $\text{TiCl}_4$ in other organic solvents such as 2-propanol or acetonitrile that have not been thoroughly dried yields colloids with similar red-shifted absorption spectra. For comparison, the onset of absorption of P1 and P2 anatase $\text{TiO}_2$ colloid occurs at 370 and 385 nm, respectively. Therefore, we suggest that the hydrolysis of $\text{TiCl}_4$ in these organic solvents results in the formation of rutile $\text{TiO}_2$ as this material has a smaller bandgap: $E_g = 3.0$ eV, corresponding to an onset of absorption at $\lambda_{on} = 415$ nm. From the actual observed spectrum, which is blue-shifted by 100 meV, a particle size of $\approx 2.5$ nm is calculated, using the material constants cited above (vide supra).

### Surface Properties

Acid-base titrations as well as coagulation studies were carried out to characterize the surface properties of the oxide particles. An oxide surface is described by acid-base equilibria involving surface hydroxyl groups:35

$$\text{MOH}^+ + \text{H}^+ \rightarrow \text{MOH}^2$$  \hspace{1cm} (12)

$$\text{MOH}^- + \text{H}^+ \rightarrow \text{MOH}^0$$  \hspace{1cm} (13)

The pH of zero point of charge is given by

$$\text{pH}_{\text{zpc}} = \frac{1}{2}(pK_1 + pK_2)$$  \hspace{1cm} (14)

Literature values for the $\text{pH}_{\text{zpc}}$ for bulk $\text{TiO}_2$ powder24 and colloid19 range between 3.5 and 6.7.

![Figure 5](image-url)  
**Figure 5.** Titration curve of 20 mM $\text{TiO}_2$ colloid (P1) yielding the pH of zero point of charge (arrow), ionic strength $= 10$ mM. Insets: absorption changes at $\lambda = 600$ nm during the course of a titration. (a) Slow titration of 100 ml of 0.5 mM P1 with 1 mM NaOH (0.5 mM min$^{-1}$). The arrow indicates the point where the coagulation rate is highest. (b) Fast titration of 100 ml of 1 mM P1 with 10 mM NaOH (1 mM min$^{-1}$).

Two approaches were chosen to determine the $\text{pH}_{\text{zpc}}$ of $\text{TiO}_2$ colloid (P1). From the inflection point of a titration curve (Figure 5, arrow), obtained by titrating a concentrated suspension of colloid, a value of $\text{pH}_{\text{zpc}} 5.0$ is inferred.

In addition titration-coagulation studies were carried out. The coagulation rate—ass derived from absorption changes at 600 nm (see insets of Figure 5)—passes through a maximum as the $\text{pH}_{\text{zpc}}$ is reached. At 600 nm an increasing absorption stems only from back scattering of light from larger particles while there is no interference due to electronic transitions. The pH values at which the coagulation rate is a maximum (inset a of Figure 5, arrow) differ slightly when an acid colloid is slowly titrated with base or when an alkaline colloid is titrated with acid. This is expected since coagulation of the particles starts before the $\text{pH}_{\text{zpc}}$ is attained. The average value of both titrations yields $\text{pH}_{\text{zpc}} 5.1$.

The effect of a fast titration is shown in inset b of Figure 5. Again, the maximum coagulation rate is observed at pH 5.0. In this case the surface charge is reversed so rapidly that some of the loosely agglomerated particles are redispersed above pH 5.7 and an absorbance decrease is noted. Thus, very fast titration is a method to prepare transparent colloids on both sides of the $\text{pH}_{\text{zpc}}$.

$\text{TiO}_2$ colloids can be dissolved readily at low pH. Figure 6 shows how the absorption spectrum of a suspension of $4 \times 10^{-4}$ M $\text{TiO}_2$ colloid decays when 0.1 M of HCl is added rapidly. The residual (stable) spectrum observed after long reaction times is ascribed to $\text{Ti(IV)}$ oligomers that have been previously found under similar pH conditions.37 The absorption decay at 235 nm has been analyzed in terms of first-order kinetics, i.e., $\ln (A - A_0) = -kt$, and good fits ($R^2 \geq 0.99$) are obtained over at least 2 half-lives.

![Figure 6](image-url)  
**Figure 6.** Acid-catalyzed dissolution of $\text{TiO}_2$ colloid. The dissolution of a preparation of $4 \times 10^{-4}$ M $\text{TiO}_2$ colloid is started by rapidly changing the pH to 1 at $t = 0$ min. Inset: Arrhenius plot of rate constants obtained from first-order decay of $4 \times 10^{-4}$ M, pH 1, $E_a = 58 \pm 4$ kJ mol$^{-1}$, $R^2 = 0.98$.

![Figure 7](image-url)  
**Figure 7.** Photocatalytic oxidation of iodide on $\text{TiO}_2$ colloids, $[\text{P}1] = 5$ mM, $[\text{I}^-] = 1$ mM, air, $t_{\text{exposure}} = 5$ mJ. (a) P1; (b) P2; (c) without colloid.

Two approaches were chosen to determine the $\text{pH}_{\text{zpc}}$ of $\text{TiO}_2$ colloid (P1). From the inflection point of a titration curve (Figure 5, arrow), obtained by titrating a concentrated suspension of colloid, a value of $\text{pH}_{\text{zpc}} 5.0$ is inferred.
An Arrhenius plot of the rate constants $k$ (inset of Figure 6) yields an activation energy for the dissolution of TiO$_2$ colloid (P1) of $E_a = 58 \pm 4$ kJ mol$^{-1}$. From the observation that the spectrum decays but does not blue-shift, we conclude that the rate-determining step of this dissolution is the initial attack of the crystallites by protons. Further degradation of smaller particles appears to proceed quickly. It is interesting to note that TiO$_2$ powder (P25, $2.5 \times 10^{-4}$ M) does not dissolve at pH 1, even under drastic conditions (i.e., refluxing for 3 h).

Figure 7 shows the oxidation of iodide by photogenerated holes in air-saturated suspensions of TiO$_2$ colloids (P1 and P2) that have been illuminated with 5 mM photons at 330 nm. Quantum yields for the oxidation are given as a function of pH. As is obvious from the plot oxidation of I$^-$ (eq 15) occurs only in the acid pH domain. Virtually no iodine or iodate is formed at pH $>7$. We conclude that I$^-$ has to be adsorbed to the positively charged surface such that efficient hole scavenging can occur. The quantum yields shown in Figure 7 compare with a value of $\approx 2\%$ reported previously by Herrmann and Pichat, who illuminated a suspension of P25 TiO$_2$ powder at pH 0 ([I$^-$] = 10 mM) with UV light (300-400 nm); note, however, that at the low pH of their study the rate of the homogeneous oxidation of I$^-$ (i.e., without TiO$_2$) is considerable (cf. Figure 7).

**Summary**

We have shown that controlled hydrolysis of TiCl$_4$ yields extremely small quantum-size TiO$_2$ particles ($d < 3$ nm, pH$_{pzc} 5.1 \pm 0.2$) that possess anatase structure when prepared in aqueous solution. Excess negative charges created either by charge injection into the conduction band or by deprotonated surface hydroxyl groups lead to a blue-shift in the optical absorption spectrum of the transparent colloidal solution, which is understood in terms of an electrostatic model. Bandgap illumination of the semiconducting material results in the formation of blue Ti$^{3+}$ centers under anoxic conditions with a quantum yield of 3%. The photocatalytic properties of the particles have been further demonstrated by the oxidation of I$^-$; the marked pH dependence of the quantum yield of this process reveals that surface adsorption of iodide ions is a prerequisite for iodine formation.

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**Registry No.** TiO$_2$, 13463-67-7; HCl, 7647-01-0; I$, 20461-35-5; TiCl$_4$, 7550-45-0; Ti, 7440-32-6.
Chapter 4

PHOTOCATALYTIC PRODUCTION OF $\text{H}_2\text{O}_2$ AND ORGANIC PEROXIDES
IN AQUEOUS SUSPENSIONS OF $\text{TiO}_2$, $\text{ZnO}$, AND DESERT SAND

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Photocatalytic Production of H$_2$O$_2$ and Organic Peroxides in Aqueous Suspensions of TiO$_2$, ZnO, and Desert Sand

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The formation of H$_2$O$_2$ and organic peroxides in illuminated aqueous suspensions of ZnO, TiO$_2$, and desert sand in the presence of O$_2$ and organic electron donors has been studied. The photocatalytic rate of formation of H$_2$O$_2$ on ZnO was shown to depend on the O$_2$ partial pressure, on the concentration of organic electron donors, and on the concentration of H$_2$O$_2$. During the initial phase of irradiation the rate production of H$_2$O$_2$ is given by

$$\frac{d[H_2O_2]}{dt} = (\Phi_0 - \Phi_1[H_2O_2]) \frac{d[hv]}{dt}$$

where $\Phi_0$ is the quantum yield for H$_2$O$_2$ formation, $\Phi_1$ is the quantum yield for H$_2$O$_2$ degradation, and $d[hv]/dt$ is the photon flux. The steady-state concentration of H$_2$O$_2$ was shown to be independent of the absorbed photon flux as predicted by the above equation; $[H_2O_2]_{ss} = \Phi_0/\Phi_1$. Steady-state concentrations of H$_2$O$_2$ in excess of 100 $\mu$M were obtained in illuminated suspensions of ZnO. In the case of ZnO, the quantum yield for H$_2$O$_2$ formation, $\Phi_0$, approached 15% at 350 nm, whereas the photodegradation reactions were relatively insensitive. On the other hand, $\Phi_0$ for TiO$_2$ (1% at 350 nm) was found to be an order of magnitude less than the value for ZnO. $\Phi_0$ for a sample of desert sand (Death Valley, CA) was found to be $10^{-4}$. Photooxidation of acetate and other organic electron donors on colloidal ZnO has been shown to produce substantial concentrations of organic peroxides, ROOH. Illumination of ZnO suspensions containing acetate produced greater than 40% of the measured total peroxide (H$_2$O$_2$ and ROOH) as ROOH.

Introduction

Overview. Hydrogen peroxide, H$_2$O$_2$, is the most effective oxidant of S(IV) in haze aerosols, clouds, and hydrometeors at low pH (1). Oxidation of S(IV) by H$_2$O$_2$ appears to be the major pathway for the formation of sulfuric acid in humid atmospheres (2-4).

In 1874, Schöne reported that H$_2$O$_2$ was present in rainwater (5). Since then, hydrogen peroxide concentrations as high as 60 $\mu$M in rainwater and 250 $\mu$M for cloudwater samples have been reported (6-8). Gas-phase concentrations in the range of 1-30 ppb have been predicted (9, 10), while concentrations in the range of 0.2-4.1 ppb have been measured by Heikes et al. (11) in the lower troposphere over the eastern United States. Measurements of H$_2$O$_2$ in polar ice samples clearly show that H$_2$O$_2$ was abundant in the atmosphere for more than 1000 years (12). Hydrogen peroxide can be generated in the gas phase due to the combination of hydroperoxyl radicals, HO$_2$ (13), at the air-water interface due to photoinduced redox processes (8) and in the aqueous phase via photocatalyzed reactions with humic/fulvic acid and green algae as mediators (14-16). Furthermore, HO$_2$ radicals that are produced in the gas phase can be scavenged by the water droplets where they then form H$_2$O$_2$. In situ generation of hydrogen peroxide together with H$_2$O$_2$ scavenged from the gas phase is thought to be the main source for the H$_2$O$_2$ accumulated in cloudwater droplets (13, 17, 18).

In addition to these pathways for H$_2$O$_2$ formation several other mechanisms are possible. For example, many metal oxides, some of which are abundant in the environment, have been shown to act as photocatalysts for a wide variety of reactions (19) such as the photoassisted reduction of N$_2$ to NH$_3$ (20). Atmospheric particulate matter originates mainly from natural sources (720-1850 Tg yr$^{-1}$ in 1979 globally) but also from man-made emissions (125-385 Tg yr$^{-1}$ in 1982 in the U.S.) with iron, titanium, and zinc being some of the most abundant transition metals detected in ambient samples (21).

Organic peroxides constitute another very important group of potential environmental oxidants. They have been detected in surface waters (22), on pine needles (23), and in rainwater and cloudwater (7). While their formation in the atmosphere has been established (9, 24), there are few reports in the literature of their formation in the aqueous phase (14). Recent review articles clearly indicate that mechanistic and quantitative aspects of the appropriate photochemical processes occurring in natural waters are still far from being understood (25-26).

Background. Many metal chalcogenides and oxides are known to be semiconductors. These materials can act as sensitizers for light-induced redox processes due to their electronic structure consisting of a valence band with filled molecular orbitals (MO’s) and a conduction band with empty MO’s. A conduction band with empty MO’s can act as reductants (35-37). For a broad range of semiconductors and pH, the redox potential of the e$_{aq}$ $-$ varies from +0.5 to -1.5 V [vs normal hydrogen electrode (NHE)] and that of the h$_{aq}^+$ from 1.0 to >3.5 V. This wide range of redox potentials fully covers the redox chemistry of the H$_2$O/O$_2$ system (38).

H$_2$O$_2$ can be formed either by the reduction of O$_2$ by e$_{aq}^-$ or by the oxidation of H$_2$O by h$_{aq}^+$:

$$O_2 + 2e_{aq}^- + 2H_2O \rightarrow H_2O_2$$

(2)

$$2H_2O + 2h_{aq}^+ \rightarrow H_2O_2 + 2H_2^+$$

(3)

Photoassisted dioxygen reduction has been studied in great detail (39-46) since Baur and Neuweiler (39) in 1927 observed the formation of H$_2$O$_2$ when they illuminated aqueous zinc oxide suspensions in the presence of gycerin and glucose. Appreciable yields of hydrogen peroxide are detected only when appropriate electron donors D are added prior to illumination. The electron donor D, which must be adsorbed on the particle surface, reacts with the valence band hole:

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D + hν → D⁺

(4)

Electron donors bound to the surface of the semiconductor particles interfere with e⁻/h⁺ recombination allowing e⁻ (conduction band electrons) to react with molecular oxygen via reaction 2. Calvert et al. (42) have shown that H₂O₂ formed in irradiated suspensions of ZnO contained oxygen atoms derived exclusively from O₂. Cadmium sulfide, CdS, and ZnO showed the highest catalytic activity for dioxygen reduction (43, 44), while TiO₂ has been reported to have negligible activity with respect to H₂O₂ production (43, 45-47). The oxidation of water via eq 3, however, has not yet been demonstrated unambiguously. For example, Rao et al. (49) reported on the formation of H₂O₂ during photolysis of aqueous suspension of ZnO and TiO₂, while Salvador and Decker (50) were unable to verify this observation. The intermediate production of H₂O₂ as the first molecular step of the four-hole oxidation of water to dioxygen has been predicted (50, 51), and a variety of free radical intermediates has been detected (52-54). However, when the oxidation of H₂O proceeds with high yields, there is little evidence of hydrogen peroxide formation (55-56). In addition to photocatalytically forming hydrogen peroxide, stable hydroperoxides may form as a byproduct of the photooxidation of organic electron donors or by the nucleophilic addition of H₂O₂ to RCHO to yield alkyl hydroperoxides (59).

