# Tris-2,2'-Bipyridylruthenium(II) Peroxydisulphate as a Photosensitizer in the Oxidative Degradation of 4-Chlorophenol

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The photolysis of aerated aqueous solutions of 4-chlorophenol in the presence of  $Ru(bpy)_3^{2+}$  and peroxydisulphate has been followed by UV/visible absorption spectroscopy, and reveals a relatively rapid oxidative decomposition of the phenol. Confirmation of the formation of benzoquinone and dihydroxybenzene as the principal products comes from product separation and spectroscopic characterization, HPLC, and TLC. 4-Chlorocatechol is also produced, while the main inorganic products are shown to be chloride and sulphate ions.  $Ru(bpy)_3^{2+}$  is regenerated in the reaction scheme, making this an overall catalytic process. Prolonged irradiation leads to further degradation into CO<sub>2</sub> and HCl. From the study of the kinetics of the reactions and considerations of literature data, a mechanistic scheme is presented.

#### 1. Introduction

New chemical methods are required for the more rigorous control of organic pollutant levels in waste waters, and the photochemical treatment of such effluents is now an area of active research.

Chlorinated phenols are an important class of environmental pollutants and among them, monochlorophenols and dichlorophenols are known for their fungicidal and hercibical effects [1] and for their general resistance to chemical, and biological degradation in the environment. The possibility of water contamination with chlorophenols is very high, as these compounds are involved in many different syntheses and formulations [2] (pesticides, disinfectants, dyes, drugs, etc.). They can also be formed during bleaching by chlorination in the paper industry or in chlorinated drinking water [3] where a chemical reaction of aromatic compounds with chlorine can take place.

Both direct photolysis [4] using vacuum ultraviolet light (172 nm) and photocatalysis [5] have been successfully employed in the complete mineralization of many organic pollutants from waste waters. Direct VUV photolysis has the advantage of producing high concentrations of strongly oxidative radicals such as OH<sup>•</sup> from water photolysis without the addition of any supplementary oxidant or catalyst. However, photocatalytic methods, which use longer wavelength light, are often prefered. Because of its low cost and high efficiency, titanium dioxide [5-7] is one of the most widely used photocatalysts for such processes. The OH<sup>•</sup> radical [5] has also been suggested to be one of the primary oxidants. But TiO<sub>2</sub> has the economic disadvantage that it does not absorb in the visible region, and so ultraviolet lamps are required for irradiation.

We have been studying the photophysics and photochemistry of transition metal complexes [8], and in particular the sensitizer tris-2,2'-bipyridylruthenium(II) (Ru(bpy)<sub>3</sub><sup>2+</sup>) and related compounds. This sensitizer has several useful attributes [8–11]: it is water soluble, absorbs strongly in the visible ( $\varepsilon \sim 1.4 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ , at  $\lambda = 450 \text{ nm}$ ) and has an easily detected emission ( $\lambda = 620$  nm) which facilitates mechanistic studies by fluorescence quenching. It is reasonably photostable to substitution with light in the visible and near-UV wavelength region so that direct photolysis presents no complication. The lowest excited state is a low lying triplet charge transfer (<sup>3</sup>MLCT) state, having an energy of 205 kJ mol<sup>-1</sup> above the ground state and a reasonably long lifetime. Further,  $Ru(bpy)_3^{2+}$  can readily be immobilized by fixing to a polymer support. This will be particularly important for application in waste water treatment, since ruthenium compounds are generally thought to be highly toxic [12] and their presence in effluent waters must be avoided. Whereas the behaviour of  $Ru(bpy)_3^{2+}$ makes it one of the most widely studied and used complexes in inorganic photochemistry [10], its potential in the photomineralization of waste effluents has not previously been demonstrated. The aim of this work is to discuss the application of the  $Ru(bpy)_3^{2+}/S_2O_8^{2-}$  system to the photomineralization of 4-chlorophenol.

