Visible Light-Induced Degradation of Carbon Tetrachloride on Dye-Sensitized TiO₂

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This study investigated an application of TiO₂ photocatalyst sensitized with tris(4,4′-dicarboxy-2,2′-bipyridyl)ruthenium(II) complex to CCl₄ degradation under visible light irradiation. By injecting electrons from the photoexcited sensitizer to the conduction band, the sensitized TiO₂ degraded CCl₄ under the irradiation of λ > 420 nm. The quantum yield of CCl₄ dechlorination was about 10⁻³. The dechlorination rate of CCl₄ was reduced in the presence of dissolved O₂ due to its competition for conduction band electrons. The photolysis rate was dependent on pH due to the strong pH dependence of the sensitizer adsorption on TiO₂ surface with a maximum degradation rate achieved at pH ~3. A two-site Langmuirian model successfully described the adsorption of the sensitizer on TiO₂ particles. The monolayer coverage was achieved at the added sensitizer concentration of 10 μM at [TiO₂] = 0.5 g/L. However, the photolysis rate of CCl₄ showed a maximum at a sensitizer surface coverage of 0.3 monolayer. Since the photoinduced electron injection gradually depleted active sensitizer molecules on TiO₂, sacrificial electron donors to regenerate the sensitizer were sought. 2-Propanol as an electron donor was efficient in the present RuIIL₃/TiO₂/CCl₄ system, which showed no sign of deceleration in the dechlorination rate up to 6 h of irradiation.

Introduction

The photocatalytic degradation of organic pollutants using TiO₂ has demonstrated successful performance in various remediation systems of polluted water and air (1–5). The pollutants that have been degraded or remediated using TiO₂ photocatalysis include almost any kind of organic compounds, various inorganic and metal ions, and even biological pathogens such as bacteria and viruses. Although TiO₂ is very popular as a photocatalyst, it suffers from the lack of visible light absorption.

Photosensitization is widely used to extend the photoresponse of TiO₂ into the visible region. The principle of photosensitization of TiO₂ is illustrated in Scheme 1 that indicates the primary electron pathways. The visible light excites the sensitizer molecules adsorbed on TiO₂ and subsequently inject electrons to conduction band (CB) of TiO₂. While the CB acts as a mediator for transferring electrons from the sensitizer to substrate electron acceptors on TiO₂ surface, the valence band (VB) remains unaffected in a typical photosensitization. Although the basic processes of TiO₂ photosensitization have been extensively studied using ruthenium-based complexes (6) and various inorganic/organic dyes (7–13) as a sensitizer in relation to photoelectrochemical cells and water splitting systems, the studies of photosensitization applied to the degradation of pollutants using visible light are few.

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In this work, we investigated the photoreductive decomposition of CCl₄ using visible light on TiO₂ sensitized by tris(4,4′-dicarboxy-2,2′-bipyridyl)ruthenium(II) complexes. On sensitized TiO₂, the electrons injected from the excited sensitizer can directly transfer to CCl₄ as illustrated in Scheme 1. The resulting -CCl₃ radicals degrade through a series of complex reactions (22–24). The characteristics and performance of the ruthenium sensitizer in the photosensitized degradation of CCl₄ under visible light irradiation are quantitatively described. A regenerative photosensitization system using electron donors is also discussed.

Experimental Section

Materials. Tris(4,4′-dicarboxy-2,2′-bipyridyl)ruthenium(II) chloride ([RuIII(bpy-(COOH)₂)₃]Cl₂, abbreviated as RuIIL₃) was synthesized according to the method described in the literature (21). The TiO₂ (Degussa P25) suspension concentration was 0.5 g/L. The suspension was dispersed by simultaneous sonication and shaking in an ultrasonic cleaning bath (Branson 3210). CCl₄ (J. T. Baker) was purified by distillation. All other chemicals used were of reagent grade and used without further treatments.