The above discussion indicates that a detailed study of the mechanism of the light-induced hydrogen peroxide production on various oxide surfaces is warranted in order to determine the viability of these pathways in environmental systems. Hence, our research has been focused on the kinetics and mechanisms of the formation of H₂O₂ and organic peroxides in irradiated suspensions of metal oxides and naturally occurring aluminum silicate mineral matrices such as desert sands.

**Experimental Section**

**Materials.** Titanium dioxide was obtained from Degussa (P25); it had a Brunauer-Emmett-Teller (BET) surface area of 50 ± 15 m² g⁻¹ and an average particle diameter of 30 nm (60). Suspensions of 0.5 g L⁻¹ (pH 4) were freshly prepared by sonication. This concentration resulted in an absorption of more than 95% of the incident photons at 330 nm. Transparent ZnO colloids with an average particle diameter of 5 nm were prepared as described previously (61). Suspensions of desert sand (Death Valley, dunes near Stovepipe Wells) were purified by a sequence of acidic leachings and centrifugations (4 × 0.1 N H₂SO₄, 0.05 M HF, 1 × 0.1 M HNO₃, and at least 3 × H₂O) in order to remove (photoinactive) carbonates, to oxidize trace organic materials, and to leach the more soluble cations that may be active in degrading H₂O₂ (such as traces of Fe³⁺ ions). In fact, a considerable amount of magnetite (Fe₃O₄, black dust) could be retrieved with the aid of a stirring bar from the suspension prior to this procedure. p-Hydroxyphenylacetic acid (POPHA) (Kodak) was recrystallized twice from water. All other chemicals were of reagent grade and used without further purification. The water employed in all preparations was purified by a Milli-Q/RO system with an attached OD-GANEX-Q unit; the resulting water had a resistivity of >18 MΩ cm.

**Apparatus.** The irradiation apparatus consisted of an Oram XBO 450W xenon lamp in a Müller LX 1450-2 lamp housing and a GM 252 (Kratos) monochromator. An additional 300-nm UV cutoff filter was placed at the monochromator outlet. The collimated beam of ~1.6 cm² cross section was focused onto quartz irradiation vessels (3-16 mL) that were equipped with a small Teflon stirring bar and were bubbled with air (TiO₂) or calibrated O₂/N₂ mixtures (ZnO) to ensure constant O₂ content and to keep particles in suspension. In general, samples were bubbled at least 10 min before illumination. Actinometry was performed with (E)-2-(1-(2,5-dimethyl-3-furyl)-ethylidene)-3-isopropylidenesuccinic anhydride in toluene according to the method of Heller (62) yielding I = (50-1200) × 10⁻⁶ M h⁻¹ min⁻¹, depending on the reaction volume and the monochromator exit slit. Reaction temperatures were 24 ± 1 °C. TiO₂ suspensions were irradiated at 350 nm, which corresponds to an energy that is above the bandgap of TiO₂ (3 eV) (63). ZnO colloids were illuminated at 320 and 330 nm, i.e., energies that lie above the bandgap energy for the material (3.4 eV) (61). For colloidal suspensions the amount of photons absorbed could be calculated accurately from the absorption spectrum of the colloid and the actinometry.

Fluorescence spectra were measured on a Shimadzu RF-540, whereas absorption spectra were measured on a HP8451A instrument. UV filters were used when appropriate.

**Analysis.** Hydrogen peroxide concentrations were determined by three different methods. A polarographic technique allowed the in situ measurement of H₂O₂ with a sensitivity of 10⁻⁶ M and a time constant of 1 s (YSI-Clark 2510 oxidase probe connected to a YSI Model 25 oxidase meter). The electron donor was calibrated following each kinetic experiment by standard additions of H₂O₂. The second method, sensitive to ~2 × 10⁻⁴ M H₂O₂, involved determination of p-hydroxyphenylacetic acid (POPHA) in the presence of H₂O₂ and horseradish peroxidase to yield a detectable fluorescent product (λₑₓ = 315 nm, λₑᵢₘ = 406 nm) (64). Aliquots (2 mL) of the irradiated P25 suspensions were rapidly filtered through 0.2-µm HPLC filters (Gelman Sciences) to 0.1-0.5 mL amounts of PHA reagent (8.0 ± 0.1 mg of POPHA, 2.0 ± 0.1 mg of peroxidase, and 50 mL 0.1 M pH 8.8 Tris buffer). Calibration was performed again by standard additions of H₂O₂ to the mixture and was found to be linear in the concentration ranges of interest. A reproducible background fluorescence, which we attribute to reagent impurities, amounted to ~10⁻⁴ M H₂O₂.

Stock solutions of H₂O₂ were calibrated iodometrically by eq 5: (52 nm) = 26 400 M⁻¹ cm⁻¹ (65, 66). The iodide method (detection limit of ~10⁻⁵ M) allows one to distinguish between H₂O₂ and organic peroxides since the latter react more slowly with the molybdenum-iodide system. Aliquots (1.5 mL) of P25 suspensions were filtered, and then 0.75 mL of 0.1 M potassium biphthalate was added. At t = 0 min, 0.75 mL of iodide reagent (0.4 M potassium iodide, 0.06 M NaOH, 1 × 10⁻⁴ M ammonium molybdate) was added, and the absorbance vs time profile was recorded. Addition of the biphthalate buffer to ZnO colloids led to the dissolution of the colloid; this result was desirable in that it eliminated the absorbance interference of colloid. No interference due to the presence of 10⁻⁵ M zinc ions was observed.

**Results**

Before the actual experimental results are presented, we wish to compare the different analytical techniques that were employed for the determination of inorganic and organic peroxides. The PHA fluorescence technique responds to both H₂O₂ and organic peroxides, whereas the polarographic method only detects H₂O₂. A typical result for the iodide method is given in Figure 1, which shows an absorbance (λ = 352 nm) vs time profile for an aerated suspension of TiO₂ following the absorption of 2.8 × 10⁻⁴
of 1- is noted within 30 s, followed by a further slow increase that eventually levels off at long (≈1 h) reaction times. Hydrogen peroxide reacts substantially faster than I- than does ROOH (59). These results show that more than 40% of the total peroxide formed during acetate oxidation is ROOH. The evolution of the absorbance at 352 nm, which is due to the faster reacting H2O2, is complete within 30 s. A slight reproducible color increase due to autoxidation (i.e., reaction with O2) of I- is noted over prolonged reaction time (≈1 h). Suspensions of TiO2 with 3 × 10^{-5} M acetate in dark controls result in a very low absorption increase due to the nonphotolytic autoxidation of I-. Figure 2 illustrates the formation of organic peroxides on ZnO colloids. It shows the "slow" part of color evolution of the I2+ ion that is observed when I- is oxidized by organic peroxides. This plot is corrected for the absorption increase due to the autoxidation of I- (e.g., less than 10% of the total absorption after 1 h). The amount of H2O2 formed is calculated from the I2+ formed within the first 2 min of reaction, while the concentration of total peroxide is derived from the absorbance after 2 h when the absorption increases are due solely to the autoxidation of I-. Figure 3 shows the H2O2 concentration vs illumination time profile for an aerated suspension of TiO2 particles irradiated with UV light (350 nm) in the presence of acetate. From the initial slope of this plot a quantum yield of 1% is calculated for the formation of H2O2. When a H2O2 concentration of ≈1 μM is reached, the increase levels off. The solid line represents a fit according to a simple rate expression (eq 9) that will be discussed below.

Figure 4 shows an analogous profile for an irradiated (320 nm) suspension of ZnO colloid. The quantum yield determined from the initial slope is 10%. The production of H2O2 is linear (i.e., zero order) over a wide concentration range (up to 60 μM).

The use of the iodide method is appropriate to probe the higher peroxide concentration range as is shown in Figure 5 for an aerated sample of ZnO (λmax = 390 nm). At higher H2O2 concentrations, the initial slope decreases, and a steady state is attained. The solid line represents a fit according to the mechanism given in the discussion.

Figure 6 shows an increase in the yield of total peroxide with an increase in acetate concentration in a suspension of TiO2 with a fixed amount of adsorbed photons (i.e., 1.2 × 10^{-5} M). In the absence of acetate, more than 2 × 10^{-7} M of peroxide is formed during illumination. Small amounts (3 × 10^{-5} M) of added acetate strongly enhance the peroxide yield. A kinetic analysis of the H2O2 evolution (using the polarographic method) shows that for acetate

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**Figure 1.** Detection of peroxides by the iodide method (RO2H + 2I- + 2H+ --> RO2 + I2). (---) Suspensions of TiO2 (0.5 g/L), 30 mM acetate, air, illuminated with 2.8 μmol photons (λmax = 350 nm). (••••) 5 μM standard addition of H2O2 to a suspension of TiO2 of identical composition kept in the dark.

**Figure 2.** Detection of organic peroxides (iodide method) in a suspension of ZnO colloid (1 mM) that has been illuminated with 5.5 μmol photons (330 nm); [acetate] = 2 mM, pH 7.7, O2 bubbled.

**Figure 3.** Hydrogen peroxide formation as function of illumination time in a suspension of 0.5 g/L TiO2 (P25); [acetate] = 10 mM, air, λmax = 350 nm, I = 4.7 × 10^{-1} M photons per min. (+) Polarographic detection; (---) mathematical fit obtained by integration of eq 9 with the data of Table I.

**Figure 4.** Hydrogen peroxide formation on colloidal ZnO (1 mM); [acetate] = 2 mM, pH 7.7, O2 bubbled, λmax = 320 nm, quantum yield = 10% (polarographic detection).

**Figure 5.** Hydrogen peroxide formation as function of illumination time in a suspension of ZnO colloid (1 mM); [acetate] = 2 mM, pH 7.7, air, λmax = 330 nm, I = 3.4 × 10^{-2} M photons per min. (+) Two different batches of colloid. Detection by iodide method. (---) Mathematical fit obtained as described for Figure 3.
concentration in the initial phase of irradiation a quantum yield of more than 15% was reached. In this case, the yield of organic peroxides is comparable to the yield of \( \text{H}_2\text{O}_2 \) at higher 2-propanol concentrations. Overall quantum yields of more than 15% are obtained.

The yield of hydrogen peroxide as a function of \([\text{O}_3]\) in illuminated suspensions of ZnO colloid is illustrated in Figure 8. At an oxygen concentration that corresponds to the \([\text{O}_3]\) content in air, a limiting value for the quantum yield of \( \text{H}_2\text{O}_2 \) formation is reached. Minute amounts of \( \text{H}_2\text{O}_2 \) were observed in samples purged with \( \text{N}_2 \), but the \( \text{H}_2\text{O}_2 \) yield increased sharply upon introduction of \( \text{O}_3 \). Steady-state concentrations of hydrogen peroxide in irradiated \( \text{TiO}_2 \) suspensions are functions of the relative rates of formation and degradation of \( \text{H}_2\text{O}_2 \). Figure 9 illustrates this point for a sample of \( \text{TiO}_2 \) with \( 30 \text{ mM acetate} \). From the sharp increase of hydrogen peroxide concentration in the initial phase of irradiation a quantum yield of 5% is calculated. In this experiment, for which the concentration of electron donors is relatively high, the steady-state concentration of 5 \( \mu\text{M} \) \( \text{H}_2\text{O}_2 \) is reached slowly. After turning off the light source, a slight decrease (\( \approx 1 \mu\text{M} \)) of \( \text{H}_2\text{O}_2 \) is noted over 10 min, possibly due to adsorption of \( \text{H}_2\text{O}_2 \) to the particle surfaces or a slow reaction of \( \text{Ti}^{IV} \) with \( \text{H}_2\text{O}_2 \). A standard addition of \( 10^{-6} \text{ M} \) \( \text{H}_2\text{O}_2 \) establishes the concentration scale of the plot. \( \text{H}_2\text{O}_2 \) is stable on \( \text{TiO}_2 \) in the dark. However upon turning on the light source, \( \text{H}_2\text{O}_2 \) concentrations that are initially above the steady-state concentrations are rapidly depleted to the level of the steady state.

**Figure 6.** Peroxide formation on \( \text{TiO}_2 \) (P25) as function of acetate concentration. 0.5 g/L \( \text{TiO}_2 \), 1.2 mM photons (\( \lambda_{\text{ex}} = 350 \text{ nm} \)), air (fluorescence method).

**Figure 7.** Quantum yield of \( \text{H}_2\text{O}_2 \) and organic peroxide formation on \( \text{ZnO} \) colloid (1 mM) as function of 2-propanol. [acetate] = 2 mM, 4.8 \( \pm 0.3 \) mM photons (\( \lambda_{\text{ex}} = 350 \text{ nm} \)), \( \text{O}_2 \) bubbled. Detection of peroxides with the iodide method (cf. Figure 1). \( \text{H}_2\text{O}_2 \), \( t \), \( = 2 \text{ min} \); total peroxide, \( t \), \( > 80 \text{ min} \).

**Figure 8.** Quantum yield of \( \text{H}_2\text{O}_2 \) formation on \( \text{ZnO} \) colloid (1 mM) as function of \( \text{O}_2 \) content; [acetate] = 2 mM, 5.4 \( \pm 0.3 \) mM photons absorbed (\( \lambda_{\text{ex}} = 330 \text{ nm} \)). Detection of \( \text{H}_2\text{O}_2 \) with the iodide method. (O, ○) Two different batches of colloid.

**Figure 9.** Photocatalytic hydrogen peroxide formation and degradation on \( \text{TiO}_2 \) (0.5 g/L) (P25); [acetate] = 30 mM, air, (350 nm) = 4.7 \( \times 10^{-4} \) M photons per minute. Polarographic detection.