The excited state,  $*Ru(bpy)_3^{2+}$ , can be efficiently quenched by  $S_2O_8^{2-}$  to give  $Ru(bpy)_3^{3+}$ ,  $SO_4^{2-}$  and  $SO_4^{-\bullet}$ radical anion. Like  $Ru(bpy)_3^{3+}$ ,  $SO_4^{-\bullet}$  is a strong oxidant and is able to oxidize various organic and inorganic compounds. The reactivity of the sulphate radical anion is well documented [13], and the species has the advantage that the final product is the non-pollutant sulphate anion. Although direct reaction between  $*Ru(bpy)_3^{2+}$  and phenolic compounds has been observed [14], this is only important at high pH values (>9.5).

#### 2. Experimental Data

Materials: 4-chlorophenol (4-CP or 4-Cl-PhOH), potassium peroxydisulphate, barium nitrate, silver nitrate, ethanol, methanol, chloroform and dichloromethane were p.a. reagents from Merck. Tris-2,2'-bipyridylruthenium(II) dichloride hexahydrate,  $Ru(bpy)_3Cl_2 \cdot 6H_2O$ , was p.a. reagent from Fluka.

All compounds were used without further purification. All solutions were prepared with distilled water immediately before use.

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Reaction procedure: typically, an aqueous solution of  $\text{Ru}(\text{bpy})_3^{2^+}$  was added to a quartz cell containing a solution of 4-CP/S<sub>2</sub>O<sub>8</sub><sup>2^-</sup> in water. Solutions were not buffered and had an initial pH ~ 4. Irradiation was performed continuously in the reaction vessel with a 125 W medium pressure Hg lamp, using a short wavelength cut-off filter (transmission for  $\lambda > 370$  nm) (kv 370). For studies on degassed solutions, nitrogen was bubbled through the reaction vessel for 15 min.

The photomineralization of 4-CP was followed by UV/visible spectra changes as a function of irradiation time and 4-CP,  $\text{Ru}(\text{bpy})_3^{2^+}$  and  $\text{S}_2\text{O}_8^{2^-}$  concentrations, using a Shimadzu UV-2100 spectrophotometer. The pH was measured with a Crison micro-pH 2000.

The analysis of 4-CP and the photoproducts was carried out by thin-layer chromatography (t.l.c., eluent 50% CH<sub>3</sub>OH/CHCl<sub>3</sub>) and by high pressure liquid chromatography (HPLC) using a Merck-Hitachi 655A-11 (eluent CH<sub>3</sub>OH/H<sub>2</sub>O, 65%/35%), with detection at 224 nm with a 655A-22 UV detector, or a Shimadzu UV-visible photodiode array detector (model SPD-M6A).

The IR spectra were measured with a FTIR 740 Nicolet spectrometer using KBr pellets. The <sup>13</sup>C NMR spectra were



Fig. 1

UV/visible absorption spectra of 4-CP:  $3.3 \times 10^{-3}$  M,  $S_2O_8^{-2}$ :  $3.3 \times 10^{-3}$  M and  $Ru(bpy)_3^{-2+}$ :  $3.3 \times 10^{-5}$  M before and during irradiation. a) The different spectra shown correspond to the following irradiation times. — 0 min, ..... 30 min, ----- 60 min and ----- 120 min. b) Difference between absorption spectra of 4-CP,  $S_2O_8^{-2-}$  and  $Ru(bpy)_3^{+2+}$  after irradiation for — 30 min, .....60 min and ------120 min, and the initial absorption spectrum

obtained on a Varian Unity 500 spectrometer operating at 125.681 MHz with off resonance decoupled, using TMS as the internal reference.

The presence of  $SO_4^{2-}$  and  $Cl^{-}$  in the photoproducts was confirmed by qualitative analysis, whilst quantitative measurements of chloride product were made by potentiometric titration with an Ag ion selective electrode; Radiometer P4011 and the Radiometer reference electrode REF 251, using the Radiometer PHM95 (detection limit: 0.41 mg/dm<sup>3</sup>).

All measurements were carried out at room temperature in the presence of oxygen or nitrogen.

#### 3. Results and Discussion

4-Chlorophenol is a model compound for many waste water pollutants. On photolysis with visible light of aerated aqueous solutions of 4-chlorophenol (4-CP) in the presence of  $S_2O_8^{2^-}$  and  $Ru(bpy)_3^{2^+}$ , changes in the UV/visible absorption spectrum were observed (Fig. 1). The absorbance of  $Ru(bpy)_3^{2^+}$  at 450 nm after photolysis was identical to that of non-irradiated solutions, showing that this is a catalytic process. It was confirmed that the simultaneous presence of  $Ru(bpy)_3^{2^+}$ ,  $S_2O_8^{2^-}$  and light was necessary to observe these changes, as degradation of  $Ru(bpy)_3^{2^+}$ , 4-CP and  $S_2O_8^{2^-}$  was not observed in the dark during the photolysis time under the experimental conditions used in this study (Fig. 2).