SCHEME 1. Photosensitized Degradation of CCl₄ on Sensitized TiO₂ Particles

* S stands for sensitizer, RuIIL₃; S⁺, electronically excited sensitizer, (RuIIL₃)⁺; S°, oxidized sensitizer, RuIIIL₃; D, sacrificial electron donor for regenerating the sensitizer. The number represents the primary electronic pathways in photosensitization: 1, excitation of S; 2, fluorescent decay of S⁺; 3, electron injection into CB; 4, back electron transfer to S°; 5, electron migration within the lattice onto the surface; 6, electron transfer to CCl₄; 7, sensitizer regeneration by electron donors.
The molar absorptivity, $\varepsilon_{\text{MLCT}}$, of the sensitized TiO$_2$ particles (TiO$_2$ suspension powder sample was prepared by evaporating the aqueous suspension of the sensitized TiO$_2$ particles) was measured using a diffuse reflectance spectrophotometer (Shimadzu UV-2401PC) with a diffuse reflectance attachment (Shimadzu ISR-2200). The Ru$^+$L$_3$-coated TiO$_2$ powder sample was prepared by evaporating the aqueous solution of Ru$^+$L$_3$ (3 $\mu$M) at pH 3. The ordinate scale in the diffuse reflectance spectra is expressed in Kubelka-Munk unit.

### Optical Measurements and Characterization

The optical absorption spectra of Ru$^+$L$_3$ solutions and Ru$^+$L$_3$-coated TiO$_2$ powders were recorded with an UV-visible spectrophotometer (Shimadzu UV-2401PC) with a diffuse reflectance attachment (Shimadzu ISR-2200). The Ru$^+$L$_3$-coated TiO$_2$ powder sample was prepared by evaporating the aqueous suspension of the sensitized TiO$_2$ particles (TiO$_2$ suspension at pH 3 with 6 mg of Ru$^+$L$_3$Cl$_2$·6H$_2$O TiO$_2$) to dryness. Figure 1 compares the diffuse reflectance spectra of the sensitized TiO$_2$ with that of pure TiO$_2$ powder. It shows the absorption spectrum of 3 $\mu$M Ru$^+$L$_3$ solution at pH 3 as well. The absorption band of the metal-to-ligand charge transfer (MLCT, d$^0 \rightarrow $d$^1$ transition) of the sensitizer was at $\lambda_{\text{max}}$ = 467 nm. The molar absorptivity, $\varepsilon$ at 467 nm, was determined to be $2.1 \times 10^4$ M$^{-1}$ cm$^{-1}$ by measuring the absorbance of the sensitizer standard solution and used in determining the concentration of Ru$^+$L$_3$ solution. This value agrees with a previously reported one (25).

### Preparation of Sensitized TiO$_2$ Suspensions

The aqueous stock solution (50–100 $\mu$M) of the sensitizer was prepared at pH > 10 for the complete dissolution of the sensitizer. A typical sample preparation procedure is as follows. A 100 mL of sensitizer solution with a desired concentration (usually 3 $\mu$M) was adjusted to pH 10 for the complete dissolution of the sensitizer. A calculated amount of TiO$_2$ was added to the remaining 80 mL of the solution to give a 0.5 TiO$_2$ g/L suspension that was then left for 20 min under magnetic stirring for adsorption equilibration. The pH of both fractions (20 mL and 80 mL) was adjusted to 3.0 in a typical experiment or to a desired value with 0.1 N HClO$_4$ or 0.1 N NaOH solutions. An aliquot (~1 mL) of the sensitized TiO$_2$ suspension was filtered through a 0.45-$\mu$m PTFE syringe filter (Millipore) and was measured for the absorbance at 467 nm ($A_{\text{max}}$). The amount of the sensitizer adsorbed on TiO$_2$ was calculated from the absorbance difference $\Delta A$ ($= A_0 - A_{\text{max}}$). The main portion of the sensitized TiO$_2$ suspension was used for photolysis experiments.

