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Sensitized photocatalytic oxidation of herbicides using natural sunlight

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Abstract

The sensitized photocatalytic oxidation (SPCO) of the herbicide terbutryne using tris(bipyridyl)ruthenium complexes as sensitizer and titanium dioxide as semiconductor was investigated. Tris(4,4′-dicarboxy-2,2′-bipyridyl)ruthenium(II) chloride is an excellent sensitizer, and on exposure to sunlight complete degradation of the pollutant occurs. The thermodynamic and kinetic requirements for successful SPCO are discussed. The adsorption of the components on the semiconductor surface, electron transfer and electron back transfer determine the efficiency of the process. © 1997 Elsevier Science S.A.

Keywords: Catalysis; Herbicide; Ruthenium(II) complexes; Sensitization; Titanium dioxide; Triazine

1. Introduction

The well-known photocatalytic oxidation (PCO) of organic compounds using near-UV-irradiated titanium dioxide is initiated by the generation of HO$^{\bullet}$ radicals in a titanium dioxide–water suspension [1–3]. The bandgap excitation of titanium dioxide proceeds only at wavelengths λ less than 380 nm, which prevents natural sunlight from being an effective driving force for the PCO process. This study deals with sensitized photocatalytic oxidation (SPCO), a method which could lead to sunlight-driven photocatalytic decontamination of water. The previously described principle of SPCO by conductive band sensitization of titanium dioxide has been applied to achieve HO$^{\bullet}$ generation [4].

Ross et al. [4] have described the successful sensitization of the PCO process by rose bengal. Irradiation of an aqueous solution of a pollutant (herbicide of the triazine type) in the presence of TiO_2 and rose bengal with light at $\lambda > 420$ nm leads to decomposition of the herbicide. The decomposition of rose bengal, via attack by the generated HO$^{\bullet}$ radicals, occurs at the same time as herbicide degradation. This irreversible decomposition reaction decelerates and, finally, stops the PCO process (sacrificial SPCO). The aim of this paper is to find a sensitizer which is stable or can be regenerated in order to yield an effective SPCO process.

The ruthenium(II) polypyridine complexes exhibit excellent properties in photoinduced reactions as light absorption sensitizers [5,6]. The fundamental requirement of a sensitizer in the SPCO process is the stability of the oxidized and/or reduced form, i.e. the reversibility of the oxidation and/or reduction process [7]. In this paper, we investigate the ability of the sensitizers tris(2,2′-bipyridyl)ruthenium(II) chloride ($Ru(bpy)_3^{2+}$), tris(4,4′-dimethyl-2,2′-bipyridyl)ruthenium(II) hexafluorophosphate ($Ru(bpy\text{-}CH_3)_3^{2+}$) and tris(4,4′-dicarboxy-2,2′-bipyridyl)ruthenium(II) chloride ($Ru(bpy\text{-}COOH)_3^{2+}$, Fig. 1) to degrade, by an SPCO process, the herbicide terbutryne (N^2-tert-butyl-N^4-ethyl-6-methylthio-1,3,5-triazine-2,4-diyldiamine, **1**), and discuss the influence of the bidentate bipyridyl ligands.

2. Experimental details

2.1. Materials

The titanium dioxide used in this work (Degussa P-25) has a specific surface area of about 55 m^2 g^{-1}. **1** was supplied by Riedel-de-Haen with 99% purity. $Ru(bpy)_3^{2+}$ was obtained from Aldrich. The syntheses of the other sensitizers are described below.