On photolysis of degassed solutions of  $\text{Ru}(\text{bpy})_3^{2^+}$ ,  $S_2O_8^{2^-}$  at the concentrations given in Fig. 1, similar spectral changes were observed but the absorbance of the product at 250 nm was slightly higher (~ 12%).

It is clear that the 4-CP compound is being transformed into various other products, which absorb light in a similar region of the spectrum to the 4-CP itself. This makes kinetic studies based on the evaluation of spectral changes of 4-CP upon irradiation problematic. Nevertheless, a preliminary study was carried out by measuring the small absorbance changes of the new absorption bands formed around 250 and 290 nm. These are close to a maximum for benzoquinone and for 1,4-dihydroxybenzene (Fig. 3), and are tentatively assigned to these species. Thin-layer chromatography of the photolyzed product after filtration confirmed the presence of dihydroxybenzene and benzoquinone, among other products. Extraction of products into dichloromethane also confirmed the presence of benzoquinone in the organic phase.

HPLC analysis (Fig. 4), of the reaction mixture taken before irradiation and after 30 min of irradiation, revealed the presence of 4-chlorophenol (4-CP), 4-chlorocatechol (4-CC), benzoquinone (BQ) and 1,4-dihydroxybenzene (HQ) from a comparison with retention times of standards and literature data [5].

In spite of the broad spectral bands observed, results of infrared (carbonyl maximum observed at  $1750 \text{ cm}^{-1}$ ) and  $^{13}\text{C}$  NMR spectra (peaks at 189 ppm and 174 ppm) are also consistent with the formation of benzoquinone and 1,4-di-hydroxybenzene [15].



UV/visible absorption spectra of a)  $Ru(bpy)_3^{2+}: 3.3 \times 10^{-5} M$ ; b) 4-CP: 3.3×10<sup>-3</sup> M, and c)  $S_2O_8^{2-}: 3.3 \times 10^{-3} M$ . Before irradiation, .... irradiation for 60 min

Formation of benzoquinone has been reported following photolysis of aerated solution of phenol and  $\text{Ru}(\text{bpy})_3^{2^+}$ . However, in the presence of O<sub>2</sub>, \*Ru(bpy)<sub>3</sub><sup>2+</sup> is quenched and it is suggested that the reaction in this case involves singlet oxygen as an intermediate [16].

The presence of  $SO_4^{2-}$  and  $CI^-$  in the photoproducts was confirmed by qualitative analysis with barium nitrate and silver nitrate respectively, whilst quantitative measurements of chloride product, using an ion selective electrode, showed an efficiency of 80% in chloride production, after two hours of irradiation. These changes were also accompanied by a decrease in the pH of the solution (Table 1).

For a typical irradiation, the efficiency of 4-CP degradation (as measured by formation of dihydroxybenzene at 290 nm) depends on time (Fig. 5),  $S_2O_8^{2-}$  and Ru(bpy)<sub>3</sub><sup>2+</sup> concentrations (Table 2). From the extinction coefficient of benzoquinone ( $\lambda = 290$  nm,  $\varepsilon = 2720 \text{ M}^{-1} \text{ cm}^{-1}$ ) under these conditions, the maximum absorbance in Fig. 5, corresponds to 13% conversion of 4-CP into dihydroxybenzene.

The results of continuous photolysis can be described according to the following reactions: as previously reported [13],  $S_2O_8^{2-}$  quenches the <sup>3</sup>MLCT of Ru(bpy)<sub>3</sub><sup>2+</sup> in water, according to the mechanism described by Eqs. (1) and (2)



UV/visible absorption spectra of \_\_\_\_\_ benzoquinone, ----- dihydrobenzene and .... quinhydrone  $(3.3 \times 10^{-4} \text{ M})$ 



Fig. 4

Typical HPLC traces recorded using a sample of the reaction solution taken at t = 0 min (trace a) and 30 min (trace b) after the start of irradiation. Retention times (min) and assignment of products: I) 2.38-4-CP; II) 1.79-4-CC; III) unknown; IV) 0.97-BQ; V) 0.75-HQ

with an oxidative quenching rate constant of  $k_q = 1.4 \times 10^9$  M<sup>-1</sup> s<sup>-1</sup>.

