

Photocatalytic degradation of chlorophenols using $\text{Ru}(\text{bpy})_3^{2+}/\text{S}_2\text{O}_8^{2-}$

M. I. Silva · H. D. Burrows · S. J. Formosinho · L. Alves · A. Godinho · M. J. Antunes · D. Ferreira

Received: 21 April 2006 / Accepted: 19 January 2007 / Published online: 21 March 2007
© Springer-Verlag 2007

Abstract Advanced oxidation processes, such as photocatalysed oxidation, provide an important route for degradation of wastes. In this study, the lowest excited state ($^3\text{MLCT}$) of $\text{Ru}(\text{bpy})_3^{2+}$ is used to break down chlorophenol pollutant molecules to harmless products. This has the advantage of using visible light and a short-lived catalytically active species. Photolysis of deaerated aqueous solutions of a variety of mono- and poly-substituted chlorophenols has been followed in the presence of $\text{Ru}(\text{bpy})_3^{2+}/\text{S}_2\text{O}_8^{2-}$ with near visible light ($\lambda > 350 \text{ nm}$) by UV/visible absorption spectroscopy, luminescence, potentiometry, NMR and HPLC techniques. Upon irradiation, a decrease is observed in the chlorophenol concentration, accompanied by the formation of Cl^- , H^+ and SO_4^{2-} ions as the main inorganic products. Benzoquinone, phenol, dihydroxybenzenes and chlorinated compounds were the dominant organic products. As the ruthenium(II) complex is regenerated in the reaction, the scheme corresponds to an overall catalytic process. The kinetics of the rapid chlorophenol photodechlorination has been studied, and are described quite well by pseudo-first order behaviour. Further studies on this were made by following Cl^- release with respect to the initial $\text{Ru}(\text{bpy})_3^{2+}$ and $\text{S}_2\text{O}_8^{2-}$ concentrations. A comparison is presented of the photodechlorination reactivity of the mono and polychlorophenols studied at acidic and alkaline pH.

Keywords Photolysis · $\text{Ru}(\text{bpy})_3^{2+}$ · Photodegradation/photodechlorination · Chlorophenols · Kinetics

Introduction

The purification of water is of great current concern, particularly the removal of toxic wastes, as reflected by the increasing number of studies in this area (Legrin et al. 1993; Mills et al. 1993).

Chlorinated phenols are among the most widespread pollutants of wastewater and natural waters. They are widely used as fungicides and herbicides, in addition to their application in wood protection, their production during the bleaching of paper pulp and their formation as by-products of water chlorination (Juris et al. 1988; Burrows et al. 1998; Silva et al. 1996 and references therein). Apart from their biological activity, these pollutants can be highly toxic (Halmann 1996), and, once in an aquatic environment, are quite persistent and resistant to chemical, photochemical and biological degradation (Pandiyan et al. 2002). Further, they may be transformed into more toxic compounds under the action of natural factors. These problems have led to the demand for limiting their use and for developing methods of treating contaminated waters in which they are present. To tackle this, techniques such as incineration and adsorption have commonly been adopted. However, these methods often transfer the pollutant from one phase to another, such that permanent disposal is still a problem. Light (photon) energy can be used as an alternative to break down such pollutants to harmless products, and both catalysed and uncatalysed photochemical processes have been used for their decomposition. The uncatalysed processes involve direct photolysis or UV photooxidation in the presence of O_3 or/and H_2O_2 as oxi-

M. I. Silva (✉) · H. D. Burrows · S. J. Formosinho · L. Alves · A. Godinho · M. J. Antunes · D. Ferreira
Chemistry Department, FCTUC, University of Coimbra,
3004-535 Coimbra, Portugal
e-mail: misilva@ci.uc.pt

dants (Benitz et al. 2001). Photocatalytic oxidation processes, such as those involving polyoxometalates (POM) (Mylonas et al. 1996) and titanium dioxide (D'Oliveria et al. 1993), have gained wide use in the treatment of hazardous organic wastes. Although efficient dechlorination of chlorinated systems has been demonstrated using aqueous dispersions of platinized TiO₂ (Horikoshi et al. 2003), this photocatalytic process suffers from the economic disadvantage that TiO₂ does not absorb in the visible region and so UV lamps are required for irradiation. Thus, alternative routes are desirable.

Because of its attractive spectral and redox properties, Ru(bpy)₃²⁺ is among the most widely studied systems in transition metal photochemistry (Juris et al. 1988). In a previous report, we have shown that this complex provides a viable alternative method for destroying the toxic organic pollutant 4-chlorophenol (Silva et al. 1996), as it does not require UV light and does not result in a transfer of the pollution problem from one place to another. However, since the photodegradation pathways of different chlorophenols may not be identical, we have extended the study to the photolysis of various mono and polychlorophenols in deaerated aqueous solutions in the presence of Ru(bpy)₃²⁺/S₂O₈²⁻. The photodegradation occurs by electron transfer initiated by the quenching of the ruthenium complex excited state either by S₂O₈²⁻ (forming the corresponding strongly oxidising intermediates Ru(bpy)₃³⁺ and SO₄⁻) or chlorophenol (with the formation of Ru(bpy)₃⁺ and chlorophenol^{+/-}).

