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Ruthenium-catalyzed oxidative dehalogenation of organics

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Contents

Abstract

Water-soluble ruthenium(II) complexes are effective catalysts for the deep oxidation of chlorinated organics in the presence of hydrogen peroxide or mono-persulfate at room temperature. Reactions are conducted either in nitromethane–water two phase or in water–acetonitrile mixtures or in water alone, in the presence of a surfactant agent (if the case) with the ruthenium(II) catalysts $[Ru(H_2O)_2(dmso)_4](BF_4)_4$, $[RuCl_2(dmso)_4]$ or [RuPcS] (dmso = dimethylsulfoxide; PcS = tetra-sulfo-phthalocyaninate). The oxidation of various chlorinated

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organics (chloro, bromo-, iodo- and nitro-benzene, polychlorobenzenes, polychlorophenols) was followed by monitoring the nature and the relative amounts of the final products: chlorinated substrates are often converted into hydrochloric acid and carbon dioxide. Factors such as solvent and oxidant affect the reactions, the most favorable conditions being achieved in aqueous media. Substituted benzenes are oxidized via an initial electrophilic attack followed by a series of faster steps, whereas with polychlorophenols, which are more sensitive to oxidation than substituted benzenes, the reaction is also radical in character.

Keywords: Oxidation; Chlorinated organics; Ruthenium complexes; Aqueous organometallic catalysis

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1. Introduction

Halogenated organics are among the most widespread and persistent contaminants of ground- and surface-water; all of the 12 persistent organic pollutants (POP) recently recommended by the UN Environment Program to be phased out of production and use are chlorinated organics [1]. The request for suitable methods of 'detoxification' (dehalogenation) of halo-organics without emission of hazardous organic materials remains a major question of environmental chemistry research [2]. The ubiquitous presence of methane–monooxygenase and Cytochrome P450 enzymatic systems indicates that they may be of principal importance on a global scale for the oxidative degradation of xenobiotics, including halo-organics, in biological systems (Fig. 1). In many instances, however, current techniques of bioremediation of contaminated groundwater involving entire micro-organisms are inadequate because of toxic pollutant concentrations, nutrient limitations, and the lack of membrane permeability (which, coupled with the absence of suitable extracellular enzymes, is the accepted basis for a molecule being recalcitrant) [3].

Water-soluble metal-catalysts are good models for the mono-oxygenase enzymes and can be a gentle alternative method for destruction of halogenated hydrocarbons [4]. The oldest catalytic oxidative system for dehalogenation is Fenton's reagent; essentially the hydroxyl radical is one of the few chemical species capable of attacking refractory halo-organic compounds (although very recently the widely-accepted radical mechanism has been the object of a serious discussion [5]). The scope of the reaction in terms of substrate-oxidation versus H_2O_2-dismutation is often however limited by sensitivity to pH and narrow H_2O_2/Fe^{2+} ratio [6]. Alternatively, $OH^{\bullet}$ radicals can be generated by semiconductor photocatalysis; TiO_2 is the most widely studied semiconductor, presumably because of its photostability and non toxicity, but strong limitations of the method have been reported with concentrated solutions of pollutants [7]. Transition metal-complexes, in particular

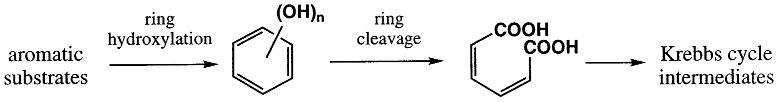

Fig. 1. Biological oxidation of aromatic compounds.