The following mechanism is suggested for photolysis of 4-CP by  $Ru(bpy)_{3}^{2+}/S_2O_8^{2-}$  system:

$$\operatorname{Ru}(\operatorname{bpy})_{3}^{2^{+}} \xrightarrow{hv} *\operatorname{Ru}(\operatorname{bpy})_{3}^{2^{+}}$$
(1)



Fig. 5

Dependence of the absorbance, at  $\lambda = 290$  nm, on the irradiation time for a mixture of  $[\text{Ru}(\text{bpy})_3^{2^+}] = 3.3 \times 10^{-5} \text{ M}$ ,  $[4\text{-CP}] = 3.3 \times 10^{-3} \text{ M}$ , and  $[\text{S}_2\text{O}_8^{2^-}] = 3.3 \times 10^{-3} \text{ M}$ 

\*Ru(bpy)<sub>3</sub><sup>2+</sup> + S<sub>2</sub>O<sub>8</sub><sup>2-</sup> 
$$\longrightarrow$$
 Ru(bpy)<sub>3</sub><sup>3+</sup> + SO<sub>4</sub><sup>-•</sup> + SO<sub>4</sub><sup>2-</sup> (2)

The SO<sub>4</sub><sup>-•</sup> product can either oxidize a second Ru(bpy)<sub>3</sub><sup>2+</sup> species (3), by thermal reaction  $(k \sim 3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1})$  [17], or react with 4-CP by electron transfer (4), addition (5) or/and hydrogen abstraction (6)

$$Ru(bpy)_{3}^{2+} + SO_{4}^{-\bullet} \longrightarrow Ru(bpy)_{3}^{3+} + SO_{4}^{2-}$$
 (3)

 $4-CP + SO_4^{-\bullet} \longrightarrow 4-CP^{+\bullet} + SO_4^{2-}$ (4)

$$4-CP + SO_4^{-\bullet} \longrightarrow 4-CP - SO_4^{-\bullet}$$
(5)

Table 1 pH dependence upon irradiation time:  $[4\text{-CP}] = [S_2O_8^{2^-}] = 3.3 \times 10^{-4}$ and  $[\text{Ru}(\text{by})_3^{2^+}] = 3.3 \times 10^{-6} \text{ M}.$ 

pH
4.02
2.98
2.90

Table 2

Dependence of the absorbance, at  $\lambda = 290 \text{ nm}$ , on the  $S_2O_8^{2-}$ ,  $Ru(bpy)_3^{2+}$  and 4-CP concentrations, for an irradiation time of 30 min.

[4-CP]	S <sub>2</sub> O <sub>8</sub> <sup>2-</sup> ]	[Ru(bpy) <sub>3</sub> <sup>2+</sup> ]	A <sub>290</sub> <sup>a</sup> )	% conversion <sup>b</sup> )
M	M	M		4-CP→HQ
$3.3 \times 10^{-3}$	$3.3 \times 10^{-3}$	$3.3 \times 10^{-5}$	0.42	4.7
$3.3 \times 10^{-3}$	$3.3 \times 10^{-3}$	$3.3 \times 10^{-6}$	0.38	4.3
$3.3 \times 10^{-4}$	$3.3 \times 10^{-3}$	$3.3 \times 10^{-5}$	0.12	13.3
$3.3 \times 10^{-3}$	$3.3 \times 10^{-4}$	$3.3 \times 10^{-6}$	0.28	3.1

<sup>a</sup>) In 1 cm cells.

b) Calculated using  $\varepsilon = 2720 \text{ M}^{-1} \text{ cm}^{-1}$ .

## Table 3

Redox potentials of some of the couples present versus NHE.