Upon prolonged irradiation, it is suggested that photomineralization of the chlorophenols occurs. As Ru(bpy)₃²⁺ is regenerated in the reaction, the scheme corresponds to an overall catalytic process. The photodechlorination kinetics associated with these processes are also reported and compared at acidic and alkaline pH. Pseudo-first order kinetic behaviour describes the rapid photodechlorination behavior quite well under our experimental conditions. The kinetics were also studied as functions of Ru(bpy)₃²⁺ and S₂O₈²⁻ concentrations for several irradiation times.

For the case of the Ru(bpy)₃²⁺/S₂O₈²⁻ sensitized photodegradation of pentachlorophenol, we also report a detailed characterization of the reaction products.

Experimental

Reagents and instruments

2, 3 and 4-chlorophenol (2-CP, 3-CP and 4-CP, respectively), 2,4-dichlorophenol (DCP), 2,4,6-trichlorophenol (TCP) and pentachlorophenol (PCP), methanol (for HPLC) and sodium sulphate were p.a. reagents from Riedel-de-Haën. Tris(2,2'-bipyridyl)ruthenium II dichloride hexahy-

drate was p.a. from Aldrich. The other compounds were p.a. reagents from Merck. All reagents were used as received. All the experiments were carried out in oxygen-free aqueous solutions at room temperature (±20°C). For high performance liquid chromatography (HPLC) studies, experiments were carried out using MilliQ system millipore deionized water.

Typical procedure

Freshly prepared aqueous solutions of chlorophenols (1.1×10^{-4} to 5.0×10^{-4} M) in the presence of Ru(bpy)₃²⁺/S₂O₈²⁻ (concentrations ranging from 5.0×10^{-7} to 6.7×10^{-6} M for the Ru(bpy)₃²⁺ complex and 6.7×10^{-4} to 8.0×10^{-3} M for S₂O₈²⁻) were purged with argon for 15 min and irradiated in 1 cm quartz cells. These used an Applied Photophysics semi micro reactor equipped with a cut-off filter ($\lambda > 350$ nm).

The time evolution of the disappearance of chlorophenols upon irradiation in the presence of Ru(bpy)₃²⁺/S₂O₈²⁻, intermediates and photoproducts formation was followed by a Gilson HPLC apparatus using an analytical cartridge [C18 water column (4.6×150 mm) with a Gilson 151 UV/vis detector. The retention times were compared with those of standards. The mobile phase consisted of a methanol/water mixture (40/60;v/v). The UV/vis absorption spectra of the irradiated and non-irradiated Ar purged solutions were measured in 1 cm quartz cells using a Shimadzu 2100 spectrophotometer. The luminescence spectra of all Ar purged solutions were monitored at the ruthenium complex maximum absorbance (around 455 nm) and the emission intensities were monitored at the wavelength of maximum emission (around 620 nm) in 1 cm quartz cells, on a Fluorlog 3.22 Isa Horiba spectrofluorimeter. The pH was measured potentiometrically using a micro-Crison pH 2000. Cl⁻ concentrations were also determined potentiometrically with a micro-Crison 2002 (mV), using a Ag/AgCl Methrom reference electrode and an Orion 94–117B chloride selective electrode. The ¹³C NMR spectra of unphotolysed and photolysed solutions were obtained at 25 ± 0.5°C, on a Varian unity 500 spectrometer operating at 126.68 MHz with off resonance decoupled. The chemical shifts were measured using TMS as the internal reference. The presence of SO₄²⁻ in the photoproducts was confirmed by qualitative analysis.

Results and discussion

Photodegradation studies

At room temperature, the UV absorption spectra corresponding to transitions of the chlorine and hydroxyl group

substituted benzene rings of aqueous solutions of monochlorophenols were observed at 275 and 225 nm, while those for the polychlorophenols occurred around 290 and 235 nm. Aqueous $\text{Ru}(\text{bpy})_3^{2+}$ solutions showed visible absorption and emission spectra with maxima at 455 and 620 nm respectively, in agreement with those of the literature (Juris et al. 1988).

The absorption spectra of mixtures of $\text{Ru}(\text{bpy})_3^{2+}$ and $\text{S}_2\text{O}_8^{2-}$ and/or chlorophenol were seen to be equal to the sum of the component spectra, showing that, under our experimental conditions, complexation between the sensitizer and the quenchers was negligible in the ground state. Oxygen-free $\text{Ru}(\text{bpy})_3^{2+}$ solutions showed almost no decrease in the steady-state luminescence intensity of the metal complex in the presence of chlorophenol in $\text{pH} < \text{chlorophenol pKa}$, in agreement with the observation of Rajagopal et al. (1992) on the lack of quenching by other phenol derivatives in neutral solutions. However, a decrease in the emission intensity was observed in alkaline solutions (NaOH ca 10^{-2} M).