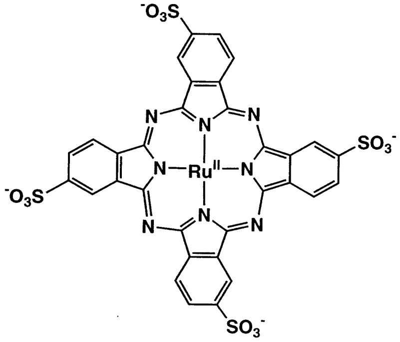

Fig. 2. Structure of the RuPcS complex.

metal-porphyrins, -corrins and -phthalocyanins, have been investigated in homogeneous aqueous systems as potential remediation catalysts. Water-soluble iron- or manganese-sulphofenylporphyrins catalyze the oxidative dechlorination of trichlorophenol with $KHSO_5$ in aqueous acetonitrile [8], whereas the corresponding sulfophthalocyanine catalysts behave similarly, in the presence of H_2O_2 [9].

Ruthenium tetroxide is a well known multipurpose stoichiometric oxidising agent for organic compounds and oxidation can often be made catalytic in the presence of a suitable secondary oxidant, conventionally periodate and hypochlorite [10]. Despite the fact that ruthenium catalysts are among the most effective systems in promoting the oxidative fission of the aromatic nuclei in mild conditions (and indeed it was shown to oxidize chlorinated aromatics in water [11]), only scattered reports have appeared on the subject and even less is known regarding the mechanism by which this important reaction takes place [12].

We focused in the past on the catalytic behaviour of non-porphyrinic complexes of ruthenium(II) for the conversion of organic compounds into the corresponding oxygenated derivatives by various mono-oxygen transfer agents [13]. Among various substrates, we also found that halogenated organics, both aromatic and olefinic, undergo oxidation, accompanied by extensive dehalogenation, in aqueous media in the presence of water soluble ruthenium catalysts, such as the dimethylsulfoxide-'solvated' ions $[Ru(H_2O)_2(dmso)_4](BF_4)_4$ and $[RuCl_2(dmso)_4]$, in conjunction with mono-persulfate [14]. Other oxidizing agents, such as iodosobenzene, magnesium peroxophthalate and potassium peroxodisulfate, were inactive. We also tried hydrogen peroxide, but the ruthenium complexes trigger a very rapid dismutation of the oxidant with little oxidation of the substrates. Now we have obtained a substantial improvement for the oxidative dechlorination of chlorophenols in water, by using dilute solutions of hydrogen peroxide in the presence of a water-soluble phthalocyanine complex of ruthenium(II), RuPcS (where PcS is sodium tetra-sulfophthalocyaninate dianion, Fig. 2). Variously substituted ruthenium–phthalocyanine complexes are known, both with Ru(II) and Ru(III) [15], which are soluble in organic media: to our knowledge RuPcS is the first water-soluble phthalocyanine-derivative of ruthenium reported so far. The green compound is diamagnetic in the solid state (Gouy's method) and a monomeric Ru(II) structure is tentatively proposed, possibly with two water molecules in apical positions.

2. Experimental

2.1. Materials

The complexes $[Ru(H_2O)_2(dmso)_4](BF_4)_2$ [12,13] and $[RuCl_2(dmso)_4]$ [16] were prepared by published procedures. A sample of [RuPcS] was prepared by template synthesis starting from ruthenium chloride, sodium 4-sulphophthalate and urea, following an early general procedure [17]. Potassium mono-persulfate was purchased from Aldrich (Oxone®: $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$).

2.1.1. Procedures

The reactions were carried out at 20°C in a 10 ml vial, by magnetically stirring an aqueous solution of the substrate (1–20 mM) and the catalyst (usually ca. 0.2 mM), to which suitable amounts of 30% hydrogen peroxide or Oxone® were added, corresponding to 100–600 mN H_2O_2 or $KHSO_5$, as determined by iodometric titration. In the experiments with the surfactant agent, 2.5% cetyltrimethylammoniun hydrogen sulfate was added; the experiments in non-acidic media were carried out in the presence of the desired phosphate buffer solutions (0.1 M solutions) or in aqueous NaOH. Reaction rates, determined for early stages of the reaction, were not affected by the presence of air and were reproducible to within 10–15%.