2.1.1. Synthesis of $Ru(bpy\text{-}CH_3)_3^{2+}$

A solution containing 50 ml ethanol, 0.3 g (1.44 mmol) ruthenium(III) chloride (Aldrich), 1 g (5.43 mmol) 4,4′-dimethyl-2,2′-bipyridine (Aldrich), 0.12 g (1.73 mmol) hydroxylamine hydrochloride and 0.14 g (1.67 mmol) sodium bicarbonate was refluxed for 8 h under nitrogen. The mixture was poured into 50 ml water and filtered. Ammonium hexafluorophosphate (0.7 g, 4.29 mmol) was added and the

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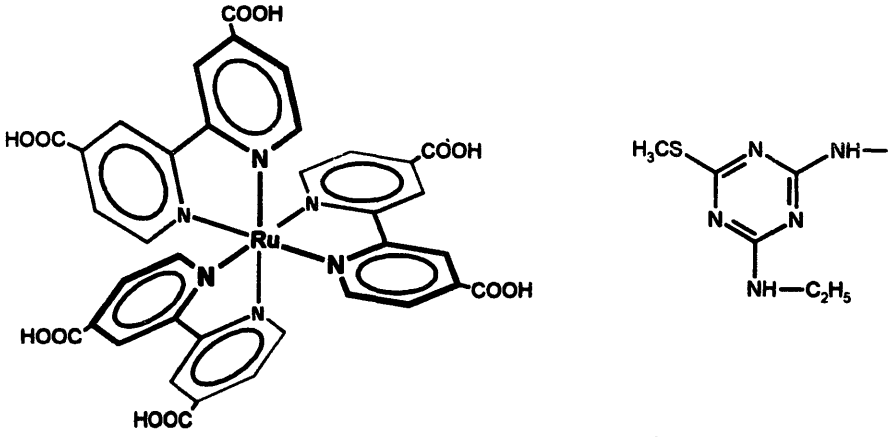

Fig. 1. Investigated compounds Ru(bpy-COOH)$_3^{2+}$ and **1**.

Table 1
Surface concentration (mol m^{-2}) of the investigated sensitizers as a function of the pH

pH	Ru(bpy)$_3^{2+}$	Ru(bpy-CH$_3$)$_3^{2+}$	Ru(bpy-COOH)$_3^{2+}$
3	$<5.0\times10^{-9}$	$<5.0\times10^{-9}$	1.8×10^{-7}
4	$<5.0\times10^{-9}$	$<5.0\times10^{-9}$	5.8×10^{-8}
5	$<5.0\times10^{-9}$	$<5.0\times10^{-9}$	1.5×10^{-8}
6	$<5.0\times10^{-9}$	$<5.0\times10^{-9}$	$<5.0\times10^{-9}$
7	$<5.0\times10^{-9}$	7.7×10^{-8}	$<5.0\times10^{-9}$
8	1.3×10^{-8}	1.2×10^{-7}	$<5.0\times10^{-9}$
9	6.6×10^{-8}	4.6×10^{-7}	$<5.0\times10^{-9}$
10	1.2×10^{-7}	7.4×10^{-7}	$<5.0\times10^{-9}$

precipitate was isolated and recrystallized from acetonitrile–chloroform (1 : 5). Yield, 52%. Analysis: calculated for $C_{36}H_{36}F_{12}N_6P_2Ru$: C, 45.82%; H, 3.85%; N, 8.91%; found: C, 45.33%; H, 4.12%; N, 8.68%.

2.1.2. Synthesis of Ru(bpy-COOH)$_3^{2+}$

A solution containing 5 ml water, 0.027 g (0.13 mmol) ruthenium(III) chloride, 0.1 g (0.41 mmol) 4,4′-dicarboxy-2,2′-bipyridine (Aldrich), 0.012 g (0.17 mmol) hydroxylamine hydrochloride and 0.084 g (1 mmol) sodium bicarbonate was refluxed for 10 h under nitrogen. The dark red precipitate was dissolved by stirring and with the addition of 5 ml water. The mixture was filtered, and the filtrate was cooled to 0 °C and acidified using concentrated HCl. The precipitate was isolated and washed with acetone and toluene. Yield, 82%.