The quenching of $^3\text{Ru}(\text{bpy})_3^{2+}$ luminescence by several chlorophenols was studied at $\text{pH} = 12$, with at least five different quencher concentrations. The Stern-Volmer plots of the luminescence intensity measurements versus $[\text{CP}]$ were linear with correlation coefficients greater than 0.997, indicating the absence of static quenching. Since the quenching of $^3\text{Ru}(\text{bpy})_3^{2+}$ by the chlorophenolate ions through electronic energy transfer should be an energetically unfavourable process, and as the chlorophenol ions are electron donors, a reductive quenching mechanism is probable. The corresponding bimolecular quenching rate constants were obtained from the slope of the Stern-Volmer plots, K_{SV} , and τ_0 , the unquenched lifetime of $^3\text{Ru}(\text{bpy})_3^{2+}$ (Juris et al. 1988). The experimental values, $k_{\text{q}} = 1.0\text{--}2.0 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$, which depend on the chlorophenols, are slightly higher than the value reported for phenol under similar conditions (Rajagopal et al. 1992), in agreement with a dominant reductive quenching mechanism.

A similar study was performed for the quenching of $^3\text{Ru}(\text{bpy})_3^{2+}$ by $\text{S}_2\text{O}_8^{2-}$ and the bimolecular quenching rate constant values, corresponding to oxidative quenching, were of the order $10^9 \text{ M}^{-1}\text{s}^{-1}$, close to previously reported values (Juris et al. 1988 and references therein).

Upon photolysis of oxygen-free aqueous solutions of mono and polychlorophenols in the presence of $\text{Ru}(\text{bpy})_3^{2+}/\text{S}_2\text{O}_8^{2-}$ with near visible light, changes were seen in the UV/visible spectra (Fig. 1a, b for acidic pH and Fig. 2a, b for alkaline pH).

From Figs. 1 and 2, it is clear that PCP ($\epsilon_{250\text{nm}} = 1,950 \text{ M}^{-1}\text{cm}^{-1}$, $\epsilon_{321\text{nm}} = 935 \text{ M}^{-1}\text{cm}^{-1}$) is transformed into various photoproducts. Among the possible photoproducts, the major components detected by HPLC are BQ ($R_{\text{f}} = 3.2$);

1,2-HQ ($R_{\text{f}} = 2.1$); and 1,4-HQ ($R_{\text{f}} = 1.8$), in addition to the observation of the peak of PCP ($R_{\text{f}} = 5.2$). The ^{13}C NMR spectra (peaks at 189–198 ppm and 172–175 ppm) are also consistent with the formation of benzoquinone and dihydroxybenzenes, while the UV/visible spectral deconvolution shows that benzoquinone and dihydroxybenzenes absorb in a similar region to mono and polychlorophenols themselves. Although this latter observation makes kinetic studies based on UV/visible absorption changes difficult, it is possible to obtain valid data by assuming that bands near 246, 275 and 289 nm correspond to BQ ($\epsilon_{246\text{nm}} = 7,715 \text{ M}^{-1}\text{cm}^{-1}$), 1,2-HQ ($\epsilon_{275\text{nm}} = 2,160 \text{ M}^{-1}\text{cm}^{-1}$) and 1,4-HQ ($\epsilon_{289\text{nm}} = 2,515 \text{ M}^{-1}\text{cm}^{-1}$) maximum, respectively. As can be seen in Table 1, photodegradation of PCP depends on the initial $\text{Ru}(\text{bpy})_3^{2+}$ and $\text{S}_2\text{O}_8^{2-}$ concentrations and on the irradiation time.