Couple	$E^0/V$	Ref.
$Ru(bpy)_{3}^{3+}/Ru(bpy)_{3}^{2+}$	1.26	20
$Ru(bpy)_{3}^{3+}/*Ru(bpy)_{3}^{2+}$	0.86	20
$*Ru(bpy)_{3}^{2+}/Ru(bpy)_{3}^{+}$	0.77	10
$Ru(bpy)_3^{2+}/Ru(bpy)_3^{+}$	-1.28	20
$SO_4^{-\bullet}/SO_4^{2-}$	2.5 - 3.1	13

4-Cl-PhOH + SO<sub>4</sub><sup>-•</sup> 
$$\longrightarrow$$
 4-Cl-PhO<sup>•</sup> + H<sup>+</sup> + SO<sub>4</sub><sup>2-</sup> (6)

However, Fessenden et al. [18] have suggested that  $SO_4^{-\bullet}$  radical does not react by addition to the aromatic ring, but most likely induces an electron transfer mechanism, producing the aromatic radical cation (reaction 4). Although we have not found literature data for the rate of oxidation of 4-CP by  $SO_4^{-\bullet}$ , rates of oxidation of phenol in neutral solutions are typically  $k \sim 10^9 \text{ M}^{-1} \text{ s}^{-1}$  [19].

On the other hand, as the resulting Ru(III) complex,  $Ru(bpy)_3^{3+}$ , is also a strong oxidant (Table 3), it can also oxidize 4-CP according to reaction (7)

$$\operatorname{Ru}(\operatorname{bpy})_{3}^{3^{+}} + 4 - \operatorname{CP} \longrightarrow \operatorname{Ru}(\operatorname{bpy})_{3}^{2^{+}} + 4 - \operatorname{CP}^{+ \bullet}$$
 (7)

As the solution is continuously irradiated, the ruthenium(II) complex produced in reaction (7) may be excited again, oxidized by further peroxydisulphate and again reduced by 4-CP to give a catalytic cycle, Scheme I, until  $S_2O_8^{2-}$  completely disappears.



Scheme I

Das et al. [21] showed that 4-methoxyphenol at pH 7 quenches the <sup>3</sup>MLCT of Ru(bpy)<sub>3</sub><sup>2+</sup> in water by the reductive quenching process described by Eq. (8) with a reductive quenching rate constant  $k_q \sim 10^7 \text{ M}^{-1} \text{ s}^{-1}$ .

\*Ru(bpy)<sub>3</sub><sup>2+</sup> + 4-CP 
$$\longrightarrow$$
 Ru(bpy)<sub>3</sub><sup>+</sup> + 4-CP<sup>+•</sup> (8)

and a very fast decay of  $Ru(bpy)_3^+$  by back electron transfer to the quencher derived radical or radical anion  $(k_b \sim 10 \times 10^9 \text{ M}^{-1} \text{ s}^{-1})$ . However, under the experimental conditions employed (pH 2 – 4), quenching of \*Ru(bpy)\_3^{2+} by  $S_2O_8^{2-}$  is at least 100 times more efficient than by the phenol.

The transient species formed during 4-CP degradation by reaction with  $SO_4^{-\bullet}$  and Ru complexes leads to the formation of the cation radical, 4-CP<sup>+•</sup> and/or its conjugated base, the phenoxyl radical 4-CP<sup>•</sup> formed in the reaction (9)

$$4 - CP^{+ \bullet} \longrightarrow 4 - CP^{\bullet} + H^{+}$$
(9)

The occurrence of this reaction explains the observed pH changes (Table 1).

Recently, Mittal et al. [22] have suggested that the  $SO_4^{-\bullet}$  radical anion reacts with several aromatic compounds to give hydroxycyclohexadienyl radical. Their formation has been explained either by a direct electron transfer from the ring to  $SO_4^{-\bullet}$ , reaction (4), followed by hydration of the resulting radical cation, reaction (10), or by addition, reac-

$$\underbrace{\stackrel{OH}{\leftarrow}_{Cl}}_{Cl} \stackrel{H}{\longrightarrow}_{Cl} \stackrel{OH}{\longrightarrow}_{Cl} \stackrel{OH}{\longleftarrow}_{H} + H.$$
 (13)

$$\begin{array}{c} OH \\ \hline \\ \bigcirc \\ CI \\ OH \end{array} \longrightarrow \begin{array}{c} OH \\ OH \end{array} + CI^{*}$$
 (14)