**Figure 10.** Quantum yield of photodegradation of \( \text{H}_2\text{O}_2 \) on illuminated \( \text{TiO}_2 \) as function of acetate concentration. Calculated from declining slopes of plots such as Figure 9.
Discussion

Pathways for $\text{H}_2\text{O}_2$ Formation. Three qualitatively different pathways for the photocatalytic production of hydrogen peroxide are plausible. (1) $\text{H}_2\text{O}_2$ can be produced through reduction of $\text{O}_2$ by conduction band electrons (eq 2). The yield of photogenerated conduction band electrons can be increased by adding electron donors. Higher oxygen concentrations are expected to enhance the removal of the electrons. Both assumptions are consistent with the experiments illustrated in Figures 6–8. (2) $\text{H}_2\text{O}_2$ can be produced via the oxidation of water (eq 3). This process most likely occurs in the absence of added electron donors. (3) $\text{H}_2\text{O}_2$ can be generated by secondary reactions of oxidized organic molecules such as the dimerization and decomposition of the methylperoxy (67) or the $\alpha$-peroxyacetic acid radicals (68), or by reaction of $\alpha$-hydroxy-methylene radicals with oxygen (69, 69, 70). These reactions may be important at high concentrations of organic molecules and/or after long illumination.

In the presence of electron donors, pathway 2 can be neglected. It has been shown by Bahmann et al. (71) that the oxidation of organic molecules by valence band holes is the principal process. The relative importance of pathways 1 and 3 can be evaluated with the aid of a complete product analysis. However, this task is complicated by the multitude of organic molecules that may be formed (vide infra). Nonetheless, an empirical expression for the rate of formation of $\text{H}_2\text{O}_2$ can be obtained which shows that pathway 3 is negligible during the initial phase of illumination or that its contribution to the formation of $\text{H}_2\text{O}_2$ is independent of the $\text{H}_2\text{O}_2$ concentration.

Given an excess concentration of electron donors to scavenge photogenerated valence band holes and a constant $\text{O}_2$ concentration to accept conduction band electrons, the rate of formation of $\text{H}_2\text{O}_2$ will be zero order (eq 5). We have shown in a previous study that a low concentration of $\text{O}_2$ is sufficient to lead to an efficient transfer of conduction band electrons to adsorbed oxygen molecules (61). On the other hand, $\text{H}_2\text{O}_2$ may also be photodegraded. It can be reduced to water (eq 6) or oxidized to $\text{O}_2$ (eq 7).

$$\text{H}_2\text{O}_2 + 2\text{e}_\text{aq}^- \rightarrow 2\text{H}_2\text{O}$$

$$\text{H}_2\text{O}_2 + 2\text{h}_\text{aq}^+ \rightarrow \text{O}_2 + 2\text{H}^+$$

Both processes are first order in $\text{H}_2\text{O}_2$ for low concentrations of $\text{H}_2\text{O}_2$. The combination of these reactions will result in the attainment of a steady-state concentration of hydrogen peroxide during continuous illumination. The rate of formation can be assumed to be given by eq 5, whereas the rate of degradation of $\text{H}_2\text{O}_2$ should follow

$$-\frac{d[H_2O_2]}{dt} = f_2/[\text{O}_2][H_2O_2] = \Phi_2[H_2O_2]d[\text{hv}]_{\text{abs}}$$

Hence the overall production of $\text{H}_2\text{O}_2$ is given by eq 9.

$$\frac{d[H_2O_2]}{dt} = (\Phi_2 - \Phi_1)[H_2O_2]d[\text{hv}]_{\text{abs}}$$

Under these conditions the steady-state concentration of $\text{H}_2\text{O}_2$ is independent of the absorbed photon flux during the experiment (eq 10).

$$[\text{H}_2\text{O}_2]_{\text{ss}} = \Phi_2/\Phi_1$$

The initial phase of $\text{H}_2\text{O}_2$ formation on TiO$_2$ and on ZnO can be described with this simple rate law as shown by the solid lines of Figures 3 and 5. The parameters corresponding to these fits are summarized in Table I. High concentrations of $\text{H}_2\text{O}_2$ are obtained readily in illuminated suspensions of ZnO not only because of the relatively high quantum yield for $\text{H}_2\text{O}_2$ formation but...
provides radical, the corresponding peroxy radical is unstable: (or D'). Carbon-centered radicals add oxygen at diffusion-controlled rates (eq 11) to form the corresponding peroxy radical.

\[ R^\bullet + O_2 \rightarrow R^\bullet + O_2 \rightarrow R^\bullet + \text{H}_2\text{O}_2 \]  

Depending on the nature and concentration of the peroxy radicals, first- or second-order decay kinetics prevail. Under environmental conditions low steady-state concentrations are likely to favor first-order decay processes.

Depending on the other substrates on the carbon atom, two different reaction patterns have been observed by pulse radiolysis and analyzed in terms of reaction kinetics and products (59, 67-70, 75-77). If one of the substrates is OH, O\(^2\)\(^-\), or NO\(_2\) (e.g., CH\(_3\)CHOH (70), CO\(_2\) (76), or CH\(_3\)N(CH\(_3\))\(_2\) (77)) (i.e., a heteroatom with a non-antibonding electron pair), the peroxy radical is unstable and decays within a few milliseconds to yield the corresponding aldehyde, ketone, acid, or imine and a superoxide radical (O\(_2\)\(^-\)).

\[ R^\bullet + \text{H}_2\text{O}_2 \rightarrow R^\bullet + \text{H}_2\text{O} + O_2 \]  

Specific and general base catalysis further accelerates the elimination of O\(_2\)\(^-\) from \(\alpha\)-hydroxyalky peroxy radicals (69). Superoxide (O\(_2\)\(^-\)) ultimately forms peroxy peroxide in a bimolecular process (eq 12) (78). No organic peroxy radicals are formed according to this route.

\[ O_2^\bullet + \text{H}_2\text{O}_2 \rightarrow H^\bullet + \text{H}_2\text{O}_2 + O_2 \]  

If none of the substrates R\(^1\), R\(^2\), or R\(^3\) (eq 11 and 12) provides a nonbonding electron pair to the carbon-centered radical, the corresponding peroxy radical (e.g., \(\text{O}_2\text{H}_2\text{CO}_2\)) is stable toward unimolecular or base-catalyzed elimination of O\(_2\)\(^-\). For example, only trace amounts of H\(_2\)O\(_2\) were observed when this radical was generated by the photolysis of NO\(_3\)\(^-\)-acetate solutions (79). The reactivity of such peroxy radicals has been described by Sheldon and Kocli (80). Organic hydroperoxides result after abstraction of weakly bound [2OX(II) < 90 kcal/mol] hydrogen atoms from such sources as H\(_3\)O\(^+\), aldehydes, tertary carbon centers, or hydrogen atoms in \(\alpha\)-position to a carbon–carbon double bond (e.g., from toluene). These radicals may also add to olefins yielding dialkyl peroxides. Addition and abstraction ratios for various olefins have been tabulated (80).

Fraser et al. (81) proposed that 2-propanol reacts as a hole scavenger on TiO\(_2\) (eq 14 and 15) to produce only acetone as the final product even in the presence of O\(_2\). However, from Figure 7 we see that higher 2-propanol concentrations do lead to higher concentrations of organic peroxy radicals. Hence, pathways other than eq 14 and 15 must be considered.

\[ (\text{CH}_3\text{)CHOH} + h^\bullet \rightarrow (\text{CH}_3\text{)COH} + \text{H}_2^\bullet \]  

\[ (\text{CH}_3\text{)COH} + h^\bullet \rightarrow (\text{CH}_3\text{)CO} + \text{H}_2^\bullet \]  

\[ \text{OH}^\bullet + \text{H}_2\text{O}_2 \rightarrow \text{OH}_\bullet + \text{H}_2\text{O}_2 \]  

Radiolysis is known that OH\(^\bullet\) radicals will oxidize 2-propanol to yield 85% (CH\(_3\)COH) and 11% (CH\(_3\))\(_2\)CHOH (i.e., \(\alpha\)- and \(\beta\)-carbon-centered radicals), respectively (82, 83). While reactions of the strongly reducing \(\alpha\)-isopropyl radical will ultimately yield only acetone and H\(_2\)O\(_2\), the reactivity of the \(\beta\) radical is expected to be different. The \(\beta\) radical may add O\(_2\) in a diffusion-controlled reaction (74) according to eq 17 in analogy to similar reactions of organic peroxy radicals (75). This radical may either be stabilized on the particle surface until a further reduction to an alkylhydroperoxide (eq 18) or it may dimerize and fragment to yield several products among which organic peroxydes and H\(_2\)O\(_2\) are expected to be found (67, 68, 75).

\[ (\text{CH}_3\text{)CH(OH)} + \text{O}_2 \rightarrow (\text{CH}_3\text{)CH(OH)} + \text{H}_2\text{O}_2 \]  

\[ (\text{CH}_3\text{)CH(OH)} + \text{H}_2\text{O}_2 \rightarrow (\text{CH}_3\text{)CH(OH)} + \text{H}_2\text{O}_2 \]  

As is obvious from Figure 1 the oxidation of acetate also yields organic peroxydes, a finding that can be explained as follows. Krüttler et al. assumed the intermediacy of the methyl radical in their study of the oxidation of acetate of illuminated TiO\(_2\) suspensions (84). They observed the formation of methane and ethane. When oxygen was present, their mechanism accounted for only \(\sim\)30% of the rate of decomposition of acetic acid, and they did not attempt to analyze the remaining 70%. In the presence of oxygen, methyl radicals may react to yield methylyperoxy radicals, which in turn dimerize and decompose to yield an array of products such as CH\(_3\)OH, CH\(_3\)OOCCH\(_2\), CH\(_3\)OH, HCO\(_2\), CH\(_3\)O, and H\(_2\)O\(_2\) (67).

Over the pH domain of this study (TiO\(_2\), pH 4.0-4.7; ZnO, pH 7.7), the particle surfaces are positively charged since the pH of zero point of charge (p\(\text{H}_{\text{zpc}}\)) is 6.0 for TiO\(_2\) (85) and 9.3 for ZnO (61). Under these conditions anions such as acetate are adsorbed to the oxide surfaces (85). Variation of the acetate concentration was found to have a pronounced effect on the photocatalytic process. In addition to increasing the yield of formation of H\(_2\)O\(_2\), an increase in [CH\(_3\)CO\(_2\)] was found to decrease the rate of photodegradation of H\(_2\)O\(_2\). This latter effect may be at-
tributed to either a steric effect in which acetate blocks the sites where $H_2O_2$ is degraded or an efficient competition of acetate with $H_2O_2$ for valence band holes.

It is noteworthy that neither Figure 6 nor Figure 10 yield linear plots but resemble adsorption isotherms. If Figure 10 were interpreted as an adsorption isotherm, one would conclude that at an acetate concentration of $\approx 2 \times 10^{-5} M$ half of the surface sites were covered. This amount of surface coverage may be considered an upper limit. In fact, the presence of fewer acetate molecules may be sufficient to promote the electronic effects observed, as will be demonstrated for the adsorption of oxygen.

Figure 8 shows again an adsorption isotherm-type behavior of the quantum yield of $H_2O_2$ formation on the $O_2$ partial pressure. An increase in the oxygen content from 20% to 100% of saturation did not result in a corresponding increase in the quantum yield of $H_2O_2$ production. However, even at 100% $O_2$ (i.e., $pO_2 = 1$ atm, hence $cO_2 = 1.2 \times 10^{-5} M$) the reactive sites on the particle surfaces are not expected to be saturated with $O_2$. Water is likely to form much stronger bonds to reactive sites on the surface under the $pH$ conditions of our experiments (e.g., $[[=\text{Zn}^+] = [\approx \text{Ti}^{+}]$) than $O_2$, thus only a few $O_2$ molecules appear to be adsorbed on each particle. At an $O_2$ content of $\approx 10%$ where the quantum yield has reached half of its final value (Figure 8), we estimate on a numerical basis that half of the particles interact with only one molecule of $O_2$ each. Fluorescence spectroscopy of the ZnO colloid supports this interpretation (61).

$H_2O_2$ Formation in the Absence of Sacrificial Electron Donors. Water can be oxidized photochemically on TiO$_2$ as follows (51, 87-89):

$$2H_2O \rightarrow 4e^{-} + 2H_2 + O_2 \quad (19)$$

$$2H_2O \rightarrow 3e^{-} + H_2 + H_2O_2 \quad (20)$$

$$2H_2O + O_2 \rightarrow 2e^{-} + 2H_2O_2 \quad (21)$$

In the absence of deposited noble metal catalysts, hydrogen fixation on titanium dioxide seems unlikely. Isotopic exchange experiments have shown the absence of D or H exchange between D$_2$ and surface hydroxyls of TiO$_2$ both in the dark and under intense bandgap irradiation (90). Hence, the reaction given in eq 21 appears to be the most plausible stoichiometry for $H_2O_2$ production in illuminated suspensions of pure TiO$_2$.

In the case of a nonstoichiometric TiO$_2$ such as "blue" TiO$_2$ (49) or an n-type TiO$_2$, oxygen may be reduced by the excess electrons according to eq 22, yielding $O_2^-$ and hence $H_2O_2$ (eq 23). The release of $O_2^-$ may occur in the dark but may also require activation by light.

$$(TiO_2)_x e^{-} + xO_2 \rightarrow [(TiO_2)_x(O_2)]^{x-} \rightarrow (TiO_2)_x + xO_2^- \quad (22)$$

$$xO_2^- + xH^+ \rightarrow (1/2x)H_2O_2 + (1/2x)O_2 \quad (23)$$

We have shown that $H_2O_2$ is detectable in the homogeneous phase after illumination of an aqueous suspension of TiO$_2$, although the concentration is low, $\approx 10^{-6} M$. The initial rate of formation was relatively high, but the maximum steady-state concentration ($7 \times 10^{-7} M$) was attained after a small number of photons had been absorbed (Figure 11). This initial phase of $H_2O_2$ production may be due to photoactivated release of $O_2^-$ according to eq 22 or it may result from degradation of trace amounts of organics (eq 4, 11-13) initially present in the system.

The steady-state concentration of $H_2O_2$ production due to water oxidation ($2 \times 10^{-7} M$) is low because of efficient degradation of the molecule.