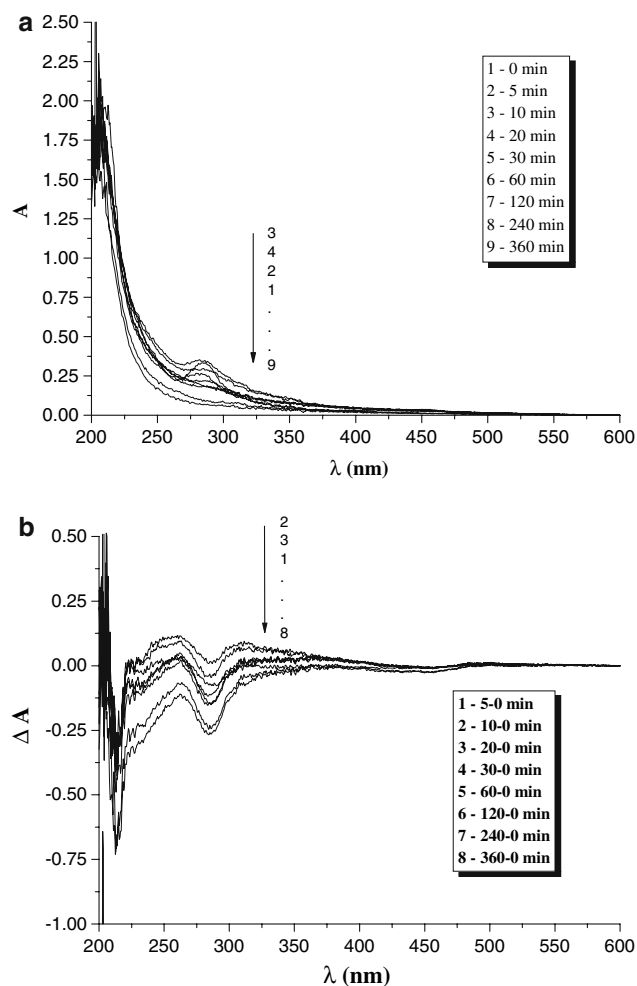


Fig. 1 a UV/visible absorption spectra of pentachlorophenol. $[\text{PCP}] = 1.1 \times 10^{-4} \text{ M}$, $[\text{Ru}(\text{bpy})_3^{2+}] = 2.7 \times 10^{-4} \text{ M}$, $[\text{S}_2\text{O}_8^{2-}] = 6.7 \times 10^{-3} \text{ M}$, before (1) and after irradiation times: 2–5, 3–10, 4–20, 5–30, 6–60, 7–120, 8–240 and 9–360 min. $\lambda_{\text{irr}} = 350 \text{ nm}$. Acidic pH. **b** Difference in absorption spectra from **a** between systems after and before irradiation

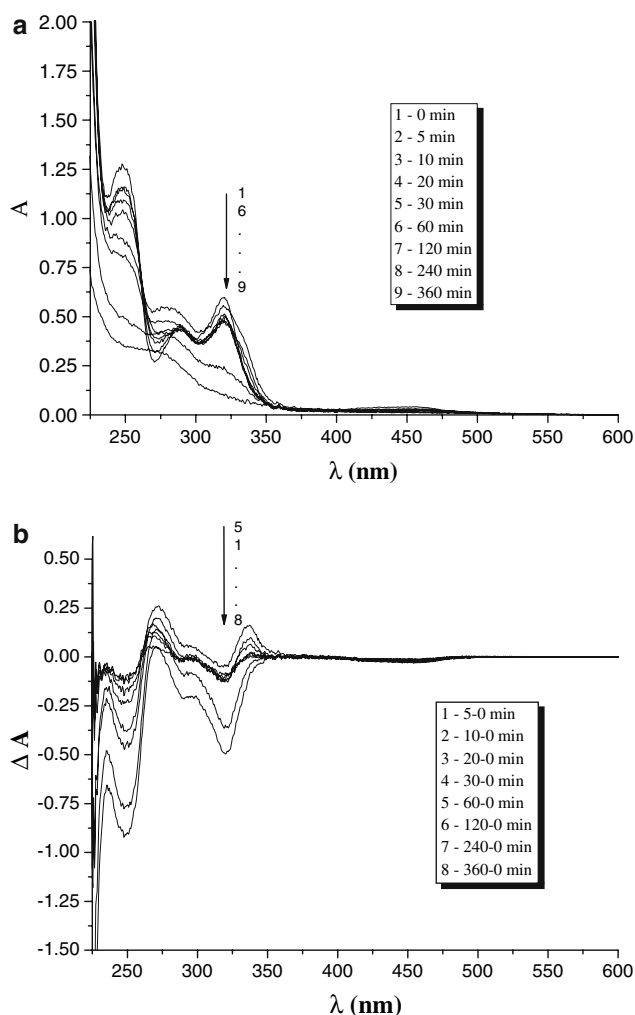


Fig. 2 **a** UV/visible absorption spectra of pentachlorophenol. $[PCP] = 1.1 \times 10^{-4}$ M, $[Ru(bpy)_3^{2+}] = 2.7 \times 10^{-4}$ M, $[S_2O_8^{2-}] = 6.7 \times 10^{-3}$ M, before (1) and after irradiation times: 2–5, 3–10, 4–20, 5–30, 6–60, 7–120, 8–240 and 9–360 min. $\lambda_{irr} = 350$ nm. Alkaline pH. **b** Difference absorption spectra from **a** between systems after and before irradiation

From this table and Figs. 1a, b and 2a, b it can also be seen that at longer irradiation times not only is the formation of intermediates enhanced, but also secondary reactions resulting from the degradation of these intermediates become important, as seen by absorptions at 310, 270 and 246 nm. These may result in the photomineralization of PCP at longer irradiation times.