2.2. Methods

The concentration of the sensitizer on the TiO_2 surface (surface concentration Γ in moles per square metre), as a function of the pH value, was determined by UV–visible spectroscopy. For this purpose, 10 ml of aqueous sensitizer solution (Ru(bpy)$_3^{2+}$, Ru(bpy-COOH)$_3^{2+}$: $c = 1\times10^{-4}$ mol l^{-1}; Ru(bpy-CH$_3$)$_3^{2+}$: $c = 5\times10^{-5}$ mol l^{-1}) and 100 mg TiO_2 were agitated ultrasonically and the pH value was adjusted. The suspension was then filtered using an RC15 filter (0.45 μm, Sartorius). From the absorbance of the sensitizer solution before and after treatment with TiO_2, the amount of sensitizer adsorbed (n_{ads} in moles) was determined, and Γ was calculated using

$$\Gamma = n_{ads}/(m_A O_A) \qquad (1)$$

where m_A is the amount of TiO_2 and O_A is the specific surface area of TiO_2. The results are summarized in Table 1.

The maximum surface concentration of the sensitizer (Γ_{max}) was estimated using the adsorption isotherm [4]. The degree of coverage was calculated using $\Theta = \Gamma/\Gamma_{max}$.

The photolysis was carried out using a 500 W high-pressure xenon lamp (Oriel) equipped with a cut-off filter ($\lambda > 420$ nm). The following concentrations/amounts were used: $c(\mathbf{1}) = 2\times10^{-5}$ mol l^{-1}; c(sensitizer) $= 1\times10^{-5}$ mol l^{-1}; $m_A = 100$ mg per 100 ml suspension; $\Gamma \approx 0.5\Gamma_{max}$. The concentrations of **1** and its degradation products [1] were determined by high performance liquid chromatography (HPLC) using a UV–visible detector (LCD 502, GAT), pump (64, Knauer), Eurosil-Bioselect column (100-G187, 7 μm, Knauer), methanol–water at different ratios as mobile phase and a detection wavelength λ of 235 nm.

The UV–visible spectra were recorded with a UVICON 930 spectrophotometer (Kontron). The pH values were measured using a pH meter (CG825) and a glass electrode (N 42A, Schott).

3. Results

The investigated sensitizers absorb in the visible spectral region. The maxima of the metal-to-ligand charge transfer (MLCT) bands are located as follows: Ru(bpy)$_3^{2+}$, $\lambda_{max} = 453$ nm ($\epsilon = 13\,000$ l mol^{-1} cm^{-1}); Ru(bpy-CH$_3$)$_3^{2+}$, $\lambda_{max} = 460$ nm ($\epsilon = 13\,200$ l mol^{-1} cm^{-1}); Ru(bpy-COOH)$_3^{2+}$ at pH 3, $\lambda_{max} = 467$ nm ($\epsilon = 12\,850$ l mol^{-1} cm^{-1}). The absorption spectrum of Ru(bpy-COOH)$_3^{2+}$

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[1] The degradation products of the SPCO process are very similar to those of the PCO process [8]. The PCO process of the triazine herbicide has been described by Pelizzetti et al. [9,10]. The toxicity of the intermediate products was not reported. The final organic product, cyanuric acid, is non-toxic [11].

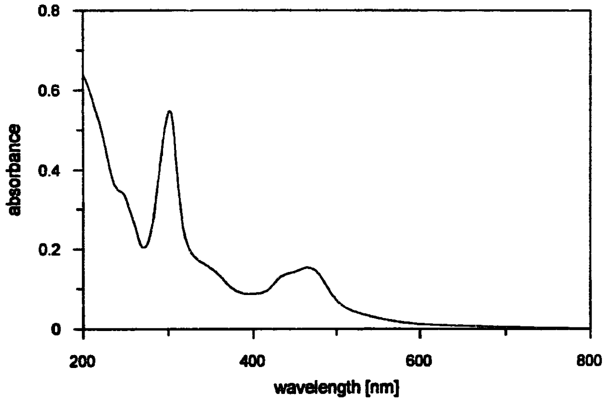

Fig. 2. Absorption spectrum of Ru(bpy-COOH)$_3^{2+}$ in aqueous solution ($c = 1 \times 10^{-5}$ mol l^{-1}) at pH 11.