### Photolysis and Analysis

Photolyses were performed with a 450 W Xe-arc lamp (Oriel). Light passed through a 10-cm IR water filter and an UV cutoff filter ($\lambda > 420$ nm). The filtered light was focused onto a 30-mL quartz reactor with minimized headspace and a rubber septum. Light intensity ($I_i$) through the UVC cutoff filter was about 6 $\times$ 10$^{-3}$ Einstein L$^{-1}$ min$^{-1}$ in the wavelength range 420–550 nm. The suspension was bubbled with O$_2$ or N$_2$ for 30 min before adding CCl$_4$. A calculated amount of CCl$_4$ was injected directly into the reactor cell with a GC syringe through a rubber septum. A typical concentration of CCl$_4$ was 1 mM.

For the complete dissolution of CCl$_4$ into the solution, the suspension was stirred magnetically for 30 min before photolysis began. Sample aliquots of 1 mL were obtained from the illuminated reactor with a 2-mL syringe filtered through a 0.45-$\mu$m PTFE filter, and injected into a 2-mL glass vial. The chloride production from the CCl$_4$ dechlorination was followed with an ion chromatograph (IC). The IC system was a Dionex DX-120 with a conductivity detector and a Dionex IonPac AS-14 wide bore column (4 mm $\times$ 250 mm).

### Results and Discussion

**Photosensitized Degradation of CCl$_4$**

The irradiation of the sensitized TiO$_2$ suspension with visible light ($\lambda > 420$ nm) led to the decomposition of CCl$_4$. Figure 2 shows the photolysis results. The initial photonic efficiency of CCl$_4$ dechlorination, $\phi$ (mol C/phot.), which does not take the light scattering loss into account, is $1 \times 10^{-4}$ for the N$_2$-saturated system. Since the sensitized TiO$_2$ suspension absorbed only a fraction of the incident light, the photonic efficiency, should be taken as a lower limit of the true quantum yield. When either the sensitizer or TiO$_2$ was absent, CCl$_4$ did not degrade. This proves that there is no direct electron transfer between an excited sensitizer and a CCl$_4$ molecule in the homogeneous solution and that the degradation of CCl$_4$ proceeds through a sensitized photocatalysis on TiO$_2$. The CB of TiO$_2$ seems to play an essential role of a mediator of electron transfer between an excited sensitizer and a CCl$_4$ molecule in the homogeneous solution and that the degradation of CCl$_4$ proceeds through a sensitized photocatalysis on TiO$_2$. Table 1 lists elementary reaction steps for the photoreductive dechlorination of CCl$_4$ on Ru$^+$L$_3$-sensitized TiO$_2$ under visible light irradiation.

When the sensitizer molecule is excited in the solution, it quickly relaxes into the ground state through fluorescence (reaction T11) with little chance of electron transfer to a CCl$_4$ molecule (reaction T13). However, in the presence of TiO$_2$, the electron injection from the excited sensitizer to the CB of TiO$_2$ is faster than the direct relaxation to the ground state. A quantum yield of 0.6 ± 0.1 was reported for the electron injection process in the Ru$^+$L$_3$/TiO$_2$ system (27). In the present Ru$^+$L$_3$/TiO$_2$ system at pH 3, the estimated driving force for the electron injection (E(Ru$^+$L$_3^{0.5}$)/Ru$^+$L$_3^{0.5}$) - $E_{\text{CB}}$ is about 0.45 V (21), while the driving force sufficient for electron injection is as small as about 0.1 V (6). Since the rate of electron injection...
TABLE 1. Initial Elementary Reaction Steps in the RuII-TiO2/CCl4/Visible Light System