This is confirmed by HPLC, although some traces of unknown photoproducts are still present. The UV/visible absorbance near 450 nm, corresponding to the $Ru(bpy)_3^{2+}$ MLCT band is almost identical after photolysis to that of non-irradiated solutions, showing that there is no overall complex degradation and that this is a catalytic process. The weak absorbance near 450 nm upon irradiation times between 20–120 min may result from the absorbance of a

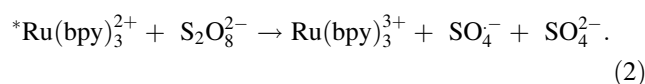
chlorophenol intermediate formed via ring contraction (Bonnichon et al. 2001), while the appearance of the new band at 520 nm can be attributed to an intermediate ruthenium species, $Ru(bpy)_3^+$ (Juris et al. 1988). However, at longer irradiation times, a decrease in this absorbance at 520 nm and in the intermediate band at 450 nm is observed, supporting the catalytic process and the PCP photomineralization.

The quantification of Cl^- in the photoproducts was obtained by potentiometric analysis as a function of the initial $Ru(bpy)_3^{2+}$ and $S_2O_8^{2-}$ concentrations at various irradiation times (Fig. 3a, b). In acidic media, the photodegradation of PCP is also accompanied by a pH decrease of the irradiated solutions (Table 1).

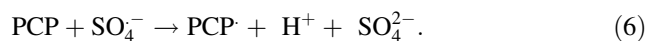
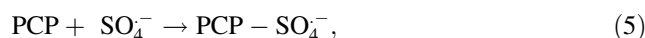
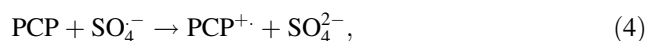
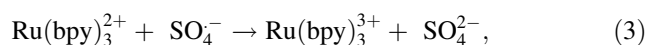
The results of continuous photolysis can be described according to the following reactions (1–7) initiated by the formation of the 3MLCT excited state of $Ru(bpy)_3^{2+}$ (1)



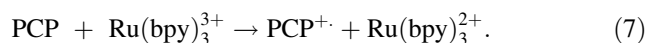
Then $S_2O_8^{2-}$ quenches the 3MLCT excited state of $Ru(bpy)_3^{2+}$, (2)



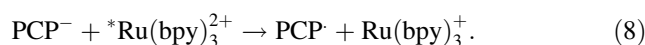
The anion radical $SO_4^{\cdot-}$ can either oxidize a second $Ru(bpy)_3^{2+}$ species (3) by thermal reaction or react with PCP by electron transfer (4), addition (5) and/or hydrogen abstraction (6)



The ruthenium(III) complex is also a strong oxidant (Juris et al. 1988) and can oxidize PCP according to reaction (7),



PCP quenches the 3MLCT of $Ru(bpy)_3^{2+}$ by a reductive quenching process, reaction (8), as is observed, at pH 12



The transient species formed during PCP degradation by reaction with $SO_4^{\cdot-}$ and/or the ruthenium complexes lead to the formation of the cation radical $PCP^{\cdot+}$, and/or its

Table 1 UV/visible absorbance changes occurring on the photodegradation of pentachlorophenol. $\lambda_{\text{irr}}=350 \text{ nm}$ [PCP]= $1.1 \times 10^{-4} \text{ M}$

Systems	$t_{\text{irr}}/\text{min}$	$\Delta A_{321 \text{ nm}}$	$\Delta A_{250 \text{ nm}}$	$\Delta A_{452 \text{ nm}}$	$\Delta A_{270 \text{ nm}}$	pH
[Ru(bpy) ₃ ²⁺] = $2.7 \times 10^{-6} \text{ M}$	0 ^a	0.087	0.345	0.036	0.129	2.66
	5–0	0.041	0.005	0.008	0.018	2.61
	10–0	0.071	0.099	0.012	0.078	2.60
[S ₂ O ₈ ²⁻] = $6.7 \times 10^{-3} \text{ M}$	20–0	0.062	0.071	0.019	0.059	2.57
	30–0	0.030	0.002	0.023	0.012	2.60
Acidic pH	60–0	0.013	-0.028	0.016	0.001	2.58
	120–0	-0.024	-0.005	0.020	0.001	2.55
	240–0	-0.033	-0.128	0.008	-0.054	2.47
	360–0	-0.044	-0.176	0.001	-0.076	2.45
	0 ^a	0.590	1.248	0.041	0.278	12.53
[Ru(bpy) ₃ ²⁺] = $2.7 \times 10^{-6} \text{ M}$	5–0	-0.084	-0.088	0.010	0.048	12.52
	10–0	-0.088	-0.121	0.013	0.090	12.53
[S ₂ O ₈ ²⁻] = $6.7 \times 10^{-3} \text{ M}$	20–0	-0.090	-0.158	0.016	0.115	12.54
	30–0	-0.092	-0.218	-0.006	0.141	12.52
Alkaline pH	60–0	-0.042	-0.379	-0.010	0.261	12.52
	120–0	-0.115	-0.433	-0.018	0.198	12.52
	240–0	-0.359	-0.756	-0.020	0.139	12.53
	360–0	-0.483	-0.899	-0.002	0.047	12.52
	0 ^a	0.590	1.248	0.041	0.278	12.53