Formation of Hydrogen Peroxide on a Suspension of Desert Sand. Illumination of a suspension of desert sand containing acetate as a hole scavenger (Figure 12) resulted in $H_2O_2$ formation with the attainment of a steady-state concentration of $2 \times 10^{-7} M$. Desert sand suspensions show photochemical behavior similar to that of TiO$_2$ and ZnO. However, $H_2O_2$ is also degraded in the dark on desert sand. This may be due to a "Fenton-type" reaction between $H_2O_2$ and Fe$^{3+}$ (91). Our sample contained a substantial amount of magnetite (Fe$_5$Fe$^{III}_{38}$O$_{40}$); some of the magnetite may have remained within the sample after the cleanup procedure. Also, the photocatalytic dissolution of Fe$_2$O$_3$ yielding ferrous ions when electron-donating molecules are present has been observed and may be of importance in this reaction system (92). Further studies are in progress to characterize the photocatalytic activity of desert sands.

Emissions and Transport of TiO$_2$, ZnO, and Sand in the Atmosphere. Titanium and zinc minerals are found in dust in the atmosphere (83). Weathering of crustal rocks of the continents is thought to be the main source of this atmospheric dust. Estimates of the amount of mineral dust capable of long-range transport are on the order of hundreds of million tons annually with the Sahara being a predominant source (260-400 x 10$^6$ tons per year) (94). While dust concentrations over the oceans are diluted to less than a few micrograms per cubic meter, higher concentrations were found over land ($10 \mu g \cdot m^{-3}$) and over the Sahara ($\approx 100 \mu g \cdot m^{-3}$) (94). Considerable amounts—about $5 \times 10^8$ tons originating from the Sahara—of dust particles of the appropriate size range (0.1-1 µm) are transported over several thousand kilometers (95). The concentration of Ti in sand was found to range between 4000 and 16 000 ppm (53, 96); zinc is a somewhat less abundant mineral: $\approx 200$ ppm (93). Thus about 1 000 000 tons of Ti minerals, mostly oxides (50 000 tons of Zn), are emitted naturally into the atmosphere above the Sahara. Man-made atmospheric emissions in the U.S. were $\approx 90 000$ tons of TiO$_2$ (1973) (97) and 160 000 tons of zinc (1969) (98). In urban areas, typical concentrations of inorganic material are about 5 µg m$^{-3}$ with average Ti contents of 2% and Zn of 1.6% (99), while typical concentrations of organic carbon/soil are near 20 µg m$^{-3}$ (100). Assuming that this material was incorporated fully into a cloud with a liquid water content (LWC) of 0.1 g m$^{-3}$, the concentration of zinc oxide would be approximately 8 µM. In our experiments the [ZnO] colloid was 1.0 mM. In haze aerosol, the concentration of ZnO can be as large as 10 mM due to the smaller LWC of these droplets (i.e., LWC $\approx 10^{-5}$-10$^{-4}$ g m$^{-3}$). In terms of potential electron donors a large fraction of 20 µg m$^{-3}$ of suspended organic carbon may be suitable as electron donor substrates. Munger et al. (101) have found concentrations of acetate in cloud and fog Southern California that range from 14 to 581 µM and concentrations of formate that range from 43 µM to 1.5 mM. Both of these anions would be suitable electron donors for the photocatalytic production of peroxide. From our studies we have found that an increase in electron donor concentration would result in a higher quantum yield for the formation of peroxides, a lower rate of degradation, higher steady-state concentrations under constant illumination, and a higher yield of ROOH relative to $H_2O_2$.

Acknowledgments

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Chapter 5

PHOTOCATALYTIC PRODUCTION OF HYDROGEN PEROXIDE

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Chapter 10

Photocatalytic Formation of Hydrogen Peroxide

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The two-electron reduction of molecular oxygen to hydrogen peroxide can be catalyzed by metal oxide semiconductor particles in the presence of visible and near-UV light. Even though very high quantum yields for this process are observed, rather low steady-state concentrations of \( \text{H}_2\text{O}_2 \) are reached. Detailed mechanisms are presented to explain these experimental findings. Metal oxide particles are found in atmospheric and surface waters. The environmental significance of photocatalytic formation of \( \text{H}_2\text{O}_2 \) on these particles in natural systems is discussed.

Hydrogen peroxide, \( \text{H}_2\text{O}_2 \), is one of the most powerful oxidants in haze aerosols, clouds, and hydrometeors at low pH (1). A major pathway for the formation of sulfuric acid in humid atmospheres below pH 5 seems to be the oxidation of sulfur dioxide by \( \text{H}_2\text{O}_2 \) (2-4). Hydrometeor concentrations of hydrogen peroxide as high as 50 \( \mu \text{M} \) have recently been reported by Kok and co-workers (5-7), while typical atmospheric \( \text{H}_2\text{O}_2 \) levels up to 5 ppb have been predicted from Henry’s law calculations (8,9). Various sources for the production of \( \text{H}_2\text{O}_2 \) in the atmosphere have been proposed: it can be generated in the gas phase by the combination of hydroperoxyl radicals, \( \text{HO}_2^- \) (10), at the air-water interface due to photoinduced redox processes (11), and in the aqueous phase via photo-catalyzed reactions with humic/fulvic acid and green algae as mediators (Zepp, R. G., EPA Environmental Research Laboratory at Athens, personal communication). Furthermore, \( \text{HO}_2^- \) radicals...
Photocatalytic Formation of Hydrogen Peroxide

which are produced in the gas phase can be scavenged by the water droplets where they then form H₂O₂. This in situ generated hydrogen peroxide together with the H₂O₂ scavenged from the gas phase is thought to be the main source for the H₂O₂ accumulated in cloudwater droplets (10, 12, 13). Another very likely possibility for H₂O₂ production, however, has so far been neglected in the design of models for aerosol-, fog-, and cloudwater chemistry. Various metal oxides, some of which are very abundant in natural environments, have been shown to act as photocatalysts for a large variety of reactions (14), e.g., the photolysis of desert sands resulted in the production of ammonia from dinitrogen (15).

Atmospheric particulate matter originates mainly from natural sources (721–1850 Tg yr⁻¹ in 1979 globally) but also from man-made emissions (125–385 Tg yr⁻¹ in 1982 in the USA) with iron, titanium, and zinc being some of the most abundant transition metals detected in ambient samples (16). These metals are present as hydroxides but also frequently as the respective oxides, depending upon the environmental conditions (17). Hence the present work addresses the question of hydrogen peroxide formation in aqueous solutions as catalyzed by metal oxides upon irradiation with visible and near-UV light.

Photocatalysis with Semiconductors

Many metal chalcogenides and oxides are known to be semiconductors. These materials can act as sensitizers for light-induced redox processes due to their electronic structure consisting of a valence band with filled molecular orbitals (MO's) and a conduction band with empty MO's. Absorption of a photon with an energy above the bandgap energy Eg generally leads to the formation of an electron/hole pair in the semiconductor particle (18):

\[
\text{semiconductor} + h\nu \rightarrow e^- (cb) + h^+ (vb) \quad (1)
\]

In the absence of suitable scavengers, recombination occurs within a few nanoseconds (19). Valence band holes (h^+ (vb)) have been shown to be powerful oxidants (20–23) whereas conduction band electrons (e^- (cb)) can act as reductants (24, 25). The redox potentials of both, e^- and h^+, are determined by the relative position of the conduction and valence band, respectively. Bandgap positions are material constants which have been determined for a wide variety of semiconductors (26). Most materials show "Nernstian" behavior which results in a shift of the surface potential by 59 mV in the negative direction with a pH increase of APH = 1. Consequently electrons are better reductants in alkaline solutions while holes have a higher oxidation potential in the acid pH-range (26). Thus, with the right choice of semiconductor and pH, the redox potential of the e^- (cb) can be varied from +0.5 to −1.5 V (vs. NHE) and that of the h^+ (vb) from +1.0 to more than +3.5 V. This sufficiently covers the full range of redox chemistry of the H₂O/O₂ system (27).
$\text{H}_2\text{O}_2$ can therefore be formed via two different pathways in an aerated aqueous solution provided $e^-(\text{cb})$ and $h^+(\text{vb})$ are generated:

$$\text{O}_2 + 2e^-(\text{cb}) + 2\text{H}^+_{\text{aq}} \rightarrow \text{H}_2\text{O}_2$$  \hspace{1cm} (2)

$$2\text{H}_2\text{O} + 2h^+(\text{vb}) \rightarrow \text{H}_2\text{O}_2 + 2\text{H}^+_{\text{aq}}$$  \hspace{1cm} (3)

Reaction 2 has been studied in great detail \((28-44)\) since Baur and Neuweiler \((28)\) in 1927 observed the formation of $\text{H}_2\text{O}_2$ when they illuminated aqueous zinc oxide suspensions in the presence of glycerin and glucose which in turn were oxidized. Appreciable yields of hydrogen peroxide are detected only when appropriate electron donors, $D$, are added prior to illumination. This strongly indicates that it is the electron donor, $D$, which is adsorbed on the catalyst's surface and hence sacrificed via Reaction 4.

$$D + h^+(\text{vb}) \rightarrow D^*.$$  \hspace{1cm} (4)

The presence of surficial $D$ interferes with the $e^-/h^+$ recombination leaving $e^-(\text{cb})$ (conduction band electrons) behind which then react with dioxygen via Reaction 2. Small quantities of $\text{H}_2\text{O}_2$ detected in the absence of added donors contained only oxygen atoms from $\text{O}_2$ as shown by labelling studies \((34)\) which indicates the presence of contaminants in the semiconductor that are able to fill the $h^+(\text{vb})$. Cadmium sulfide, CdSe, and ZnO showed the highest catalytic activity for dioxygen reduction \((35,36)\). Titanium dioxide, on the other hand, which seems to be the material with the greatest potential for water splitting is reported to have negligible activity \((35,41-43)\). The oxidation of water via Reaction 3, however, has not yet been demonstrated unambiguously. While Rao et al. \((45)\) reported the formation of $\text{H}_2\text{O}_2$ in water splitting experiments on ZnO and TiO$_2$, Salvador and Decker \((46)\) could not verify this observation. The intermediate production of $\text{H}_2\text{O}_2$ as the first molecular step of the four-hole oxidation of water to dioxygen has been predicted \((46,47)\) and a variety of free radical intermediates have already been detected \((48-50)\). Whenever the oxidation of H$_2$O is found to proceed with high yields there is no indication of hydrogen peroxide formation \((51-54)\), but the dioxygen production seems to proceed via different intermediate peroxides as shown by Baur and Perret \((51,52)\): they studied the photocatalytic formation of O$_2$ on ZnO in the presence of silver nitrate and observed the intermediate production of silver peroxides. In the case of TiO$_2$, the absence of detectable amounts of $\text{H}_2\text{O}_2$ and O$_2$ during water photoelectrolysis experiments has been explained with the well-documented adsorption and photo-uptake of these oxo-species by the material \((55-71)\) and their incorporation into the molecular structure as peroxytinates \((68,72,73)\).

The above discussion indicates that a detailed study of the mechanism of the light-induced hydrogen peroxide production on
various oxide surfaces is warranted in order to judge its potential environmental implications. Using a newly developed polarographic technique for the kinetic analysis of hydrogen peroxide concentrations with a sensitivity of $10^{-7}$ M, we present further insight into the photocatalytic formation and destruction of $\text{H}_2\text{O}_2$.

Experimental Details

Several catalysts were prepared from chemicals of highest available grade. Mechanistic studies were performed using colloidal dispersions of zinc oxide, ZnO, which contained particles with a mean diameter of 5 nm (Bahnemann, D. W.; Kormann, C.; Hoffmann, M. R. J. Phys. Chem. submitted 11/3/86). Suspensions of such small aggregates exhibit negligible light scattering properties and conventional spectroscopic techniques can be used to study ongoing reactions (74). The preparation of titanium dioxide particles, TiO$_2$, coated with cobalt(II)tetrathiosulfophthalocyanine, Co(II)TSP, has recently been reported (Hong, A. P.; Bahnemann, D. W.; Hoffmann, M. R. J. Phys. Chem. accepted for publication 12/12/86). These particles have a mean diameter of 30 nm with 30% of the surface area covered with Co(II)TSP.

Desert sand obtained from Death Valley has been treated with several acid washing cycles and selected by size and weight (Kormann, C.; Bahnemann, D. W.; Hoffmann, M. R. unpublished data). The $\text{H}_2\text{O}_2$ concentration was measured continuously with a YSI-Clark 2510 Oxidase Probe connected to a YSI model 25 oxidase meter. The surface of the electrode was covered with a dialysis membrane (molecular weight cutoff 12,000 - 14,000) to prevent any interference caused by the catalyst particles. Equilibration times between 30 and 60 minutes were allowed to ensure a stable signal once the electrode was immersed into the reaction solution. Following equilibration, changes in $\text{H}_2\text{O}_2$ content were monitored at a sensitivity of $10^{-7}$ M and a time constant of 1 s. The electrode was calibrated following each kinetic experiment using a standard addition method; linear response was obtained between $10^{-7}$ and $2\times10^{-6}$ M $\text{H}_2\text{O}_2$. Since this polarographic method is sensitive to any species with a redox potential of 700 mV, different methods were used to verify the formation of hydrogen peroxide. Following the illumination an aliquot of the solution was taken and titrated with iodide in the presence of a catalyst (75,76) to form the $I_3^-$ anion which was quantitatively measured by spectrophotometry ($\epsilon(352\text{nm}) = 26400 \text{ M}^{-1} \text{ cm}^{-1}$) (77). As a second check and when very small concentrations of $\text{H}_2\text{O}_2$ were detected with the polarographic method a very sensitive fluorometric determination (detection limit: $1.2\times10^{-8}$ M $\text{H}_2\text{O}_2$) was employed. This latter procedure involves the reaction of $\text{H}_2\text{O}_2$ with p-hydroxyphenylacetic acid in the presence of horseradish peroxidase to yield a product which fluoresces at 400 nm ($\lambda(\text{ex}) = 320 \text{ nm}$) (78,79). Even though the polarographic method can not differentiate between $\text{H}_2\text{O}_2$ and other species with a similar electrochemical half-wave potential, the use of two alternative chemical analysis techniques eliminates such artifacts. Interferences by other chemicals such as ozone.
can also be excluded in this study since it is extremely unlikely that they should occur with all three methods to the same extend.