2.2. Analyses

Carbon dioxide evolved during the reaction was captured by an aqueous solution of $Ba(OH)_2$ 0.1 M, and aliquots from the filtered solution were backtitrated with 0.1 N HCl; the amount of CO_2 was also indirectly evaluated by TOC (Total Organic Carbon) measurements. Chloride ions produced upon oxidation of the chlorinated substrates were analysed spectrophotometrically by the mercury thiocyanate method; the degree of dechlorination (%) was calculated by the amount of chloride ions formed at given times relative to the total initial chlorine content of the chlorinated substrate. Organic analyses were performed on aliquots withdrawn with a hypodermic microsyringe on a HP 5890 Series II GLC instrument equipped with FID, using 30 m SE-30 capillary columns (0.25 mm i.d.) with the injection port thermostatted at 250°C (carrier gas, helium) or on a Beckman System Gold HPLC instrument equipped with UV detector, using a C-18 column (25 cm) by using 0.07% w/w H_3PO_4 solution as eluent. MS spectra were obtained with a VG 16F mass spectrometer operating in the electron ionisation mode at 70 eV. NMR spectra were measured on a Bruker Avance 300 MHz spectrometer. Derivatization of the putative oxygenated products was performed by treating the ethereal extracts of the acidified aqueous reactions mixtures with diazomethane, following standard procedures; the solutions were analysed by GC–MS.

3. Results

3.1. Oxidation of chloro-benzenes

Chlorobenzene is only slightly affected by oxidation with the conventional ruthenium trichloride–hypochlorite system in water/carbon tetrachloride (or dichloromethane), with less than 10% of the substrate oxidised after 100 h reaction at room temperature. Oxidation experiments with monopersulfate in a water–dichloromethane two phase system showed distinctly higher oxidation rates, with complete disappearance of the substrate within a few hours: CO_2 and inorganic chlorine (Cl_2 or Cl^- ions, depending upon the reaction conditions, see Section 3.3.1) were formed, together with minor amounts of chloroform, produced upon hyperchlorination of dichloromethane. To avoid the above undesirable reaction, we replaced dichloromethane with nitromethane, a non-chlorinated and non-easily oxidizable solvent alternative to acetonitrile, which caused massive salt precipitation from relatively concentrated aqueous solutions of monopersulphate. Under these conditions, the oxidative fission proceeds faster than in the chlorinated solvents by at least one order of magnitude (Table 1). The reaction can also be performed in the water phase, by adding suitable amounts of cetyltrimethylammoniun hydrogen sulfate, with oxidation rates comparable to those of the reactions conducted in nitromethane. The measured amounts of inorganic chlorine formed during the oxidation of chlorobenzene in the presence of chlorine-free catalysts and

Table 1
Oxidation of substituted-benzenes with mono-persulfate[a]

Substrate	CH_2Cl_2–H_2O[b] (%)	CH_3NO_2–H_2O[c] (%)	H_2O-surfactant[d] (%)
Benzoic acid	100 (2 h)	100 (15 min); CO_2, 75% (6 h)	n.d.[e]
Iodobenzene	100 (30 h)	100 (2 h)	n.d.[e]
Bromobenzene	65 (30 h)	85 (2 h)	n.d.[e]
Chlorobenzene	65 (30 h)	85 (2 h); HCl, 98%: CO_2, 85% (6 h)	85 (2 h)
Nitrobenzene	<1 (24 h)	55 (12 h); CO_2, 48% (12 h)	65 (12 h)
1,2-Dichlorobenzene	<1 (24 h)	<1 (24 h)	n.d.[e]
1,3-Dichlorobenzene	<1 (24 h)	70 (24 h)	75 (24 h)
1,4-Dichlorobenzene	<1 (24 h)	<1 (24 h)	n.d.[e]
1,3,5-Trichlorobenzene	<1 (24 h)	<1 (24 h)	<1 (24 h)

[a] Substrate conversion (at the time given); 20°C.