^a Absorbance for $t_{\text{irr}} = 0 \text{ min}$

conjugated base, the phenoxy radical PCP[•], is also formed in the reaction (9)



The occurrence of reactions 6 and 9 explains the observed pH decrease (Table 1). The intermediates can also eliminate HCl and yield the detected photoproducts, benzoquinone and the dihydroxybenzenes.

There are also indications that ketene (resulting from ring contraction by Wolff rearrangement, Decand et al. 1994), biphenyls (Guyon et al. 1982) and some halogenated compounds (Burrows et al. 1998) could also be formed. As the solutions are continuously irradiated, the ruthenium(II) complex can be re-excited, oxidized by further peroxydisulphate and/or reduced by PCP to give a catalytic cycle (Fig. 4), until S₂O₈²⁻ completely disappears to form sulphate ion and/or PCP is completely mineralized. The presence of SO₄²⁻ in the photoproducts was qualitatively confirmed by precipitation with Ba²⁺.

Kinetic studies

Kinetic studies of PCP degradation upon irradiation were made by studying Cl⁻ release (Fig. 3). The Cl⁻ concentration expected for complete PCP degradation was greater than what was observed experimentally. This suggests that

some chlorinated intermediates were formed and were not completely degraded with an irradiation time of 3 h. However, in spite of this, it was still possible to obtain good pseudo-first order kinetic conditions. The experimental pseudo-first order rate constants obtained were $k_1 = 2.7 \times 10^{-6} \text{ min}^{-1}$ ($\chi = 0.993$) and $k_2 = 1.9 \times 10^{-4} \text{ min}^{-1}$ ($\chi = 0.995$) when the S₂O₈²⁻ and Ru(bpy)₃²⁺ initial concentrations change, at acidic and alkaline pH, respectively. The sensitized PCP photodechlorination rate law was found to be proportional to the Ru(bpy)₃²⁺ concentration [or that of *Ru(bpy)₃²⁺] and S₂O₈²⁻ initial concentrations,

$$V = d[\text{Cl}^{-}]/dt = k [\text{Ru}(\text{bpy})_3^{2+}] [\text{S}_2\text{O}_8^{2-}]. \quad (10)$$

Assuming that PCP photodechlorination is also first order in the PCP ($1.1 \times 10^{-4} \text{ M}$) concentration under our experimental conditions, the PCP photodechlorination rate constant was $k = 5.3 \times 10^3 \text{ M}^{-2} \text{ min}^{-1}$ (acidic pH) and $k = 3.8 \times 10^4 \text{ M}^{-2} \text{ min}^{-1}$ (alkaline pH) and the photodechlorination yields obtained were 21 and 36% at acidic and alkaline pH, respectively.

We have previously shown that the system Ru(bpy)₃²⁺/S₂O₈²⁻ acts as an excellent catalyst for the photodegradation/photodechlorination of the monochlorophenols 2, 3, and 4, photodechlorination yield $\cong 80\%$, $k \cong 10^2 \text{ M}^{-2} \text{ min}^{-1}$, also of the polychlorophenols 2,4-dichlorophenol, photo-