(Fig. 2) is dependent on the pH value: with increasing pH, the MLCT band is blue shifted. However, on addition of the triazine to a solution of the ruthenium complex, no change in the absorption or fluorescence spectra of the sensitizer is observed. Therefore no remarkable association or complex formation occurs between the sensitizer and the herbicide in the ground and excited states.

A precondition for successful SPCO is the simultaneous adsorption of the herbicide and the sensitizer on the TiO$_2$ surface. The adsorption of **1** occurs in the pH range 3–10 and is described in Refs. [4,8]. The efficiency of sensitizer adsorption is dependent on the pH value (Table 1). The sensitizers Ru(bpy)$_3^{2+}$ and Ru(bpy-CH$_3$)$_3^{2+}$ are adsorbed effectively at pH > 8. The sensitizer Ru(bpy-COOH)$_3^{2+}$ shows strong adsorption on TiO$_2$ at pH < 5. At pH < 3, the solubility of Ru(bpy-COOH)$_3^{2+}$ is insufficient. Therefore the experimental pH values used are pH 10 for Ru(bpy)$_3^{2+}$ and Ru(bpy-CH$_3$)$_3^{2+}$ and pH 3 for Ru(bpy-COOH)$_3^{2+}$.

The irradiation of an aqueous solution of **1** in the presence of titanium dioxide and one of the three investigated sensitizers at $\lambda > 420$ nm (to prevent direct excitation of **1** or TiO$_2$) leads to the decomposition of the herbicide in the case of Ru(bpy-COOH)$_3^{2+}$ only. The results of this photodecomposition are presented in Fig. 3. The complete degradation of the herbicide takes place. When Ru(bpy-COOH)$_3^{2+}$ is absent, no decomposition of **1** occurs. In the same way, the system does not operate without TiO$_2$. A possible photo-oxygenation mechanism caused by singlet oxygen must be excluded. Similar results are obtained on exposure of the microheterogeneous system containing **1**, Ru(bpy-COOH)$_3^{2+}$ and TiO$_2$ to sunlight under the same spectral conditions.

4. Discussion

The proposed mechanism of the SPCO process on the semiconductor surface [4,6] is shown in Fig. 4. The sensitizer molecule adsorbed on the surface absorbs visible light (Eq. (2)), and injects an electron into the conducting band of the n-type semiconductor TiO$_2$ (Eq. (3))

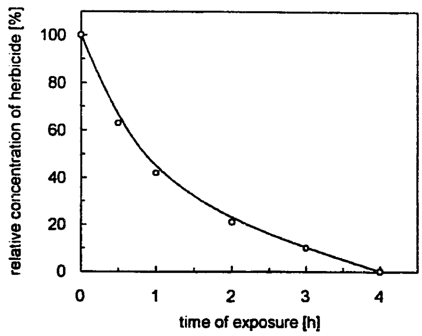

Fig. 3. Sensitized photocatalytic degradation of **1** (100 mg TiO$_2$ in 100 ml solution, $c(\mathbf{1}) = 2 \times 10^{-5}$ mol l^{-1}, c(Ru(bpy-COOH)$_3^{2+}$) $= 1 \times 10^{-5}$ mol l^{-1}, pH 3).

$$Ru(L)_3^{2+} + h\nu \rightarrow Ru(L)_3^{2+*} \qquad (2)$$

$$Ru(L)_3^{2+*} + TiO_2 \rightarrow Ru(L)_3^{3+} + (TiO_2 + e_{CB}) \qquad (3)$$

The conducting band electrons reduce dissolved oxygen to form hydrogen peroxide as an intermediate, followed by the generation of HO$^\bullet$ radicals [12]. The HO$^\bullet$ radicals rapidly attack organic compounds in their environment. The success of SPCO depends on three main points which must be fulfilled by the sensitizer–terbutryne–TiO$_2$ system under the experimental conditions (concentration, pH).