Figure 1 shows the experimental set-up for the photolysis studies. White light of a 450 W Xe lamp (Osram XBO) passes through a water filter, a monochromator (PRA B102) and an appropriate UV-filter before the continuously stirred sample is irradiated. The analog signal of the oxidase meter is amplified to give the right amplitude for the input of the A/D converter (HBC Dash 8) which digitizes the data and feeds them into an IBM PC/AT for kinetic analysis. Aberchrome 540 is used for the determination of the light flux to enable an absolute measurement of the quantum yields (80).

Results and Discussion

The formation of hydrogen peroxide upon the illumination of an air-saturated aqueous colloidal suspension of zinc oxide particles is shown in Figure 2. No \( \text{H}_2\text{O}_2 \) is produced when light energies below the bandgap energy of ZnO where employed (\( \text{E}_g(\text{ZnO}) = 3.4 \text{ eV} \) or \( \text{\lambda}(\text{ex}) = 365 \text{ nm} \)), e.g., \( \text{\lambda}(\text{ex}) = 400 \text{ nm} \). As the irradiation was performed at lower wavelengths, e.g., \( \text{\lambda}(\text{ex}) = 366 \text{ and 320 nm} \), the sudden increase of the signal from the polarographic analyzer indicated \( \text{H}_2\text{O}_2 \) formation with a wavelength-independent quantum yield of 6%. No hydrogen peroxide is formed or depleted in the absence of light. Prolonged illumination leads to the formation of a steady-state in \([\text{H}_2\text{O}_2]\) of \(1.2 \times 10^{-4} \text{ M} \) in irradiated samples. The quantum-yields \( \phi \) determined from the initial slope of the \([\text{H}_2\text{O}_2]\) vs. time plots depended strongly on the oxygen-content of the solution: \( \phi \) increased to 10% in \( \text{O}_2 \)-saturated samples and decreased sharply below \(2 \times 10^{-6} \text{ M} \text{O}_2 \). No \( \text{H}_2\text{O}_2 \) is produced when anoxic solutions were irradiated. The following mechanism explains these observations. Electrons and holes are formed in the zinc oxide particles under bandgap irradiation (Reaction 1). Their recombination is prevented by the presence of 2 mM acetate ions which are strongly adsorbed onto the ZnO surface and are oxidized via:

\[
\text{CH}_3\text{COO}^- + h^+ (\text{vb}) \rightarrow (\text{CH}_3\text{COO})^* \quad (5)
\]

\[
(\text{CH}_3\text{COO})^* \rightarrow \text{CH}_2\text{COO}^-/\text{H}^*\text{aq} \text{ and/or } \text{CH}_3/\text{CO}_2 \quad (6)
\]

The fate of the radicals produced via Reaction 6 is currently being investigated. Initial results indicate the formation of organic peroxides and suggest the intermediate formation of peroxy-radicals (Kormann, C.; Bahnhann, D. W.; Hoffmann, M. R. unpublished results). With the inhibition of charge recombination conduction band electrons are now available to reduce molecular oxygen yielding \( \text{H}_2\text{O}_2 \) (Reaction 2). The observed steady-state concentration of hydrogen peroxide can be understood as a competition between Reactions 2 and 7.
Figure 1. Experimental configuration used for irradiations and hydrogen peroxide detection.

Figure 2. $\text{H}_2\text{O}_2$ formation upon illumination of an aqueous colloidal suspension of zinc oxide in the presence of 2 mM acetate (other exp. cond. are given in the figure).
H₂O₂ + 2e⁻(cb) + 2H⁺\text{aq} \rightarrow 2\text{H}_2\text{O} \quad (7)

The value \([\text{H}_2\text{O}_2]\) measured in air-saturated solutions suggests that Reaction 7 is about twice as efficient as the initial dioxygen reduction.

H₂O₂ is also produced in the absence of hole scavengers provided the right catalyst is used. Figure 3 shows the formation of hydrogen peroxide upon bandgap illumination of an oxygenated aqueous suspension of TiO₂ coated with Co(II)TSP which acts as an electron relay to transfer e⁻(cb) onto O₂ (Hong, A. P.; Bahnemann, D. W.; Hoffmann, M. R. J. Phys. Chem. accepted for publication 12/12/86). It is clearly obvious from Figure 3 that the same steady-state concentration of H₂O₂ is reached once the system is perturbed by the addition of H₂O₂ during prolonged irradiation. As in the case of ZnO no formation or depletion of hydrogen peroxide is observed in the absence of light. An octahedrally coordinated surface complex, e.g., Ti-O⁻-Co(III)TSP-O₂⁻*, has been identified as the catalytically active species in the TiO₂-Co(II)TSP system. With dioxygen being bound in the form of superoxide, O₂⁻*, this complex proved to be extremely stable but acts as an effective acceptor for conduction band electrons produced upon irradiation of the bulk TiO₂:

\[
\text{Ti-O}^{-}\text{-Co(III)TSP-O}_2^{-}\cdot + e^{-}(\text{cb}) \rightarrow \text{Ti-O}^{-}\text{-Co(III)TSP-H}_2\text{O} + \text{H}_2\text{O}_2 \quad (8)
\]

\[
+ 2 \text{H}^+\text{aq}
\]

The aquo complex formed in Reaction 8 readily accepts another e⁻(cb) to form a reduced metal center which then quickly reacts with O₂:

\[
\text{Ti-O}^{-}\text{-Co(II)TSP-H}_2\text{O} + \text{O}_2 \rightarrow \text{Ti-O}^{-}\text{-Co(III)TSP-O}_2^{-}\cdot \quad (9)
\]

yielding again the stable O₂⁻* complex.

H₂O₂ is formed in quantum yields close to 50% by this reaction sequence. The observed net formation of H₂O₂ indicates that the valence band holes, h⁺(vb), are able to oxidize water via Reaction 3. The low steady-state concentrations \([\text{H}_2\text{O}_2]\) which are reached during these experiments (5 - 25 µM depending on the nature of the catalyst) suggest that oxidation of H₂O₂ via

\[
\text{H}_2\text{O}_2 + 2\text{h}^+(\text{vb}) \rightarrow \text{O}_2 + 2\text{H}^+\text{aq} \quad (10)
\]

efficiently competes with Reaction 3. When present at high concentrations, hydrogen peroxide can also compete with molecular oxygen (Reaction 9) for the open coordination site on Co(II)TSP:

\[
\text{Ti-O}^{-}\text{-Co(II)TSP-H}_2\text{O} + \text{H}_2\text{O}_2 \rightarrow \text{Ti-O}^{-}\text{-Co(III)TSP-OH} + \text{OH}^{-} \quad (11)
\]

Reaction 11 is analogous to Reaction 8 in that it leads to the overall reduction of H₂O₂ by two e⁻(cb). The major difference
between the zinc oxide and the TiO₂-Co(II)TSP systems is that the surface complex (Co(II)TSP) acts as an electron relay in one case while sacrificial electron donors such as acetate are a prerequisite for interruption of the e⁻/h⁺ recombination in the other case.

Following the studies of these rather well-defined model systems aerated aqueous suspensions of desert sand particles were irradiated (λ(ex) = 350 nm) in the presence of sodium acetate. The very rapid formation of a steady-state concentration of 0.2 µM H₂O₂ upon illumination is shown in Figure 4. This, however, decays very quickly when the light is turned off. A similar depletion is apparent when H₂O₂ is added in the dark. If the light is turned on during this decay period a steady-state of 0.2 µM is again established. These cycles can be repeated many times without any apparent loss in activity. It has already been demonstrated (15) that desert sand contains minerals such as hematite, α-Fe₂O₃, and anatase, TiO₂, and can thus be photocatalytically active. We envision a mechanism similar to that proposed for the model systems above to account for the observed formation of H₂O₂ on desert sands. In this case the e⁻/h⁺ pair (Reaction 1) is intercepted by the donor acetate (Reactions 5 and 6) leaving e⁻(cb) behind to reduce O₂ via Reaction 2. The efficient destruction of H₂O₂, on the other hand, might be caused by metal ion contaminants (M⁺) adsorbed on the sand particles (81-85). Hydrogen peroxide can thus react with M⁺ in a Fenton type reaction (81,82).

\[
M^{xx⁺} + H₂O₂ \rightarrow M^{(xx⁺)⁺} + OH⁻ + OH⁺
\]  
(12)

followed by the free radical Reactions 13 to 17 (87,88).

\[
H₂O₂ + OH⁻ → H₂O + HO₂⁺
\]  
(13)

\[
HO₂⁺ ↔ O₂⁻ + H⁺
\]  
(14)

\[
HO₂⁺ + O₂⁻ + H⁺ \rightarrow H₂O₂ + O₂
\]  
(15)

\[
HO₂⁺ + OH⁻ → H₂O₂ + O₂
\]  
(16)

\[
OH⁻ + OH⁻ → H₂O₂
\]  
(17)

This reaction sequence results in the overall disproportionation of H₂O₂ and thus explains its rapid disappearance in the dark. Finally, a word of caution should be added regarding other possibilities to photogenerate hydrogen peroxide in such an ill-defined natural system. In spite of the rigorous pre-treatment it is possible that trace amounts of organic adsorbates are still present on the desert sand samples employed in this study. On the other hand, it is well documented that naturally occurring humic type materials can also be photochemically active (89). Thus we cannot exclude the possibility that part of the observed rather low steady-state
Figure 3. Formation and depletion of \( \text{H}_2\text{O}_2 \) upon irradiation \((\lambda(\text{ex}) = 366 \text{ nm})\) of an oxygenated aqueous suspension of 0.3 g \( \text{TiO}_2-\text{Co(II)TSP} \) at pH 12.

Figure 4. Formation and depletion of \( \text{H}_2\text{O}_2 \) upon illumination and in the dark observed in an aerated aqueous suspension of Death Valley desert sand (other exp. cond. are given in the figure).
Concluding Remarks

We have shown that hydrogen peroxide can be produced photocatalytically in the presence of semiconductor particles. Quantum yields up to 50% and steady-state concentrations between 0.2 and 120 \( \mu M \) \( H_2O_2 \) have been observed. While the reduction of molecular oxygen by \( e^- (cb) \) seems to be the most likely process for \( H_2O_2 \)-formation, oxidation of water by \( h^+ (vb) \) should in principle yield the same products.

It is the observation of hydrogen peroxide production upon the illumination of an aerated aqueous suspension of desert sand particles that presents the most intriguing result of this study. Submicron sand particles are very abundant in the atmosphere where they act as condensation nuclei (90). Their involvement as catalysts and/or photocatalysts in chemical transformations occurring in natural environments has so far been neglected even though they are rather persistent in the atmosphere with half-lives of several days before precipitation takes place. We propose the surface reaction of photocatalytically formed \( H_2O_2 \) with sulfur dioxide (\( SO_2 \)) and nitrous oxides (\( NO_x \)) as an additional pathway for the formation of acid rain. Even though due to its metal-catalyzed dismutation the steady-state concentration of \( H_2O_2 \) observed in the desert sand experiment was rather low, it may nevertheless be high enough to yield reasonable quantities of oxidation products like \( H_2SO_4 \) or \( HNO_3 \). Further experiments are in progress to study the photocatalytic activity of natural systems.

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Chapter 6

[The text of this chapter is being submitted to the Journal of Photochemistry.]
INTRODUCTION

The photocatalytic reactions promoted by aqueous suspensions of colloidal metal oxides has been the subject of an abundant number of recent investigations.\[1\] Iron oxide, an n-type semiconductor with a bandgap of 2.2 eV, has been studied extensively for use in solar photoelectrolysis cells.\[2,3\] Leland and Bard\[4\] recently studied the photoelectrochemical properties of colloids and particles of different forms of iron oxide. They found $\alpha$–Fe$_2$O$_3$, the most stable polymorph, to be the most effective catalyst for the photo-oxidation of sulfite. Frank and Bard\[5\] investigated the photocatalytic oxidation of cyanide and sulfite at several semiconductor powders. They found TiO$_2$ to be an active photocatalyst for cyanide oxidation, while no oxidation was seen for $\alpha$–Fe$_2$O$_3$. Cunningham et al.\[6\] obtained evidence for the photocatalytic formation of OH$^-$ radicals in illuminated suspensions of $\alpha$–FeOOH. Pronounced differences in the activities of two Fe$_2$O$_3$ samples were found when Pichat and Co–workers examined the photocatalytic behavior of various semiconductor oxide powders dispersed in oxalic acid solutions.\[7\] The photocatalytic activity of $\alpha$–Fe$_2$O$_3$ (hematite) has also been studied by several authors in the context of the dissolution of solid oxide phases.\[8,9\] Stramel and Thomas\[10\] studied the photochemistry of iron oxide colloids but were unsuccessful in promoting chemical reaction by irradiating into the Fe$_2$O$_3$ absorption band. Ferric oxides and oxyhydroxides ($\alpha$–Fe$_2$O$_3$, Fe$_3$O$_4$, $\alpha$–FeOOH, $\gamma$–FeOOH) are ubiquitous constituents of the aqueous environment and have also been identified as components of airborne particles.\[11\] Their potential importance in the photocatalytic transformation of sulfur compounds in the aqueous atmospheric environment has been evaluated by Hoffmann and Co–workers.\[12\]
In the work described below, the photocatalytic activity of $\alpha$–Fe$_2$O$_3$ colloids are compared to the activities of ZnO and TiO$_2$. The formation of H$_2$O$_2$ is investigated and the oxidation of organic molecules is studied with high sensitivity.

EXPERIMENTAL

Materials

Transparent $\alpha$–Fe$_2$O$_3$ colloids were prepared by the controlled hydrolysis of FeCl$_3$ which was followed by membrane dialysis until the residual Cl$^-$ concentration was below $10^{-5}$ M. Particle diameters were found to be between 3 and 20 nm. Details of the synthesis and characterization of this catalyst have been described elsewhere.$^{[12]}$ Titanium dioxide (bandgap energy: 3 eV)$^{[13]}$ was obtained from Degussa (P25); it had a BET surface area of 50 ±15 m$^2$ g$^{-1}$ and an average particle diameter of 30 nm. Zinc oxide (bandgap energy: 3.4 eV)$^{[13]}$ was u.s.p. grade from Baker. Suspensions were freshly prepared by sonication (<60 seconds in Bransonic 5200 cleaning bath). The concentrations employed resulted in an absorption of more than 95% of the incident photons at 330 nm. Chloroacetic acid (MCB) contained ±2 mol% of Cl$^-$ as detected by HPIC. All chemicals were of reagent grade and used without further purification. The water employed in all preparations was purified by a Milli–Q/RO system with an attached ORGANEX–Q unit ($\rho$>18 M$\Omega$ cm).
Apparatus

Illumination apparatus and actinometry have been described elsewhere.[14] Typically a volume of 2 ml suspension was illuminated with the collimated beam of an Osram XBO 450 W lamp through a 300 nm UV cutoff and an IR filter. The incident photon flux between 300 and 400 nm was \( I \approx 5 \cdot 10^{-3} \text{ M } h\nu \text{ min}^{-1} \). Reaction temperatures were between 25 and 30 °C.