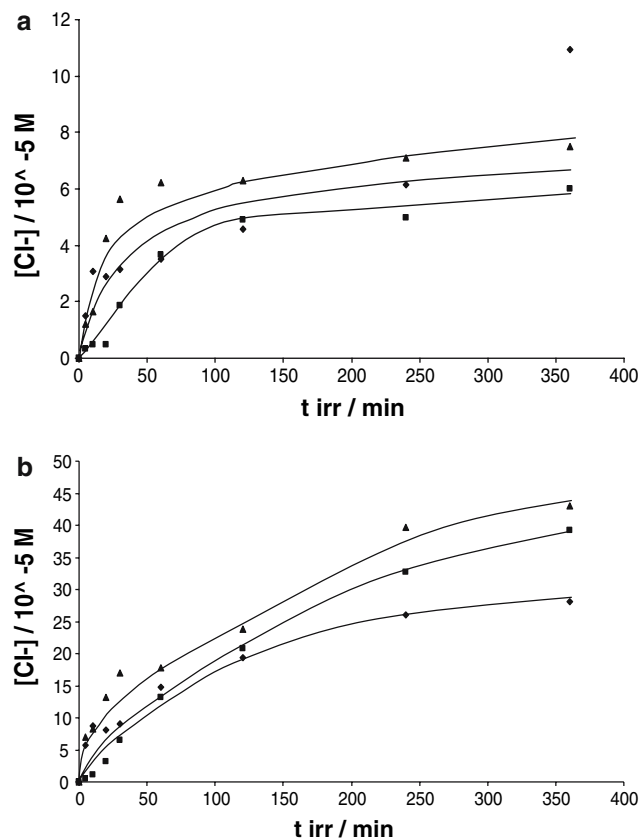


Fig. 3 **a** Pentachlorophenol dechlorination as a function of the irradiation time in acidic pH. $\lambda_{\text{irr}} = 350 \text{ nm}$. $[\text{PCP}] = 1.1 \times 10^{-4} \text{ M}$. Filled diamond $[\text{Ru}(\text{bpy})_3^{2+}] = 1.0 \times 10^{-6} \text{ M}$, $[\text{S}_2\text{O}_8^{2-}] = 3.3 \times 10^{-4} \text{ M}$; filled triangle $[\text{Ru}(\text{bpy})_3^{2+}] = 2.7 \times 10^{-6} \text{ M}$, $[\text{S}_2\text{O}_8^{2-}] = 3.3 \times 10^{-4} \text{ M}$; filled square $[\text{Ru}(\text{bpy})_3^{2+}] = 1.0 \times 10^{-6} \text{ M}$, $[\text{S}_2\text{O}_8^{2-}] = 3.3 \times 10^{-3} \text{ M}$. **b** Pentachlorophenol dechlorination as a function of the irradiation time at alkaline pH. $\lambda_{\text{irr}} = 350 \text{ nm}$. $[\text{PCP}] = 1.1 \times 10^{-4} \text{ M}$. Filled diamond $[\text{Ru}(\text{bpy})_3^{2+}] = 1.0 \times 10^{-6} \text{ M}$, $[\text{S}_2\text{O}_8^{2-}] = 3.3 \times 10^{-4} \text{ M}$; filled triangle $[\text{Ru}(\text{bpy})_3^{2+}] = 2.7 \times 10^{-6} \text{ M}$, $[\text{S}_2\text{O}_8^{2-}] = 3.3 \times 10^{-4} \text{ M}$; filled square $[\text{Ru}(\text{bpy})_3^{2+}] = 1.0 \times 10^{-6} \text{ M}$, $[\text{S}_2\text{O}_8^{2-}] = 6.7 \times 10^{-4} \text{ M}$

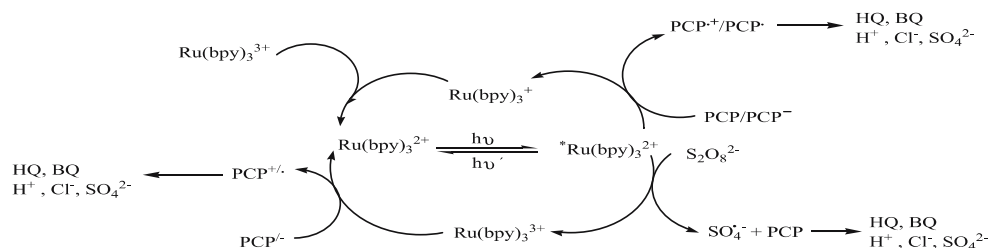
dechlorination yield $\cong 60\%$, $k \cong 10^3 \text{ M}^{-2} \text{ min}^{-1}$ and 2,4,6-trichlorophenol, photodechlorination yield $\cong 56\%$, $k \cong 10^3 \text{ M}^{-2} \text{ min}^{-1}$, at acidic pH and slightly higher at alkaline pH, assuming that all chlorine atoms were released during photolysis. The observed increase in the photodechlorination rate constants when the number of chlorine atoms and

the pH increase can be explained by the increasing acidic character of the chlorophenols ($\text{pK}_a = 9.43\text{--}6.23$), in general, and pentachlorophenol, in particular ($\text{pK}_a = 4.7$), with the dissociated species being more reactive towards oxidants such as the ruthenium complexes and the anion radical $\text{SO}_4^{\cdot -}$. In contrast, the photodechlorination yield decreases with increasing benzene substitution or decreasing pH.