[b] Substrate (0.1 mmol) and $[RuCl_2(dmso)_4]$ catalyst (0.01 mmol) dissolved in CH_2Cl_2 (1 ml); $KHSO_5$ (0.3 mmol) dissolved in water (6 ml).

[c] Substrate (0.1 mmol) dissolved in CH_3NO_2 (1 ml); $[Ru(H_2O)_2(dmso)_4](BF_4)_2$ catalyst (0.01 mmol) and $KHSO_5$ (0.3 mmol) dissolved in water (6 ml).

[d] Substrate (0.01 mmol), $[Ru(H_2O)_2(dmso)_4](BF_4)_2$ catalyst (0.001 mmol), cetyltrimethylammonium hydrogen sulfate (17 mg) and $KHSO_5$ (0.03 mmol) dissolved in water (7 ml).

[e] n.d. = non detected.

solvents indicate quantitative dechlorination of the substrate, whereas the amount of carbon dioxide was constantly smaller than the chlorobenzene destroyed. No evidence of carbon monoxide was found, but examinations of the acidic aqueous phase indicate the presence of formic acid (ca. 2%) and of minor amounts of a variety of organic products. Polychlorobenzenes are scarcely affected by the oxidation, even in the more favourable reaction conditions, and only 1,3-dichlorobenzene, which has a relatively reactive and accessible ring position (position 5), undergoes oxidative fission, with slow degradation to CO_2 and inorganic chlorine. The oxidation completely failed for the other two isomeric dichlorobenzenes and for other polychlorinated benzenes, such as 1,3,5-trichlorobenzene.

Oxidations of iodo- and bromo-benzene proceed slightly faster than chlorobenzene, again with formation of carbon dioxide and formic acid, whereas the fate of the halogens is more complicated, by being irreversibly converted into the corresponding oxyacids in higher oxidation states. Among simple benzene-derivatives, nitrobenzene is the most resistant to the oxidation: yet, to our knowledge, very few oxidising systems are capable of effectively degrading this recalcitrant substrate [18]. In the case under investigation, no evidence of mineralization was observed when the ruthenium-catalyzed oxidation was carried out in a water–dichloromethane two phase system both with hypochlorite and with monopersulfate. Only when the reaction was conducted in water–nitromethane or in water in the presence of the surfactant, a significant oxidative degradation took place in the presence of monopersulfate, leading to the complete disappearance of nitrobenzene within 24 h: about 90% of the carbon is transformed into CO_2 (together with smaller amounts of HCOOH), whereas the organic nitro-group is converted into nitrate ions.

The degree of deactivation of the aromatic nuclei plays a key role in the oxidation of substituted benzenes: (a) the introduction of further chlorine into the benzene ring rapidly enhances the resistance to the oxidative fission; (b) the observed sensitivity to the oxidation of mono-substituted benzenes is in a strictly inverse relationship to the dipole moments of the substrates, which are conventionally related to the degree of deactivation of the aromatic ring (Fig. 3). Deuterium kinetic isotopic measurements for the monopersulfate-oxidation of chlorobenzene in the presence of the $[RuCl_2(dmso)_4]$ catalyst gave k_H/k_D values constantly equal or (slightly) smaller than one, which are typically found in electrophilic aromatic substitutions involving only a change of hybridization at carbon ($sp^2 \rightarrow sp^3$) without C–H bond cleavage. Electrophilic attack at the benzene ring by the oxo-metal reagent [19] is likely followed by a series of kinetically inaccessible steps leading to the complete oxidative degradation of the substrates, which also accounts for the fact that we never observed accumulation of intermediate organic products during the course of the reactions.

3.2. Oxidation of chloro-phenols

Phenols are known to undergo oxidation by monopersulfate alone (Elbs oxidation) with formation of products of further hydroxylation of the aromatic ring [20]: under these conditions however chloro-phenols are not significantly dechlorinated.