1. The surface properties of TiO$_2$ and the concentrations of sensitizer and herbicide must guarantee simultaneous adsorption. The lifetime of the generated HO$^\bullet$ radicals is too short for diffusion processes to occur.
2. The free enthalpy of the electron transfer process must guarantee a high population of the conducting band of the semiconductor.
3. The efficiency of electron transfer from the conducting band of TiO$_2$ to the reduced sensitizer (back transfer) must be small.

On the basis of these three basic requirements, the successful SPCO of Ru(bpy-COOH)$_3^{2+}$ and the failed degradation experiments using Ru(bpy)$_3^{2+}$ and Ru(bpy-CH$_3$)$_3^{2+}$ are discussed.

The adsorbing power of the sensitizers is strongly influenced by the surface charge. Within the alkaline pH range, the TiO$_2$ surface is negatively charged; at acid pH values (isoelectric point at pH 6.1 [13]), the TiO$_2$ surface is protonated. This explains the different adsorption behaviour of Ru(bpy)$_3^{2+}$ and Ru(bpy-CH$_3$)$_3^{2+}$ on the one hand and Ru(bpy-COOH)$_3^{2+}$ on the other. The positively charged sensitizer complex ions Ru(bpy)$_3^{2+}$ and Ru(bpy-CH$_3$)$_3^{2+}$ show strong adsorbing power at pH 8–10 (Table 1), caused by the negatively charged TiO$_2$ surface. The sensitizer Ru(bpy-COOH)$_3^{2+}$ is an acid (pK_{a1} = 2.8 [14]) and, at pH > 3, the complex ion has the structure Ru(bpy-COO)$_3^{4-}$. This explains the highest adsorption efficiency within the pH range 3–4 (Table 1). For the three sensitization experiments, the simultaneous adsorption of both the sensitizer and terbutryne was realized by considering the dependence of the sensitizer adsorbing power on the pH value (sensitizer-specific pH values, see Table 2).

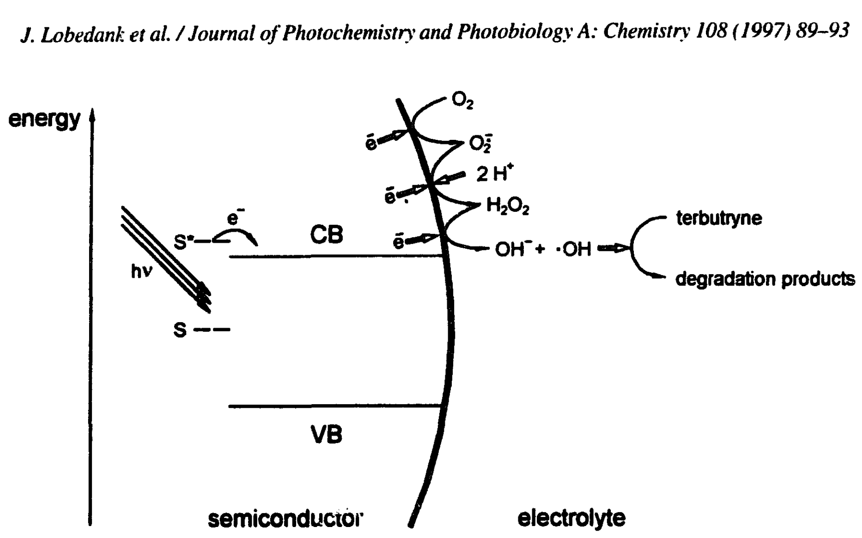

Fig. 4. Scheme of the postulated SPCO process.