Hydrogen peroxide concentrations were determined by an enzymatic and a polarographic method. Details have been described elsewhere.[14] Ion Chromatography (HPIC) was performed with a Dionex 2020i instrument (Column: AS4A with AG4 pre-column, eluant: 0.005 M \( \text{Na}_2\text{B}_4\text{O}_7 \), flow rate: 2.0 ml min\(^{-1}\), detection: suppressed conductivity, sample volume: 50 µl). Chloride concentrations were also determined using a chloride sensitive electrode (Orion 94–17). In a typical illumination experiment 25–50 µl aliquots were taken, diluted in 2500 µl of water (in the case of the \( \text{Fe}_2\text{O}_3 \) colloid, 0.5 mM \( \text{NaOH} \) was used to precipitate the colloid) and subsequently analyzed by HPIC. The degradation of volatile chlorinated hydrocarbons was monitored by gas chromatography (HP 5880A Level Four instrument, column: 12m HP–1, isothermal at 35 °C, carrier gas: nitrogen at 1ml min\(^{-1}\), electron capture detector (300 °C). Typically, 10 µl of the headspace of the aqueous sample solutions were injected.
RESULTS AND DISCUSSION

Metal oxide particles such as Fe$_2$O$_3$, ZnO, and TiO$_2$ behave as short-circuited electrochemical cells where both cathodic and anodic electron transfer occur on the same particle. Excitation of the metal oxide (MO) particle with light (hv > $E_{\text{gap}}$) leads to the formation of an electron–hole pair:

$$\text{MO} + \hbar \nu \rightarrow \text{MO}(e_{cb}^- + h_{vb}^+)$$

While electron donors such as acetate fill the photogenerated valence band holes

$$D + h_{vb}^+ \rightarrow D^+$$

the remaining conduction band electrons can reduce oxygen to yield hydrogen peroxide

$$e_{cb}^- + \frac{1}{2} O_2 + H^+ \rightarrow \frac{1}{2} H_2O_2$$

The formation of H$_2$O$_2$ in illuminated aqueous suspensions of ZnO, TiO$_2$, and desert sand has been studied previously.$^{[14]}$ It has been shown that during the initial phase the rate production of H$_2$O$_2$ is given by

$$\frac{d[\text{H}_2\text{O}_2]}{dt} = (\phi_0 - \phi_1[H_2\text{O}_2]) \cdot \frac{d[\text{hv}]_{\text{abs}}}{dt}$$

where $\phi_0$ is the quantum yield for H$_2$O$_2$ formation, $\phi_1$ is the quantum yield for H$_2$O$_2$ degradation, and $d[\text{hv}]_{\text{abs}}/dt$ is the photon flux.$^{[14]}$ A steady state
concentration of \( \text{H}_2\text{O}_2 \), \([\text{H}_2\text{O}_2]_{ss} = \phi_0/\phi_1\), is reached because \( \text{H}_2\text{O}_2 \) itself accepts or donates electrons and is degraded.

No hydrogen peroxide is found when suspensions of \( \alpha-\text{Fe}_2\text{O}_3 \) colloids or powders are illuminated with intense light \( \lambda > 300 \) nm. The upper limit for the quantum yield for \( \text{H}_2\text{O}_2 \) formation is calculated to be \( \phi_0 < 10^{-5} \), considering the amount of photons absorbed and the detection limits of the methods used. The experimental conditions were comparable to the experiments with the other oxides and were varied as follows: \([\alpha-\text{Fe}_2\text{O}_3] = 5 \cdot 10^{-4} \text{--} 1 \cdot 10^{-3} \) M, electron donor: \([\text{isopropanol}] = 1 \) M or \([\text{acetate}] = 10 \) mM, \([\text{O}_2] = 2.3 \cdot 10^{-4} \text{--} 1.3 \cdot 10^{-3} \) M, pH \( 2 - 5 \), ionic strength \( I = 10^{-3} \text{--} 10^{-2} \) M (KCl).

The different behavior of the three oxides can be explained if one takes into account the redox potentials of the conduction band electrons and of individual electron transfer reactions. While the redox potentials of the conduction band for bulk ZnO and TiO\(_2\) electrodes have been reported to be \( E_{cb} = 0.0 \) V and \( E_{cb} = +0.05 \) V, respectively, the corresponding value for \( \alpha-\text{Fe}_2\text{O}_3 \) is \( E_{cb} = +0.3 \) V at pH 2.\(^{[13]} \) The redox potential of photogenerated conduction band electrons in small particles may be somewhat more negative (by ca. 0.1 V) than the redox potential of the conduction band for bulk electrodes due to characteristic size effects.\(^{[15,16]} \)

On the other hand, the reduction of oxygen yielding the hydroperoxy radical is endothermic:

\[
e_{cb^-} + \text{O}_2 + \text{H}^+ \longrightarrow \text{HO}_2^-
\]

In homogeneous solution a value of \( E^0 = \text{ca.} -0.15 \) V (at pH 2) has been given.\(^{[17]} \) This value may be more positive when dioxygen is bound to the surface. It is obvious that the reduction of \( \text{O}_2 \) by a conduction band
electron is most endothermic \((\Delta G^0 = -0.45 \text{ V or } +44 \text{ kJ/mol})\) in the case of \(\alpha-\text{Fe}_2\text{O}_3\). Hence, it is not surprising that the oxygen molecule is not photo-reduced on \(\alpha-\text{Fe}_2\text{O}_3\) particles.

**Photocatalytic oxidation**

Oxidation of organic or inorganic molecules occurs by photogenerated holes or via intermediate \(\text{OH}^*\) radicals after the photogenerated conduction band electrons have reacted with oxygen \((\text{TiO}_2, \text{ZnO})\)\(^{[14]}\) or with ferric ions.\(^{[8,9]}\) It has been shown that the presence of oxygen is necessary for photocatalytic oxidations to occur \(^{[14]}\) or to prevent the reductive dissolution of \(\alpha-\text{Fe}_2\text{O}_3\) particles via \(^{[8,9]}\)

\[
D + \{\alpha-\text{Fe}_2\text{O}_3\}(\text{Fe}^{3+}) + h\nu \rightarrow \{\alpha-\text{Fe}_2\text{O}_3\} + D^+ + \text{Fe}^{3+}_{\text{aq}}
\]

In the present study chloroacetate was chosen as electron donor because its disappearance as well as the formation of its degradation product, chloride, can be detected with accuracy and high sensitivity by HPIC. Over the pH range of this study (pH 5–8) the molecule is negatively charged (\(pK_a= 2.9\)) and is adsorbed to the positively charged particle surfaces, since \(\text{pH}<\text{pH}_{ZPC}\) (pH of zero point of charge).\(^{[18]}\)

Millimolar concentrations of chloroacetate are degraded with the concomitant formation of chloride ions in a 1:1 ratio when aqueous suspensions containing \(\text{ZnO}\) (Fig.1a) or \(\text{TiO}_2\) (Fig.1b) particles are irradiated with UV light. Although the detailed mechanism of such photocatalytic oxidations is still unknown, it has been shown that photocatalytic oxidations of various chlorinated hydrocarbons proceed to complete degradation with quantitative formation of
carbonate, chloride, and protons,\textsuperscript{[19,20]} e. g.

\[ \text{CH}_2\text{ClCO}_2^- + \frac{3}{2} \text{O}_2 + \text{H}_2\text{O} \rightarrow 2 \text{HCO}_3^- + \text{Cl}^- + 2 \text{H}^+ \]

From the slope of the plots (Fig. 1a–b) and the actinometry of the experiment quantum yields of degradation are calculated to be ca. 3% for TiO\(_2\) and 0.1% for ZnO.

Figure 1c shows that illumination of \(\alpha\)-Fe\(_2\)O\(_3\) colloid in the presence of chloroacetate and oxygen does not lead to the release of chloride ions or to a degradation of the organic acid. An upper limit for the quantum yield of degradation of \(\phi<10^{-6}\) can be calculated from the amount of light absorbed after 7 hours of illumination (\(\lambda > 300\) nm) and the variation of the chloride signal (HPIC).

Figure 2 shows how chloroform is degraded when a suspension of TiO\(_2\) particles is illuminated with UV light. The initial quantum yield is found to be 2% in agreement with similar experiments by Pruden et al.\textsuperscript{[21]} The reaction stoichiometry

\[ 2 \text{CHCl}_3 + \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 6 \text{H}^+ + 6 \text{Cl}^- \]

has been confirmed by measuring the chloride production rate,\textsuperscript{[21]} the formation of carbonate,\textsuperscript{[21,22]} the rate of hydroxide consumption at constant pH,\textsuperscript{[22]} and the depletion of oxygen.\textsuperscript{[22]} Under the same experimental conditions, chloroform is not degraded (quantum yield as determined by GC headspace technique \(\phi<<0.1\%\)) and no chloride is formed when \(\alpha\)-Fe\(_2\)O\(_3\) colloids are illuminated in the presence of oxygen. Chloral (\(\text{CCl}_3\text{CH(OH)}_2\)) is a molecule carrying a hydrophilic group which facilitates adsorption to the particle surfaces, however
no photodegradation ($\phi<0.1\%$) of this molecule is found when $\alpha$-$\text{Fe}_2\text{O}_3$ colloids are illuminated with UV light at pH 2.6 ($[\text{CCl}_3\text{CH(OH)}_2]=10^{-4} \text{ M}$).

The absence of photocatalytic activity of $\alpha$-$\text{Fe}_2\text{O}_3$ in the oxidation of such molecules as chloroform, chloroacetic acid, and chloral cannot be explained in terms of the redox potential of the valence band. This oxidation potential is sufficiently positive, i.e. $E_{\text{vb}} = +2.5 \text{ V}$, to oxidize water yielding $\text{OH}^\cdot$ radicals. The $\text{OH}^\cdot$ radicals in turn are known to oxidize all of the above organic molecules. It must be concluded that neither the oxidizing power of a valence band hole nor the intermediate $\text{OH}^\cdot$ radical are available at the surface of a $\alpha$-$\text{Fe}_2\text{O}_3$ particle after light excitation. Kennedy and Frese proposed that two optical absorption processes occur in ferric oxide, one of which leads to a second type of hole, similar to a $\text{Fe}^{4+}$ species, of relatively low oxidizing power.[2] It appears that the presence of the crystal lattice of $\text{Fe}_2\text{O}_3$ provides effective relaxation channels for the excited state.

Our experimental observation that organic molecules such as acetate, chloral or CHCl$_3$ are not oxidized on $\alpha$-$\text{Fe}_2\text{O}_3$ particles does not contradict other reports on the photocatalytic activity of this material.[5,7–9,23,24] Thus, there are reports on the photocatalytic oxidation of sulfite,[9] thiols,[23] and iodide.[24] Note, however that these molecules are much better reducing agents that react easily with ferric ions in the dark.[25–27] Light excitation in these cases helps to overcome relatively small activation energies. In fact, Waite et al.[23] preferred to term the reaction with thiols "photoassisted", as they observed substantial dark reaction rates.

Other "photocatalytic" reactions involve such electron donors as oxalate or citrate that are also strong complexing agents, i.e. they form inner sphere complexes with ferric ions. Pichat and co–workers studied the oxidation of oxalate on (uncharacterized) $\text{Fe}_2\text{O}_3$ specimens.[7] Oxalate is known to be an
excellent complexing agent which may dissolve iron oxide under formation of the ferritrioxalate complex.\cite{28,29}

It is conceivable that the photoactive species is a monomolecular iron complex rather than a $\alpha$–Fe$_2$O$_3$ particle. Faust and Hoffmann\cite{9} showed that while the quantum efficiency of the surface complexes between Fe(III) and S(IV) is high, light absorption is dominated by the $\alpha$–Fe$_2$O$_3$ particles, which are less active. Baxendale and Bridge\cite{30} found that the quantum yield for the photo-oxidation of formate in the presence of Fe$^{3+}$ decreases as the Fe$^{3+}$ concentration is increased. They concluded that polymolecular species were formed which were less reactive.

**Is iron oxide an active photocatalyst?**

Clearly, the answer will depend on the system studied. While TiO$_2$ and ZnO appear to be active photo-oxidation catalysts with virtually any electron donor,\cite{1,14,19–21} $\alpha$–Fe$_2$O$_3$ particles appear to react only with a select set of molecules (i. e., with strong reducing agents, that already react in the dark, and with multidentate ligands). Table 1 summarizes quantum yields for photocatalytic reactions of iron oxide particles obtained from the literature and from this work. In the majority of the studies strongly binding and reducing agents were used as electron donors. While sulfite or oxalate were found to be effectively oxidized, other electron donors such as citrate, benzoate or cyanide did show only little or no activity.