$$\begin{array}{ccc} OH \\ \hline & & & OH \\ \hline & & & & & OH \\ \hline & & & & & & O \\ CI & OH \end{array} + CI^{*}$$
(15)

$$\begin{array}{c} OH \\ \hline \\ O \\ O \\ O \\ \end{array} \longrightarrow \begin{array}{c} OH \\ OH \\ OH \\ \end{array} + \begin{array}{c} O \\ O \\ O \\ O \\ O \\ \end{array}$$
(16)

$$\begin{array}{c} OH \\ \hline \\ \hline \\ \hline \\ C \\ C \\ \end{array} \end{array} \longrightarrow \begin{array}{c} O^{\bullet} \\ \hline \\ O \\ \hline \\ C \\ C \\ \end{array} + H^{+}$$
 (17)

Scheme II

tion (5), of  $SO_4^{-\bullet}$  to the benzene ring, followed by hydrolysis, reaction (11), or/and heterolysis, reaction (12),

 $4-CP^{+\bullet} + H_2O \longrightarrow 4-CP-OH^{\bullet} + H^+$ (10)

$$4\text{-}CP\text{-}SO_4^{-\bullet} \longrightarrow 4\text{-}CP^{+\bullet}\text{+}SO_4^{2-}$$
(11)

$$4-CP-SO_4^{-\bullet} + H_2O \longrightarrow 4-CP-OH^{\bullet} + SO_4^{2-}$$
(12)

of the geminal C-H or C-Cl bonds in further steps, producing hydrogen atoms and 4-chlorocatechol (4-CC), reaction (13), or chlorine atoms and 1,4-dihydroxybenzene (HQ), reaction (14), in either case by radical substitution.

In the presence of oxygen, the hydrogen atoms are expected to react to form hydroperoxyl (HO<sub>2</sub>·) radicals. The fact that oxygen has only a slight effect shows that reaction (13) is only a fairly minor process. This is in agreement with the small yield of 4-chlorocatechol.

The intermediate radical formed by addition to the para position can also eliminate HCl to yield quinhydrone (Q), reaction (15), which disproportionates subsequently to 1,4dihydroxybenzene (HQ) and p-benzoquinone (BQ), reaction (16), Scheme II.

The phenoxyl radical can be formed either by direct hydrogen abstraction from 4-CP by  $SO_4^{-\bullet}$ , reaction (6), and/or by the additional channel reaction (17), from 4-CP<sup>+•</sup>, leading to pH changes (Table 1).

The phenoxyl radical can also undergo various degradation products including dimerization [23].

Prolonged irradiation of the reaction mixture leads to further oxidation of the products into  $CO_2$  and HCl which explains the decrease in the absorbance at  $\lambda = 290$  nm (Figs. 1 and 5), and the pH changes shown in Table 1.

Scheme III summarises the overall mechanism suggested

# 4. Conclusions

The tris-2,2'-bipyridylruthenium(II) peroxydisulphate system is shown to be an effective catalyst for the oxidative degradation of 4-chlorophenol, chosen as a model substrate for organic pollutants in water, which is rapidly degraded in the presence of oxygen.



Analysis of the spectral changes during the reaction of  $*\text{Ru}(\text{bpy})_3^{2+}/\text{S}_2\text{O}_8^{2-}$  with 4-chlorophenol reveals that the reaction mechanism probably involves both direct electron transfer and addition-elimination processes, eventually leading to the formation of 4-chlorodihydroxycyclohexadienyl radicals.

Further irradiation of the reaction mixture produces 1,4dihydrobenzene and p-benzoquinone, among other products. Prolonged irradiation leads to further oxidation into  $CO_2$  and HCl. The results suggest that the photomineralization of 4-chlorophenol sensitized by  $Ru(bpy)_3^{2+}$  is a photooxidation initiated by the quenching of the excited state of the metallic complex by  $S_2O_8^{2-}$  and/or 4-CP, leading to the formation of the cation radical 4-CP<sup>+•</sup> and/or the corresponding phenoxyl radical. These species react with another radical or molecule present in solution leading to dechlorination and complete degradation of 4-CP into  $CO_2$ .

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