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Ferrous Hemin Oxidation by Organic Halides at Nanocrystalline TiO₂ Interfaces

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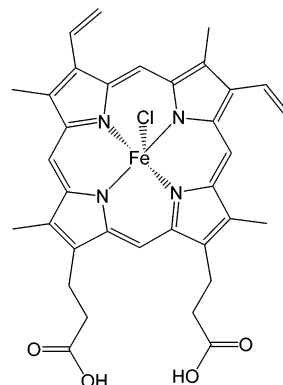
Received May 29, 2003; Revised Manuscript Received June 19, 2003

ABSTRACT

The photoreduction of organic halides CCl₄, CBr₄, and CHCl₃ and chloroacetanilides alachlor (2-chloro-2',6'-diethyl-*N*-(methoxymethyl)acetanilide) and propachlor (2-chloro-*N*-isopropylacetanilide) by iron(III) protoporphyrin IX chloride (hemin) in fluid solution and anchored to a mesoporous nanocrystalline (anatase) TiO₂ thin film immersed in solution is reported. Band gap illumination resulted in the reduction of Fe(III) to Fe(II) when the films were immersed in acidic water (pH 4) and in dimethyl sulfoxide with photochemical quantum yields of $(2.0 \pm 0.3) \times 10^{-3}$ and $(1.6 \pm 0.3) \times 10^{-2}$, respectively. The ferrous hemes were reacted with organic halides in the dark. Second-order kinetic rate constants were quantified and were found to be larger than the corresponding rate constants for ferrous hemin in fluid solution.

Organic halides can present serious health risks, and their prevalence in groundwater is of considerable environmental concern. Many organic halides have been present in groundwater for decades, but others, such as chloroacetanilide herbicides, continue to be introduced.^{1–3} The remediation of organic halide (RX) pollutants by inorganic solids and molecular compounds has been reported in the literature.^{3–14} Inorganic solids, such as iron particles, are often reactive toward RX, but the reaction chemistry generally leads to distributions of products.^{3–6} A potential advantage of molecular compounds is that they can be fine-tuned to react selectively with specific pollutants to yield desired environmentally benign products. However, molecular RX catalysts are generally active only in highly reduced^{7–11} (or oxidized)^{12–14} states, and it is unclear how this state can be maintained in the environment. In principle, the oxidation state of molecular catalysts can be controlled electrochemically or photochemically if they are supported on an appropriate inorganic material. If the support material is also catalytic toward RX, one could potentially take advantage of the specificity of molecular catalysts and the redox stability of the solid-state material to produce hybrid molecular-material catalysts that are more active than the individual parts.

In this letter, we report the reduction of organic halides by ferrous hemin anchored to nanocrystalline TiO₂ thin films. The ferrous state was generated through band gap illumination of the hemin-modified semiconductor. We indeed find that the reactivity of hemin/TiO₂ exceeds that of hemin or TiO₂ alone.



Iron (III) protoporphyrin IX chloride (hemin)

Organic halides CCl₄, CBr₄, and CHCl₃ and chloroacetanilides alachlor (2-chloro-2',6'-diethyl-*N*-(methoxymethyl)acetanilide) and propachlor (2-chloro-*N*-isopropylacetanilide) were used as received. Titanium(IV) isopropoxide and iron(III) protoporphyrin IX chloride (hemin) were obtained from Aldrich Chemical Co., and L-cysteine was obtained from Avocado Research Chemicals. All solvents were of HPLC grade and were obtained from Fisher Scientific.

Transparent TiO₂ films consisting of ~10-nm-diameter TiO₂ anatase particles were prepared by the hydrolysis of Ti(iOPr)₄ using a sol–gel technique as described previously in the literature.¹⁵ The attachment of hemin to the TiO₂ surface was achieved by soaking the TiO₂ films for 24 h in an 8 μM hemin solution in DMSO. The concentration of hemin adsorbed on the TiO₂ surface was typically ~2 μM.

The nanocrystalline thin films were placed diagonally in a standard quartz cuvette. Absorption spectra and steady-

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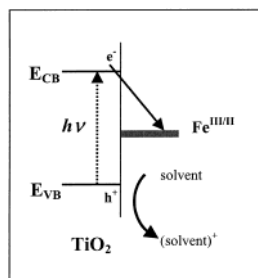


Figure 1. Schematic representation of the proposed mechanism for hemin photoreduction on TiO₂.

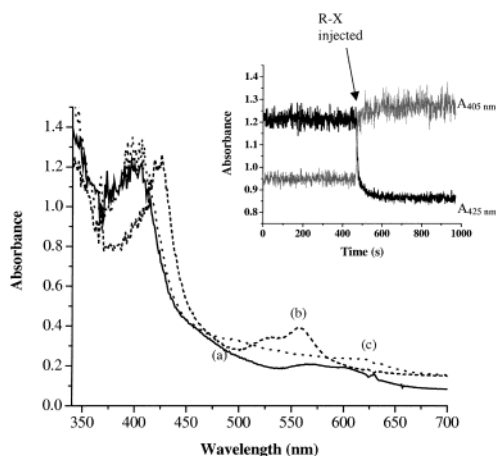


Figure 2. UV-visible absorbance spectra of (a) hemin on TiO₂ surface (—) and (b) after 10 min of irradiation, producing ferrous Fe(II) hemin (---). Spectra (c) was obtained after adding RX to the ferrous hemin/TiO₂ (···). The inset shows time-resolved absorbance changes monitored at 405 nm and at 425 nm following the addition of RX. Note that the S/N ratio is significantly low at $\lambda < 400$ nm because of the fundamental TiO₂ absorption.

state kinetic measurements were acquired using a Cary 50 UV-visible spectrophotometer. Irradiations of hemin/TiO₂ films or hemin in solution were carried out using a 1000-W Xe lamp with a KV 370 filter. In each case, samples were illuminated for 15 min.