Conclusions

The system $\text{Ru}(\text{bpy})_3^{2+}/\text{S}_2\text{O}_8^{2-}$ acts as an excellent catalyst for the photodegradation of mono and polychlorophenols using near visible light. In the present study, we have shown that this system is very efficient in the photodegradation/photodechlorination of pentachlorophenol. The main organic products among the intermediates formed during photolysis appear to be benzoquinone (or its chloro derivatives) and dihydroxy benzenes (and its respective chloro derivatives), while the inorganic ions Cl^- , SO_4^{2-} and H^+ are also formed. The results suggest that the photodegradation of PCP sensitized by $\text{Ru}(\text{bpy})_3^{2+}/\text{S}_2\text{O}_8^{2-}$ is an oxidative process, initiated by $\text{SO}_4^{\cdot -}$ and/or $\text{Ru}(\text{III},\text{II})$ formed in the quenching of the excited state of the metallic complex by $\text{S}_2\text{O}_8^{2-}$ or $\text{PCP}^{\cdot -}$. The reaction mechanism probably involves both direct electron transfer and addition–elimination processes. The intermediate species may react with each other or another PCP molecule, leading to dechlorination and the observed pH changes in acidic solutions. As the $\text{Ru}(\text{bpy})_3^{2+}$ complex is regenerated in the overall reaction of PCP, photodechlorination in the presence of the pair $\text{Ru}(\text{bpy})_3^{2+}/\text{S}_2\text{O}_8^{2-}$ makes the scheme a catalytic process. The kinetic studies carried out under pseudo-first order conditions, show that PCP photodechlorination is a fast reaction and is first order in both $\text{Ru}(\text{bpy})_3^{2+}$ and $\text{S}_2\text{O}_8^{2-}$ initial concentrations. If the ruthenium complex can be immobilized on an appropriate solid support, the system has considerable potential for general applications for decomposition of chloroaromatic pollutants using sunlight.

Fig. 4 Scheme of the photocatalytic degradation of pentachlorophenol in the presence of the pair $\text{Ru}(\text{bpy})_3^{2+}/\text{S}_2\text{O}_8^{2-}$



References

- Benitz FB, Heredia JB, Acero JL, Rubio FJ (2001) Oxidation of several chlorophenols derivatives by UV irradiation and hydroxyl radicals. *J Chem Technol Biotechnol* 76:312–320
- Bonnichon F, Richard C, Grabner G (2001) Formation of an α -ketocarbene by photolysis of aqueous 2-bromophenol. *Chem Commun* 73:1–5
- Burrows HD, Ernestova LS, Kemp TJ, Skurlatov YI, Purmal AP, Nermakov AN (1998) Kinetics and mechanism of photodegradation of chlorophenols. *Prog React Kinet* 23:145–207
- Decand J, Bollag JM (1994) Dehalogenation of chlorinated phenols during oxidative coupling. *Environ Sci Technol* 28:484–490
- Guyon C, Boule P, Lemaire J (1982) Photochemie et Environnement Formation d'Acid Cyclopentadiénique par Irradiation du Chloro-2-Phenol en Solution Aqueuse Basique. *Tetr Lett* 23:1581–1584
- Halmann M, (1996) *Water Pollutants*. CRC, Finland
- Horikoshi S, Hidaka H, Serpone N (2003) Environmental remediation by an integrated microwave/UV-illumination technique. Non thermal effects in the microwave-assisted degradation of 2,4-dichlorophenoxy-acetic acid in UV-irradiated $\text{TiO}_2/\text{H}_2\text{O}_2$ dispersions. *J Photochem Photobiol A Chem* 159:289–300
- Juris A, Balzani V, Barigelletti F, Campagna S, Belser P, Zelewski AV (1988) Ru(II) polypyridine complexes: photophysics, photochemistry, electrochemistry and chemiluminescence. *Coord Chem Rev* 84:85–277
- Legrin O, Oliveros E, Braun AM (1993) Photochemical processes for water treatment. *Chem Rev* 93:671–698
- Mills A, Morris S, Davis R (1993) Photomineralization of 4-chlorophenol sensitised by titanium dioxide: a study of intermediates. *J Photochem Photobiol A Chem* 70:183–191
- Mylonas A, Papaconstantinou E (1996) On the mechanism of photocatalytic degradation of chlorinated phenols to CO_2 and HCl by polyoxometalates. *J Photochem Photobiol A Chem* 94:77–82
- D'Oliveria JC, Minero M, Pelizzetti E, Pichat P (1993) Photodegradation of dichlorophenols and trichlorophenols in TiO_2 aqueous solutions: kinetic effects of the position of the Cl atoms and identification of the intermediates. *J Photochem Photobiol A Chem* 72:261–267
- Pandiyani T, Rivas OM, Martinez JO, Amezcua GB, Carrillo MM (2002) Comparison of methods for the photochemical degradation of chlorophenols. *J Photochem Photobiol A Chem* 146:149–155
- Rajagopal S, Gnanaraj GA, Mathew A, Srinivasan C (1992) Excited state electron transfer reaction of tris(4,4'-dialkyl-2,2'-bipyridine)ruthenium (II) complexes with phenolate ions: structural and solvent effects. *J Photochem Photobiol A Chem* 69:83–89
- Silva MI, Burrows HD, Miguel MG, Formosinho SJ (1996) Tris-2,2'-bipyridylruthenium(II) peroxydisulphate as a photosensitizer in the oxidative degradation of 4-chlorophenol. *Ber Bunsenges Phys Chem* 100:138–143