Except for sulfite, oxalate and iodide (cf., however, footnote b, Table 1), very low quantum yields ($3 \cdot 10^{-8} – 5 \cdot 10^{-5}$) were reported for the other molecules. It appears questionable whether such low quantum yields are relevant to environmental processes involving the oxidation of organic molecules since the rate of reaction is proportional to the product of $\phi$ times the concentration of the
semiconductor which is also low. The present study did not detect any photocatalytic activity of $\alpha$–Fe$_2$O$_3$ particles $\phi << 10^{-5}...10^{-3}$ (experimental resolution) in the oxidation of "normal" organic molecules (i.e. molecules, that are not particularly strong reducing or complexing agents).
Table 1: Photocatalytic activity of iron oxide particles

<table>
<thead>
<tr>
<th>Material</th>
<th>Quantum yield</th>
<th>System studied</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\alpha-\text{Fe}_2\text{O}_3)</td>
<td>0.027</td>
<td>Fe(II) production in the presence of sulfite at 350 nm</td>
<td>9</td>
</tr>
<tr>
<td>(\alpha-\text{Fe}_2\text{O}_3)</td>
<td>100(^a)</td>
<td>sulfite oxidation</td>
<td>4</td>
</tr>
<tr>
<td>(\gamma-\text{Fe}_2\text{O}_3)</td>
<td>60(^a)</td>
<td></td>
<td>4</td>
</tr>
<tr>
<td>(\delta-\text{FeOOH})</td>
<td>14(^a)</td>
<td></td>
<td>4</td>
</tr>
<tr>
<td>(\beta-\text{FeOOH})</td>
<td>11(^a)</td>
<td></td>
<td>4</td>
</tr>
<tr>
<td>(\gamma-\text{FeOOH})</td>
<td>124(^a)</td>
<td></td>
<td>4</td>
</tr>
<tr>
<td>(\alpha-\text{FeOOH})</td>
<td>6(^a)</td>
<td></td>
<td>4</td>
</tr>
<tr>
<td>(\alpha-\text{Fe}_2\text{O}_3)</td>
<td>3(^a)</td>
<td>oxidation of oxalate</td>
<td>4</td>
</tr>
<tr>
<td>(\gamma-\text{Fe}_2\text{O}_3)</td>
<td>41(^a)</td>
<td></td>
<td>4</td>
</tr>
<tr>
<td>(\delta-\text{FeOOH})</td>
<td>11(^a)</td>
<td></td>
<td>4</td>
</tr>
<tr>
<td>(\beta-\text{FeOOH})</td>
<td>10(^a)</td>
<td></td>
<td>4</td>
</tr>
<tr>
<td>(\gamma-\text{FeOOH})</td>
<td>29(^a)</td>
<td></td>
<td>4</td>
</tr>
<tr>
<td>(\alpha-\text{FeOOH})</td>
<td>6(^a)</td>
<td></td>
<td>4</td>
</tr>
<tr>
<td>(\text{Fe}_2\text{O}_3)</td>
<td>active</td>
<td>oxidation of oxalate</td>
<td>7</td>
</tr>
<tr>
<td>(\alpha-\text{FeOOH})</td>
<td>0.8(^b)</td>
<td>oxidation of iodide by laser photolysis</td>
<td>24</td>
</tr>
<tr>
<td>(\alpha-\text{FeOOH})</td>
<td>(3 \times 10^{-8} - 2 \times 10^{-5})</td>
<td>formation of salicylate by oxidation of benzoate</td>
<td>6</td>
</tr>
<tr>
<td>(\alpha-\text{Fe}_2\text{O}_3)</td>
<td>enhanced dissolution of (\alpha-\text{Fe}_2\text{O}_3) in the presence of thiols</td>
<td>23</td>
<td></td>
</tr>
<tr>
<td>(\gamma-\text{Fe}_2\text{O}_3)</td>
<td>(3 \times 10^{-5})</td>
<td>dissolution with citrate</td>
<td>8</td>
</tr>
<tr>
<td>(\alpha-\text{Fe}_2\text{O}_3)</td>
<td>no activity</td>
<td>oxidation of polyacrylic acid, formation of CO(_2)</td>
<td>10</td>
</tr>
<tr>
<td>(\alpha-\text{Fe}_2\text{O}_3)</td>
<td>no activity</td>
<td>oxidation of cyanide</td>
<td>5</td>
</tr>
<tr>
<td>(\alpha-\text{Fe}_2\text{O}_3)</td>
<td>no activity</td>
<td>oxidation of chloroacetate, chloroform and chloral</td>
<td>this work</td>
</tr>
<tr>
<td>(\alpha-\text{Fe}_2\text{O}_3)</td>
<td>no activity</td>
<td>formation of H(_2)O(_2)</td>
<td>this work</td>
</tr>
</tbody>
</table>

\(^a\) Relative quantum yields calculated from pseudo–first–order rate constants given in Table 1 of ref. 4

\(^b\) The authors of ref. 4, however, find equal yields of iodide oxidation in presence and absence of \(\alpha-\text{Fe}_2\text{O}_3\).
FIGURE CAPTIONS

Figure 1: Photocatalytic degradation of chloroacetate with concomitant formation of chloride in aqueous suspensions of metal oxides.

a) $2 \cdot 10^{-2}$ M ZnO powder, pH 8, air, UV light (300–400 nm) with $I \approx 5 \cdot 10^{-3}$ M $h\nu$ min$^{-1}$; b) $6.3 \cdot 10^{-3}$ M TiO$_2$ (P25) powder, pH 5, air, UV light; c) $1 \cdot 10^{-3}$ M $\alpha$-Fe$_2$O$_3$ colloid, pH 5, air, full lamp spectrum.

Figure 2: Photocatalytic degradation of chloroform in the presence of aqueous TiO$_2$ powder (P25, $6.3 \cdot 10^{-3}$ M, pH 5, air).
REFERENCES

b) Harriman, A. in Photochemistry, Bryce-Smith, D.; Gilbert, A.; Eds. Royal Society of Chemistry, London: 1988, Vol. 19, pp 509–542. Since it is not the purpose of this paper to review this abundant literature, only two references are proposed.


Figure 1a
Figure 1b
Figure 1c
Figure 2
Chapter 7

ON THE REACTIVITY OF THE OXIDIZING SPECIES GENERATED BY PHOTOEXCITED TiO$_2$ PARTICLES IN AQUEOUS SUSPENSION.
INTRODUCTION

Over the past 15 years there has been an active interest in the photoelectrochemistry of small semiconductor oxide particles (cf. references in the preceding chapters). While the photo-reduction process is thought to occur through electrons from the conduction band or from trapped states, there is still an ongoing controversy about the nature and reactivity of the oxidation process. To distinguish between oxidation of solute molecules by photogenerated holes or by intermediate OH• radicals is a subtle point in the discussion of the photoelectrochemistry of metal oxide particles. So far, only few studies concentrated on the mechanistic details of photo-oxidations by these materials. Some authors have obtained evidence for direct hole transfer, others have postulated that the active species is the OH• radical. The OH• radical may be generated from a hole reacting with surficial hydroxide, =TiOH, which involves subsequent substitution of the OH• by OH− at the Ti center.

\[
\text{OH}^− + h^+_\text{vb} \rightarrow \text{OH}•
\]  

(1)

Alternatively, an outer-sphere electron transfer may occur between an oxidized =TiO• site and hydroxide concentrated within the electrical double layer, =TiOH2+:OH−, adjacent to the charged metal oxide surface. In addition OH• radicals may be generated by reduction of O2 with conduction band electrons. In this reaction O2−/HO2 and H2O2 are expected intermediates. However, H2O2 was found to be efficiently degraded by oxidation (formation of O2). It was found to inhibit the oxidation of organic molecules such as methyl orange as it is oxidized itself. Hence, the formation of OH• radicals by reduction of O2 appears to be unlikely.
Research in this laboratory has provided strong evidence for oxidations occurring by \( \text{OH}^\cdot \) radicals at pH > pH_{zpc} (pH of zero point of charge) but it cannot rule out that some of the observed oxidation rate is due to direct electron transfer from the organic donor molecule, e.g., acetate, to the hole at the particle surface.

We decided to study the oxidative degradation of acetate molecules in illuminated aqueous suspensions of TiO\(_2\). Acetate is an ideal molecule because it can undergo two different reaction pathways depending on whether it is oxidized by an \( \text{OH}^\cdot \) radical or whether its carboxylate moiety transfers an electron to a valence band hole.

We furthermore studied the rate of oxidation of organic anions and cations as a function of pH. While the oxidative degradation of anions such as acetate as a function of pH has been reported several times \(^1,^7\) the oxidative degradation of cations has not been examined in detail. The observed pH dependence of the rate of acetate oxidation was explained in terms of band shifting of the valence band \( E_{vb} = +2.79 - 0.059 \cdot \text{pH} \) [V vs. NHE].\(^7\) The effect of surface adsorption was ignored, however. Bahnemann et al. who studied the oxidation of MV\(^{2+}\) (methylviologen) obtained evidence for \( \text{OH}^\cdot \) radical reactivity at pH 11.5.\(^4\)

Our experimental findings cannot be explained with the conventional electrochemical and solid state expressions (e.g., the Nernst equation of the flat band potential). It is found that the effect of surface adsorption of the reactant molecules to the oxide surface is a predominant factor in the electrochemical reactivity of TiO\(_2\) particles.
Background

The reaction of acetate with OH\(^{•}\) radicals has been studied by Neta et al.\(^{[8]}\) and by von Sonntag and co-workers\(^{[9]}\) using gamma- and pulse- radiolysis. The OH\(^{•}\) radicals react with acetate only \(^{[9]}\) via abstraction of a hydrogen atom:

\[
\text{CH}_3\text{CO}_2^- + \text{OH}^{•} \rightarrow \text{CH}_2\text{CO}_2^{•} \rightarrow \text{products}
\]

In aerated solutions oxygen adds rapidly to the \(\cdot\text{CH}_2\text{CO}_2\) radicals to give the corresponding peroxyl radicals which then react with each other to yield the final products. A complete material balance has been achieved for the OH\(^{•}\) reactions with acetate and the resultant products.\(^{[9]}\) Glyoxylate and glycolate were found to be the principal products in a ratio of 2.7 : 0.7 at pH 7.8; formation of formate was not observed.

On the other hand, acetate can be selectively oxidized by electron transfer from the carboxylate group:\(^{[10]}\)

\[
\text{CH}_3\text{CO}_2^- \xrightarrow{\text{ox}} \text{CH}_3\text{CO}_2^{•} \rightarrow \text{O}_2 \rightarrow \text{products}
\]

As a consequence, a different product spectrum is obtained.\(^{[12]}\) In this case formate is produced but no glyoxylate or glycolate.

In conclusion, it can be stated that the product spectrum for CH\(_3\)CO\(_2\)^{•} photo-oxidation on semiconductor surfaces will depend on the reaction pathways that are actually followed (i.e. either reaction with OH\(^{•}\) or h\(_{\text{vb}}\)).
EXPERIMENTAL

Materials, experimental methods and instruments, e.g. the irradiation apparatus have been described previously (cf. preceding Chapters). Trichloroacetic acid (Mallinckrodt) and chloroethylammonium hydrochloride (Aldrich) were used as received. The photo-degradation of acetate was performed by illuminating 2mL aliquots in a 1cm quartz cuvet with light λ> 300 nm.

A pH-stat titration technique was employed to determine the rates of degradation of organic molecules via the rates of OH⁻ consumption. The quantitative degradation (oxidation) of chlorinated hydrocarbon molecules \( C_xH_yCl_z \) according to

\[
C_xH_yCl_z + (x + \frac{y-z}{4}) O_2 \rightarrow x CO_2 + z HCl + (\frac{y-z}{2}) H_2O
\]  

leads to the formation of \( z \) protons which tend to decrease the pH. The autotitration system adds precisely \( z \) molecules of OH⁻ to keep the pH constant, while a computer records the derivative of the amount \( z \) with respect to time. The Radiometer autotitration system consisted of a pHM84 pH meter, a TTT80 titrator, and a ABU80 autoburet which was interfaced with an IBM PC-AT computer (An 8253–5 programmable timer on a MBC DASH–8 card was used to count pulses from the ABU80). The titrant solution (0.2 N NaOH) was kept under Ar gas and was calibrated with 0.100 N HCl (Baker Analyzed). The pH-stat reactor contained 100 mL of TiO₂ suspension (0.5 g/l) which was stirred and bubbled with oxygen; the actinometry (300 nm <λ< 400 nm) was \( I \approx 10^{-4} \) M hν min⁻¹. At \( pH \geq 9 \) a low rate of hydroxide consumption was observed when suspensions of TiO₂ were illuminated in the absence of added organic molecules or when suspensions containing electron donors were stirred in the dark (or in
yellow light $\lambda>500$ nm). This was due to $\text{CO}_2$ scavenging; its contribution has been factored into the analysis. At $\text{pH}<9$ no hydroxide consumption due to oxidation of organic molecules was observed in suspensions of TiO$_2$ in the dark (or in yellow light $\lambda>500$ nm).

Ion exclusion chromatography was achieved with a Dionex 2000i HPIC equipped with a HPICE–AS1 separator column, a Ag/AgCl suppressor, and a conductivity detector. The eluent was 2.5 mM HCl.
RESULTS AND DISCUSSION

When suspensions of TiO$_2$ particles ([TiO$_2$] = 0.5 g/l, pH 11, [acetate] = 2 mM, [chloroacetate] = 1 mM) are illuminated with near UV light in the presence of air the quantitative degradation of the organic molecules can be observed readily (initial quantum yield: ca. 0.6%). The disappearance of chloroacetate has been shown to occur with a concomitant release of chloride ions in a 1 : 1 ratio (Chapter 6). The overall reaction stoichiometry is:

$$\text{CH}_3\text{CO}_2^- + 2 \text{O}_2 \xrightarrow{T\text{iO}_2/h\nu} 2 \text{CO}_3^{2-} + 3 \text{H}^+ \quad (5)$$

and

$$\text{CH}_2\text{ClCO}_2^- + \frac{1}{2} \text{O}_2 + \text{H}_2\text{O} \xrightarrow{T\text{iO}_2/h\nu} 2 \text{CO}_3^{2-} + \text{Cl}^- + 4 \text{H}^+ \quad (6)$$

Glyoxylate, glycolate, and formate were found in a ratio 1 : 1 : 5 with an overall quantum yield of ≈0.3%. The production of glyoxylate and glycolate is taken as evidence for oxidation via OH$^\bullet$. However, the production of formate does not indicate unambiguously that some oxidation occurs via h$_{vb}$, because formate can also be formed via the oxidation of formaldehyde (which is a by-product in the reaction sequence of eqn 2).