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Equation</th>
</tr>
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<tbody>
<tr>
<td>T1</td>
<td>RuIIaq + TiO2 ⇌ RuII-TiO2</td>
</tr>
<tr>
<td>T2</td>
<td>RuII-TiO2 + CCl4,sol ⇌ RuII-TiO2 ... CCl4,sol</td>
</tr>
<tr>
<td>T3</td>
<td>RuII-TiO2 + O2,ads ⇌ RuII-TiO2 ... O2,ads</td>
</tr>
<tr>
<td>T4</td>
<td>RuII-TiO2 ( \frac{hν(λ &gt; 420 \text{ nm})}{hν} ) → RuII*TiO2</td>
</tr>
<tr>
<td>T5</td>
<td>RuII*-TiO2 ... O2,ads → RuII-TiO2 + O2</td>
</tr>
<tr>
<td>T6</td>
<td>RuII-TiO2 + O2 → RuII-TiO2 + O2</td>
</tr>
<tr>
<td>T7</td>
<td>RuII*-TiO2 → RuII-TiO2</td>
</tr>
<tr>
<td>T8</td>
<td>RuII-TiO2(eCB) → RuII-TiO2</td>
</tr>
<tr>
<td>T9</td>
<td>RuII-TiO2(eCB) ... CCl4,ads → RuII-TiO2 + CCl4 + Cl</td>
</tr>
<tr>
<td>T10</td>
<td>RuII-TiO2(eCB) ... O2,ads → RuII-TiO2 + O2</td>
</tr>
<tr>
<td>T11</td>
<td>RuIIaq ( \frac{hν(λ &gt; 420 \text{ nm})}{hν} ) → RuII*aq</td>
</tr>
<tr>
<td>T12</td>
<td>RuII<em>aq + O2,ads → RuII</em> + O2</td>
</tr>
<tr>
<td>T13</td>
<td>RuII<em>aq + CCl4,ads → RuII</em> + CCl3 + Cl (negligible)</td>
</tr>
</tbody>
</table>

* RuII stands for a Ru II(bpy-CH(OOH))32+ complex.

Table 1 shows the initial elementary reaction steps in the RuII-TiO2/CCl4/Visible Light System. The reaction sequence includes electron transfer to the preadsorbed substrates, followed by the scavenging of CB electrons. The reaction leaves fewer CB electrons available for CCl4 molecules, which results in lower dechlorination rates.

Dissolved Oxygen Effect. Figure 2 also shows the effect of dissolved gas on the photolysis rate of CCl4. The initial dechlorination rates of CCl4 decrease in the order of N2 > air > O2-saturated system. The presence of O2 in the suspension lowers photosensitization efficiency by two ways: direct quenching of the excited sensitizer and scavenging CB electrons. Dissolved O2 is an efficient quencher of the excited ruthenium bipyridine complex.

Dissolved oxygen competes for CB electrons with CCl4 molecules. The increasing dissolved oxygen concentration leaves fewer CB electrons available for CCl4 molecules, which results in lower dechlorination rates.

Kinetic Analysis of CCl4 Dechlorination. The following kinetic analysis quantitatively expresses the dechlorination rate of CCl4 in the RuII/Li/TiO2 system. Let us assume that CB electrons transfer to the preadsorbed substrates. From reaction T9

\[
\frac{d[ClI]}{dt} = k_{T9}[eCB][CCl4]_{ads} \tag{1}
\]

The CB electron concentration at steady state can be obtained from

\[
\frac{d[eCB]}{dt} = \frac{l_{abs}}{1 + k_{T10}[O2]_{ads} + k_{T9}[RuII* - TiO2]} \tag{2}
\]

Substituting eq 2 into eq 1 gives

\[
\frac{d[ClI]}{dt} = \frac{l_{abs}}{1 + \frac{k_{T9}[RuII* - TiO2]}{k_{T9}[CCl4]_{ads}}} \tag{3}
\]

In N2-saturated suspension where [O2]_{ads} ≈ 0

\[
\frac{d[ClI]}{dt} = \frac{l_{abs}}{1 + \frac{k_{T9}[RuII* - TiO2]}{k_{T9}[CCl4]_{ads}}} \tag{4}
\]

then the dechlorination quantum yield is

\[
Φ_{ClI} = \frac{d[ClI]/dt}{l_{abs}} = \frac{1}{1 + \frac{k_{T9}[RuII* - TiO2]}{k_{T9}[CCl4]_{ads}}} \tag{5}
\]