The attachment of hemin to the nanocrystalline TiO₂ particles produced a dark-orange film with a UV-visible absorption spectrum that was within experimental error the same as that for free hemin in solution.^{16–19} Band gap illumination in nitrogen-saturated DMSO (or H₂O pH 4) generated the absorption spectrum expected for the ferrous (Fe(II)) hemin (Figure 2).¹⁹ The Fe(II) oxidation-state assignment was established on the basis of comparisons with the literature and the spectrum of hemin following chemical or photochemical reduction in fluid solution. Steady-state actinometry measurements were used to calculate photochemical quantum yields of $(2.0 \pm 0.3) \times 10^{-3}$ and $(1.6 \pm 0.3) \times 10^{-2}$ in acidic water and dimethyl sulfoxide (DMSO), respectively. The quantum yield is defined as moles of Fe(III) consumed divided by moles of photons absorbed. The photogenerated ferrous hemin/TiO₂ was stable in the dark for days.

A proposed mechanism for the hemin photoreduction is shown in Figure 1. We note that similar mechanisms have been proposed in the literature for molecular compounds on TiO₂ interfaces^{20–22} as well as Fe(III)-doped TiO₂.^{23,24} Band

Table 1. Rate Constants for RX Reduction by Ferrous Hemin^a

RX	k (DMSO) (M ⁻¹ s ⁻¹)	k (TiO ₂ surface) (M ⁻¹ s ⁻¹)
CBBr ₄	50.31 ± 0.06	64 ± 2
CCl ₄	0.031 ± 0.003	0.06 ± 0.01
CHCl ₃	> 4 days	0.009 ± 0.002
propachlor	0.0100 ± 0.0003	0.040 ± 0.007
alachlor	> 4 days	0.010 ± 0.003

^a All measurements were made at room temperature in DMSO. The errors represent standard deviations from multiple trials.

gap excitation produces an electron–hole pair. The conduction band electron reduces ferric hemin to ferrous hemin, and the valence-band hole oxidizes solvent. Prolonged irradiation after the ferric hemin was quantitatively reduced to ferrous hemin did not yield the well-known absorption of reduced TiO₂, and no further absorption changes were observed.²⁵ This suggests that the ferrous hemin mediates electron–hole pair recombination in TiO₂.

An alternative mechanism with literature precedence is that UV excitation of ferric porphyrins promotes homolytic cleavage of the Fe–Cl bond, leading to ferrous porphyrins and the Cl• radical.^{18,26–29} This mechanism is not favored upon the basis of the relatively high quantum yields measured for hemin photoreduction on TiO₂. We and others find that the photoreduction quantum yields for ferric hemes in fluid solution are more than 2 orders of magnitude smaller.^{28,29} In fact, irradiation conditions sufficient to photoreduce all hemin/TiO₂ resulted in no measurable production of ferrous hemin in DMSO. The quantum yield for hemin photoreduction in DMSO was determined to be $(2.3 \pm 0.6) \times 10^{-6}$.

The reaction of ferrous hemin with RX pollutants was examined. These reactions were studied in the dark by the addition of RX to the external solvent *after* the photoreduction of hemin. This was done to eliminate possible contributions from the excited TiO₂ to the observed RX chemistry. The addition of RX resulted in an exponential loss of the ferrous hemin and the formation of ferric hemin (Figure 2 inset). The UV-visible absorbance spectrum of the ferric hemin produced after the addition of RX to ferrous hemin gave a Soret band identical to that of Fe(III) before photoreduction, but we observed differences in the Q-band region. These new spectral features may be a result of Fe(III) binding to a new axial ligand such as the solvent (DMSO). Reactivity was qualitatively observed for all of the RX compounds in aqueous solution and were quantitatively analyzed in DMSO. Second-order rate constants were abstracted for plots of k_{obs} versus [RX] for each organic halide and are compared to those for ferrous hemin generated by L-cysteine reduction in fluid DMSO solution (Table 1). In some cases, such as chloroform or alachlor, no reactivity was observed in solution for days, but the reaction proceeded to completion within minutes on the TiO₂ surface. For the other RX compounds, the kinetic rate constants for the ferrous hemin/TiO₂ were found to be 1–2 times faster.

In conclusion, we have shown that hemin can be photoreduced on TiO₂ and that the ferrous hemin reacts rapidly and efficiently with organic halide pollutants. The enhanced

reactivity on TiO₂ relative to that in fluid solution is encouraging for future applications and studies. An explanation of the enhanced reactivity is unknown but may result from shifts in the Fe(III/II) reduction potential upon surface binding and/or the activation of R–X by the dark TiO₂ surface. Future studies will focus on understanding these and other molecular details with a wider range of catalysts and will also identify the RX reaction products. The observation of RX photoreactivity of ferrous hemin supported on TiO₂ in water is particularly encouraging and suggests that the materials may be suitable for aqueous environmental photocatalysis.

Acknowledgment. This work was supported by the National Science Foundation. We acknowledge the Camille and Henry Dreyfus Postdoctoral program in Environmental Chemistry for the support of S.O.O.

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NL034353I