Since the quantum yield of product formation is lower than the quantum yield of acetate degradation and the ratio of glyoxylate to glycolate is 1 : 1 instead of 2.7 : 0.7, it must be concluded that other mechanisms than those outlined in eqns 2–3 are operative. One likely possibility is that the intermediate peroxyl radicals are stabilized on the particle surface where they are
photodegraded before they can dimerize and fragment:

$$\text{CH}_3\text{CO}_2^- + \text{OH}^*_{\text{surf}} \rightarrow \cdot\text{CH}_2\text{CO}_2\cdot_{\text{surf}}$$ (7)

$$\cdot\text{CH}_2\text{CO}_2\cdot_{\text{surf}} + \text{O}_2 \rightarrow \cdot\text{O}_2\text{CH}_2\text{CO}_2\cdot_{\text{surf}}$$ (8)

$$\cdot\text{O}_2\text{CH}_2\text{CO}_2\cdot_{\text{surf}} + 3 \text{OH}^*_{\text{surf}} \rightarrow 2 \text{HCO}_3^- + \text{H}^+ + \text{H}_2\text{O}$$ (9)

Similar surface stabilization effects have been observed previously in related systems. [12]

It is surprising that the photodegradation of acetate and chloroacetate occurs at all at pH 11. At this pH the particle surfaces are negatively charged due to the following surficial acid–base equilibria:[13–14]

$$\equiv\text{TiOH}_2^* \rightleftharpoons \equiv\text{TiO}^- + \text{H}^+ \quad \text{pK}_a1 = 4.5$$ (10)

$$\equiv\text{TiOH} \rightleftharpoons \equiv\text{TiO}^- + \text{H}^+ \quad \text{pK}_a2 = 8.0$$ (11)

Since pH 11 > pH_{zpc} (pH of zero point of charge; pH_{zpc} = ½ (pK_a1+pK_a2); TiO_2: pH_{zpc} = 6.25) the particle surfaces will be negatively charged and electrostatic repulsion will prevent the adsorption of acetate molecules. Adsorption to the particle, however, is a prerequisite for hole scavenging. Using the SURFEQL computer code described below the concentration of the Ti–acetate surface species is calculated to be less than 10^{-12} M. Matthews who studied the hydroxylation of benzoate in illuminated suspensions of TiO_2 found enhanced rates of oxidation at alkaline pH where benzoate is not expected to be bound to the surface.[13] It must be concluded that an oxidizing agent (i.e. the
OH• radical) diffuses away from the surface and oxidizes acetate in the homogeneous solution.

At pH < pH_{zpc} this argument does not hold. When an aerated suspension of TiO_2 is illuminated in the presence of acetate at pH 5.6 only low concentrations of formate (quantum yield ca 0.4%) are formed. Thus a different mechanism appears to be operative, e.g. oxidation of acetate by holes and/or a very efficient degradation of the surface stabilized intermediates of eqns 2–3.

The rate of photo-oxidation of organic molecules in illuminated oxygenated suspensions of TiO_2 can be studied conveniently using the pH-stat titration technique. The oxidation of trichloroacetate (pK_a = 0.66), for instance, leads to the quantitative formation of CO_2, protons and chloride according to:

\[
\text{CCl}_3\text{CO}_2^- + \frac{1}{2} \text{O}_2 + \text{H}_2\text{O} \xrightarrow{\text{TiO}_2} 2 \text{CO}_2^- + 2 \text{H}^+ + 3 \text{Cl}^- \quad (12)
\]

Quantitative degradation of chlorinated hydrocarbons in illuminated suspensions of TiO_2 yielding CO_2 and chloride has been shown to occur in a large number of cases.\textsuperscript{[15–16]} The CO_2 will be present as HCO_3^- at 6.3 < pH < 10.3 and as CO_3^{2-} at pH > 10.3 Thus, depending on the pH of the suspension n(pH) = 2–6 molecules of OH^- need to be added for each molecule of CCl_3CO_2^- that is oxidized in order to maintain the pH constant:

\[
n(pH) = 2 + \frac{2}{1+10^{(6.3-pH)}} + \frac{2}{1+10^{(10.3-pH)}} \quad (13)
\]

The rate of chloroacetate degradation is then given by the rate of hydroxide consumption divided by n(pH).
Likewise, the rate of oxidation of chloroethylammonium ions according to

\[
\text{CH}_2\text{ClCH}_2\text{NH}_3^+ + 4\frac{1}{2} \text{O}_2 \xrightleftharpoons[\frac{h}{\nu}]{\text{TiO}_2} 2 \text{CO}_2 + 3 \text{H}^+ + \text{Cl}^- + \text{NO}_3^- + 2 \text{H}_2\text{O} \quad (14)
\]

can be studied at pH < 9 (pK_a ≈ 9 is the estimated stability constant for the chloroethylammonium ion in water).

Figure 1 shows the rates of degradation of trichloroacetate and of chloroethylammonium ions (10 mM concentrations, respectively) as function of the pH. The rate of degradation of trichloroacetate is highest at low pH. Contrary to acetate and the other chloroacetates, the rate of oxidation of the trichloro derivative approaches zero as the pH → pH_{pc} (6.2) of TiO_2. This observation yields further evidence for the hypothesis that OH• radicals diffuse away from the negatively charged TiO_2 surface to oxidize anions in the bulk of the solution. All acetates with a CH bond are susceptible to hydrogen abstraction by the OH• radical. CCl_3CO_2^- has no CH bond and does not react with the OH• radical. On the other hand, at low pH the trichloroacetate molecule is bound to the oxide surface via its carboxylate moiety which can donate its electron to a photogenerated valence band hole according to

\[
\text{CCl}_3\text{CO}_2^- + h^+_b \longrightarrow \text{CCl}_3\text{CO}_2^* \longrightarrow \text{CCl}_3^* + \text{CO}_2 \quad (15)
\]

The carboxyradical will loose CO_2 yielding the CCl_3* radical that is susceptible to further degradation reactions.

The rate of degradation of the cation (chloroethylammonium) is zero at pH 3. It reaches a maximum at pH≈ 8. At pH≥9 a substantial release of acidity due to a dark reaction of the molecule —presumably an intramolecular cyclization associated with the deprotonation of the amino group— becomes
noticeable. The observed rate of oxidation at pH 9 is corrected for this dark effect (≈25%). Only a negligible release of acidity is observed when a solution (10 mM) of chloroethylammonium hydrochloride is illuminated in the absence of TiO$_2$ at pH 7.7.

The enhanced rate of oxidation of cations at alkaline pH cannot be explained by a shift of the Fermi level of the semiconductor particles. In fact, the opposite behavior would be expected (i.e., lower rates of oxidation at high pH). Surface adsorption of the electron donor to the oxide particles appears to play a dominant role in the photoactivity of the catalyst.

Under our experimental conditions only one photon is absorbed per particle per ≈4 milliseconds,

$$\text{TiO}_2 + h\nu \rightarrow \tau = 4 \text{msec} \rightarrow h_{vb}^* + e_{vb}^* \quad (15)$$

hence no significant accumulation of minority carriers (holes or surface OH$^\bullet$) will occur. Fast trapping of valence band holes as surficial hydroxyl radicals (OH$^\bullet_{\text{surf}}$) has been postulated:[6]

$$h_{vb}^* + \text{OH}_{\text{surf}} \rightarrow \text{OH}_{\text{surf}}^\bullet \quad (16)$$

Regardless of whether the excited state is described in terms of an electron–hole pair or an electron–surface hydroxyl radical pair, it is likely to be very short lived due to the well established reducing properties of the electron $^{[17]}$ and the strongly oxidizing properties of both the hole or the surface state.$^{[6]}$ The net result is that recombination will be first order for the minority carriers. The
half life of the electron hole pair has been found to be \((30\pm15)\) ns for TiO\(_2\) particles:\[18\]

\[
\begin{align*}
h_{vb}^* + e_{vb} & \xrightarrow{k_{rec}} \text{heat} \\
k_{rec} & \approx 3 \cdot 10^7 \text{ s}^{-1}
\end{align*}
\]

(17)

It is assumed that the rate determining step in the photo oxidation of organic molecules is the initial irreversible electron transfer/ hydrogen abstraction at the surface of the particle according to

\[
h_{vb}^* \text{ or } \text{OH}_{surf}^\bullet + D_{surf} \xrightarrow{k_{ox}} D^*
\]

(18)

In this treatment photo oxidations of the donor will be efficient if \(k_{ox}[D_{surf}] > k_{rec}\). On the other hand, if the concentration of organic molecules at or near the surface is too low because of electrostatic repulsion between a charged surface and the charged donor, the catalyst will become deactivated before oxidizing the donor.

The observed rate dependence of the oxidation of anions or cations in illuminated suspensions of TiO\(_2\) particles can be modeled using the SURFEQL computer code that was developed to perform equilibrium calculations of surface speciation.\[19\]

Figure 2a shows the surface speciation and the concentration of the complex between the TiO\(_2\) surface and trichloroacetate as a function of pH assuming the following stoichiometry:

\[
\begin{align*}
\equiv \text{TiOH} + H^+ + \text{Ac}^- & \quad K_{ac} \quad \equiv \text{TiAc} + \text{H}_2\text{O}
\end{align*}
\]

(19)
where $K_{ac} \approx 10^4 \text{ M}^{-2}$ [20]. The concentration of the surface complex increases steadily below pH 5 in agreement with the observed increase of the rate of degradation of the molecule (cf Figure 1). At pH 11 the concentration of the surface complex is found to be $10^{-12}$ M.

Figure 2b shows the surface concentration of the complex between the TiO$_2$ surface and the organic ammonium ion according to

$$\equiv TiOH + H^+ + RNH_2 \xrightleftharpoons{K_{am^+}} \equiv TiRNH_2^+ + H_2O$$ (20)

where $K_{am^+} = 10^{9-5} \text{ M}^{-2}$.[20]

The concentration of the surface complex increases at pH $> 4$ and reaches a maximum at pH $\approx 9$ corresponding to the pK$_a$ of the ammonium ion. Comparison with the experimental rate of oxidation of the molecule in an illuminated suspension of TiO$_2$ (cf. Figure 1) shows good qualitative agreement.

A quantitative agreement is not expected since the photo-oxidation process depends on additional factors such as the efficiency of the charge separation process, that are likely to depend on the pH and on the surface charge. For instance, Bahnemann et al.[21] have found that hole scavenging becomes less efficient at low pH as repulsion of the hole from the positively charged surface leads to an enhanced recombination with the electron in the interior of the particle.
REFERENCES


FIGURE CAPTIONS

Figure 1  
**pH Dependence of the rate of degradation of trichloroacetate (+) and chloroethylammonium (Δ) ions in illuminated suspensions of TiO₂ (0.5 g/L). Actinometry (300 nm–400nm) I ∼10⁻⁴ Einstein l⁻¹ min⁻¹.**

Surface speciation of TiO₂ particles (P25, 0.5 g/L) in the presence of 10 mM concentrations of
a) trichloroacetate, solid line: =Ti–CO₂CCl₃  
b) chloroethylamine, solid line: =Ti⁺NH₂CH₂CH₂Cl

Calculated using the SURFEQL computer code (diffuse layer model, ionic strength: 0.01, pKₐ₁=4.5, pKₐ₂=8.0, surface area = 50 m²g⁻¹). For further details see text.

+ : =TiOH₂⁺  
○ : =TiOH  
Δ : =TiO⁻
Figure 1
Figure 2a

---

- **-** : \(\equiv\text{Ti-}\text{CO}_2\text{CCl}_3\)
- **+** : \(\equiv\text{TiOH}_2^+\)
- **o** : \(\equiv\text{TiOH}\)
- **△** : \(\equiv\text{TiO}^-\)
Figure 2b

---

: $\equiv\text{Ti}^2\equiv\text{NH}_2\text{CH}_2\text{CH}_2\text{Cl}$

+ : $\equiv\text{TiOH}_2^+$

○ : $\equiv\text{TiOH}$

△ : $\equiv\text{TiO}^-$
RECOMMENDATIONS FOR FUTURE RESEARCH

In this thesis synthetic methods have been described to prepare ultrasmall colloidal oxide particles of ZnO, TiO$_2$, and $\alpha$-Fe$_2$O$_3$. Other oxide materials can also be prepared in a highly dispersed form. Two recent articles have pointed out the necessity to synthesize novel ceramic materials that encompass not only advantageous properties such as chemical resistivity, hardness, wear resistance, high melting temperature, low density, low price, but also plasticity and ductility.[1–2] Karch et al. observed substantial plasticity, at 80–180 °C, of "nanocrystalline"* TiO$_2$ (made by oxidation of nanocrystalline titanium, average crystal size: $\approx 8$ nm).[1] This could be explained by diffusion creep. Cations and anions diffuse from the compressed to the stretched side of each grain, round an intergranular circuit, thereby changing the shape of the grain. The authors estimated that the reduction of the crystal size from 10 $\mu$m (in conventional ceramics) to $\approx 10$ nm improves the strain rate by a factor of $10^9$, and the self–diffusivity by a factor of $10^3$. [1]

While the common method of preparation of nanocrystalline ceramic materials is costly and energy intensive, as inert gas atmospheres, high vacuum, and very low temperatures (77K) are required, alternative syntheses of substantial quantities (g to kg amounts) of nanocrystalline material at fairly low cost (see, for example, Chapter 3 of this thesis) can be achieved.

* A nanocrystalline material is defined as a polycrystalline material whose crystal size is of the order of a few (1–10) nm.[1]
This thesis has also described numerous photochemical experiments: the photocatalytic formation and degradation of H$_2$O$_2$ and organic peroxides, the degradation of chlorinated hydrocarbons using aqueous suspensions of TiO$_2$ and ZnO. One of the most promising applications of these catalysts is the degradation of toxic molecules (e.g. chlorinated hydrocarbons, or even NO$_3$) by using inexpensive sunlight. Several workers have already made important contributions to this field,[3-4] yet there need to be further studies to unravel mechanistic details of these photodegradation reactions and subsequent demonstrations of practicable feasibility. The transparent colloidal materials prepared as a part of this thesis research lend themselves ideally to mechanistic studies using fast optical techniques.

The efficiency of photocatalytic and photosynthetic reactions of metal oxide particles is dependent on and limited by the rather short lifetime of the excited state. Efficient relaxation channels are provided by fluorescence and radiationless transitions (ZnO, bandgap fluorescence: $\tau_\frac{1}{2}$<50 ps, surface fluorescence $\tau_\frac{1}{2}$<20 ns (Chapter 2); TiO$_2$ lifetime of an electron hole pair $\tau_\frac{1}{2}$~20 ns [5]).

Recently Hong et al. described a catalyst based on TiO$_2$ particles to which an electron relay (Co-Tetrasulfophtalocyanine) was covalently bound (Caltech Thesis, Andrew P. Hong, 1987; see also Chapter 5 of this thesis). A significant enhancement of the rate of electron transfer to oxygen was found, and enhanced rates of oxidation were postulated. It thus appears very promising to modify the colloidal catalysts prepared in this thesis research in a similar fashion in order to obtain more efficient charge separation. In view of the fact that OH$^*$ radicals are generated upon photoexcitation of TiO$_2$ particles (Chapter 7), the attached electron relay must be resistant to oxidation by this species. It is anticipated that by preparing perchlorinated or perfluorinated electron relays, this problem can be solved.
REFERENCES