If we assume that 10% of the incident light (I) is absorbed by the suspension (see Figure 1) and substitute the measured initial dechlorination rate from Figure 2 into eq 5, we get the dechlorination quantum yield, \(Φ_{ClI} \approx 10^{-4}\). This indicates that the back electron transfer (T8) is 1000 times faster than the interfacial electron transfer to CCl4 (T9) in the present system.

Adsorption of the Sensitizer and the Photoreactivity. Figure 3 shows the adsorption behavior of the sensitizer on TiO2. The following two-site model successfully describes the adsorption isotherm:

\[
\frac{[RuII\text{L}_3]_{ads}}{[RuII\text{L}_3]_{\text{mono}}} = \frac{K_1[RuII\text{L}_3]_{\text{eq}} + K_2[RuII\text{L}_3]_{\text{eq}}}{1 + K_3[RuII\text{L}_3]_{\text{eq}}} \tag{6}
\]
where \([\text{Ru}^{II}\text{L}_3]_{\text{ad}}\) is the concentration of the adsorbed sensitizer on TiO\(_2\); \([\text{Ru}^{II}\text{L}_3]_{\text{eq}}\), the equilibrium concentration of the sensitizer remaining in the solution; \([\text{Ru}^{II}\text{L}_3]_{\text{mono}}\), the surface concentration of the adsorbed sensitizer on TiO\(_2\) at a monolayer coverage; and \(K_1\) and \(K_2\), the equilibrium adsorption constant of the sensitizer for each site. The values of the fitted parameters are \([\text{Ru}^{II}\text{L}_3]_{\text{mono}} = 25.7 \, \mu\text{mol/g TiO}_2\), \(K_1 = 9.8 \times 10^6 \, \text{M}^{-1}\), and \(K_2 = 7.3 \times 10^4 \, \text{M}^{-1}\). The fitted results are shown in solid line along with its two components in dotted lines in Figure 3. The site 1 represents the strong first layer adsorption through a bidentate carboxylate linkage that is frequently assumed for the structure of the adsorbed sensitizer (31). The site 2 corresponds to loosely bound complexes through a monodentate carboxylate linkage or weak outer-sphere electrostatic interactions with multilayer deposition. While the stronger adsorption component quickly reaches a monolayer coverage, the weaker adsorption component increases slowly with \([\text{Ru}^{II}\text{L}_3]_{\text{ad}}\). Assuming a specific surface area of 50 m\(^2\)/g for the TiO\(_2\) suspension, we calculate \([\text{Ru}^{II}\text{L}_3]_{\text{mono}}\) to be 0.31 molecule/nm\(^2\), which corresponds to an average area of 3.2 nm\(^2\) occupied by a single Ru\(^{II}\text{L}_3\) molecule. The sensitizer molecule's geometric cross-section is 2 nm\(^2\) (molecular radius 8 Å) (27).