Table 2
Electrochemical (vs. normal hydrogen electrode (NHE)) and thermodynamic data of the investigated sensitizer–TiO_2 systems

Sensitizer	pH	$E_{ox}(Ru(L_3)^{2+}/Ru(L_3)^{3+})$ [14] (V)	$E_{0,0}(Ru(L_3)^{2+*})$ (eV)	$\Delta G^* - E_C$ (eV)
$Ru(bpy)_3^{2+}$	10	+1.51	2.05	+0.11
$Ru(bpy\text{-}CH_3)_3^{2+}$	10	+1.37	2.01	+0.01
$Ru(bpy\text{-}COOH)_3^{2+}$	3	+1.31	1.99	−0.45

The second precondition for SPCO is successful electron transfer (Eq. (3)). The overall free enthalpy change for an electron transfer reaction is obtained from the relative energies of the frontier orbitals (redox properties) of the reactants (Fig. 4). Thus, for the one-electron transfer (Eq. (3)), the free enthalpy change ΔG^* is given by

$$\Delta G^* = E_{ox}(Ru(L_3)^{2+*}/Ru(L_3)^{3+}) - E_{CB}(TiO_2) + E_C \tag{4}$$

The oxidation potential of the electronically excited sensitizer is described by the ground state potential and the excitation energy [15]

$$E_{ox}(Ru(L_3)^{2+*}/Ru(L_3)^{3+}) = E_{ox}(Ru(L_3)^{2+}/Ru(L_3)^{3+}) - E_{0,0}(Ru(L_3)^{2+*}) \tag{5}$$

The energy bands of the TiO_2 semiconductor depend on the pH value of the electrolyte [16]

$$E_{CB}(TiO_2) = -0.05 - 0.06\text{pH} \quad (\text{in eV}) \tag{6}$$

$$E_{VB}(TiO_2) = +3.15 - 0.06\text{pH} \quad (\text{in eV}) \tag{7}$$

The Coulomb energy (E_C) of attraction or repulsion in the electron transfer state is difficult to quantify and will be discussed later. Table 2 shows the free enthalpy changes of the three sensitizer systems. For $Ru(bpy)_3^{2+}$ and $Ru(bpy\text{-}CH_3)_3^{2+}$, the driving force for electron transfer, ΔG^*, is small and positive. Therefore the efficiency of the photoelectron transfer and the population of the conducting band are low. For $Ru(bpy\text{-}COOH)_3^{2+}$, ΔG^* is large and negative, resulting in an effective electron transfer according to Eq. (3).

An important process determining the lifetime of the "charge-separated" state generated by excited state electron transfer is back electron transfer

$$(TiO_2 + e_{CB}) + Ru(L_3)^{3+} \rightarrow TiO_2 + Ru(L_3)^{2+} \tag{8}$$

The back transfer quenches the electron transfer state and its chemical consequences, i.e. the formation of HO$^\bullet$ radicals according to Fig. 4. The free enthalpy change for back electron transfer, ΔG_{back}, described by Eq. (9) is large and negative, and there is a powerful driving force reducing the primary electron transfer efficiency

$$\Delta G_{back} = E_{CB}(TiO_2) - E_{ox}(Ru(L_3)^{2+}/Ru(L_3)^{3+}) + E'_C \tag{9}$$

In the electron transfer state of $Ru(bpy\text{-}COOH)_3^{2+}$, the competing back electron transfer is hindered by the repulsive Coulomb energy. In this case, the reverse electron transfer is directed to the negatively charged $Ru(bpy\text{-}COO)_3^{4-}$, in contrast with $Ru(bpy\text{-}CH_3)_3^{2+}$. This also explains the favourable position of $Ru(bpy\text{-}COOH)_3^{2+}$ in the SPCO process.

5. Conclusions

The SPCO process works well and can be applied to photooxidize contaminants using sunlight provided that the sensitizer, semiconductor and reaction conditions fulfil essential thermodynamic and kinetic requirements to guarantee the adsorption of the sensitizer and pollutant, the absorption of visible light by the sensitizer, the forward electron transfer and the hindrance of the reverse electron transfer. The SPCO process is sacrificial, since the sensitizer is transformed to the oxidized species $Ru(bpy\text{-}COOH)_3^+$. The reductive regeneration of the sensitizer using sulphur-containing organic compounds is described in Ref. [6].

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