In Figure 4, we also investigated the effect of the added sensitizer concentration, \([\text{Ru}^{II}\text{L}_3]_{\text{i}}\), on the dechlorination rate. While the adsorption data shown together indicate that the coverage of the sensitizer starts to be saturated above \([\text{Ru}^{II}\text{L}_3]_{\text{i}} = 15 \, \mu\text{M}\), the photoreductive dechlorination rate shows a maximum at \([\text{Ru}^{II}\text{L}_3]_{\text{i}} = 3 \, \mu\text{M}\), which corresponds to 0.3 monolayer of Ru\(^{II}\text{L}_3\) on TiO\(_2\). Since the light absorption by the sensitized TiO\(_2\) particles is proportional to \([\text{Ru}^{II}\text{L}_3]_{\text{ad}}\) (32, 33), the fact that there exists an optimal surface concentration at a submonolayer coverage implies that other competing processes are affecting the photolytic degradation of CCl\(_4\). Competition for the bare TiO\(_2\) surface sites between the sensitizer and CCl\(_4\) molecules (reactions T1 vs T2) seems to be the most plausible explanation. While the light absorption increases with increasing \([\text{Ru}^{II}\text{L}_3]_{\text{ad}}\), less bare surface sites become available for CCl\(_4\) molecules. As the photoreductive dechlorination of CCl\(_4\) requires the access of both CCl\(_4\) and the sensitizer onto the TiO\(_2\) surface, their competition for the surface sites should be compromised at a submonolayer coverage for CCl\(_4\) and the sensitizer, respectively. Their adsorbed concentrations, \([\text{Ru}^{II}\text{L}_3]_{\text{ad}}\) and \([\text{CCl}_4]_{\text{ad}}\), should be comparable at a typical experimental condition \([\text{Ru}^{II}\text{L}_3]_{\text{i}} = 3 \, \mu\text{M}; [\text{CCl}_4]_{\text{i}} = 1 \, \text{mM}\) with \(K_{\text{RuL}} \sim 10^7 \, \text{M}^{-1}\) and \(K_{\text{CCl}_4} \sim 10^8 \, \text{M}^{-1}\) (vide infra). We confirmed their competitive adsorption on TiO\(_2\) by measuring \([\text{CCl}_4]_{\text{eq}}\), as a function of \([\text{Ru}^{II}\text{L}_3]_{\text{i}}\): when the added sensitizer concentration increased from 3 to 17 \(\mu\text{M}\), the equilibrated CCl\(_4\) concentration in the solution increased by 10–20\% due to desorption.

A Langmuir–Hinshelwood equation successfully describes the dependence of \([\text{CCl}_4]_{\text{eq}}\) on the initial dechlorination rates (data not shown)

\[
\frac{d[\text{Cl}^-]}{dt} = k_{\text{CCl}} k_{\text{CCl}} [\text{CCl}_4]_0
\]

where \(k_{\text{CCl}}\) is the photoinduced dechlorination rate constant of CCl\(_4\) and \(k_{\text{CCl}}\) is the adsorption constant of CCl\(_4\) on TiO\(_2\). The corresponding constants are \(k_{\text{CCl}} = 1.9 \, \mu\text{M min}^{-1}\) and \(k_{\text{CCl}} = 595 \, \text{M}^{-1}\). Hsiao et al. (34) reported a value of \(K_{\text{CCl}_4} = 1370 \, \text{M}^{-1}\) from their photocatalytic degradation study of the CCl\(_4\)/UV/TiO\(_2\) system.

**pH Effect.** The pH dependence of the sensitizer adsorption on TiO\(_2\) is largely of the electrostatic nature. A simple electrostatic model is frequently employed to explain the adsorption of charged substrates on metal oxides (35). The surface of TiO\(_2\) in aqueous suspensions takes positive charges at \(pH < 6\) and negative charges at \(pH > 6\) (i.e., \(pH_{\text{pzc}} = 6\)). The Ru\(^{II}\text{bpy-(COOH)}_2\)\(^{3+}\) sensitizer used in this study has \(pK_a\) values of 1–2 for the first and second deprotonation step (36). Therefore, the net charge of the sensitizer molecule is negative under normal pH (> 3) conditions. The pH dependence of \([\text{Ru}^{II}\text{L}_3]_{\text{i}}\) shown in Figure 5 can be explained by the electrostatic interactions between the negatively charged sensitizer molecule and a charged TiO\(_2\) surface. The positively charged TiO\(_2\) surface at acidic conditions strongly attracts negatively charged sensitizer molecules, while the negatively charged TiO\(_2\) surface at basic conditions repels
with the back electron transfer. Further studies should be directed into resolving the problem of the slow interfacial electron transfer.

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