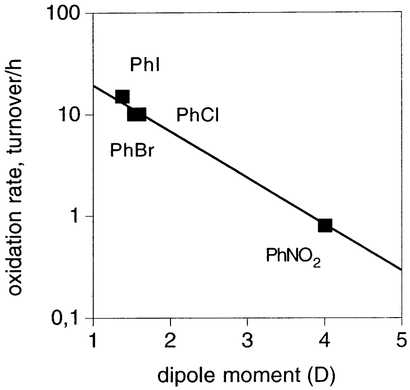

Fig. 3. Initial oxidation rate (substrate disappearance, turnover/h) versus dipole moment of PhX substrates (D). Substrate, 0.1 mmol, in 1 ml of CH_3NO_2; $[Ru(H_2O)_2(dmso)_4](BF_4)_2$ catalyst, 0.01 mmol, and $KHSO_5$, 0.3 mmol, in 6 ml of water; 20°C.

Various polychlorophenols are instead easily oxidized by monopersulfate when in the presence of the ruthenium catalysts with complete degradation and extensive dechlorination of the substrates within hours (Table 2). The presence of a phenolic group dramatically enhances the sensitivity of the aromatic rings to the oxidative fission. The measured rates of disappearance of the substrates examined, i.e. pentachloro-, 2,4,6-trichloro- and 2,6-dichloro-phenol, are much larger than the corresponding chloro-substituted benzenes. The amount of inorganic chlorine evolved indicates almost quantitative (80%) dechlorination, whereas less than 50% of carbon was converted into carbon dioxide: HPLC analyses indicate the presence of a wide variety of water-soluble organic products, among which are the *para*-dihydroxylate and the corresponding chloroquinone derivatives and various isomers of the products of radical coupling.

There are convincing indications for a radical character of the reaction, with the initial attack likely centered on the phenoxide anion: the reaction is scarcely sensitive to the presence of more chlorine into the phenolic ring, with the outstanding result that the reactivity of pentachlorophenol is similar to that of phenol.

Table 2
Oxidation of chloro-phenols with mono-persulfate[a]

Substrate	Substrate converted (%)	HCl produced (%)	CO_2 produced (%)
Phenol	100 (3 h)	=	n.d.[b]
2,6-Dichlorophenol	100 (1 h)	85 (6 h)	45 (6)
2,4,6-Trichlorophenol	100 (30 min)	80 (6 h)	50 (6)
Pentachlorophenol	100 (3 h)	n.d.[b]	n.d.[b]

[a] Conversions (at the times given); 20°C. Substrate (0.1 mmol) dissolved in CH_3NO_2 (1 ml); $[Ru(H_2O)_2(dmso)_4](BF_4)_2$ catalyst (0.01 mmol) and $KHSO_5$ (0.3 mmol) dissolved in water (6 ml).

[b] n.d. = non detected.

Table 3
Oxidation of 2,4,6-trichlorophenol (10 mM) by H_2O_2 (60-fold, equiv/mol), in water at pH 7.5 (phosphate buffer); catalyst, 0.2 mM; 20°C.

Catalyst	HCl produced (%)	CO_2 produced (%)	H_2O_2 consumed (%)
$[RuCl_2(dmso)_4]$	35 (3 h)	25 (3 h)	100 (3 h)
$[RuCl_2(dmso)_4]$[a]	3 (24 h)	n.d.[b]	10 (24 h)
RuPcS	69 (24 h)	50 (24 h)	60 (24 h)

[a] Freshly prepared solutions.
[b] n.d. = non detected.

Indeed this behaviour is in good agreement with the small effect of ring substituents expected for radical aromatic substitutions, when compared to electrophilic or nucleophilic substitutions. The reaction of ruthenium tetroxide with dichlorophenols is also reported to occur through a radical pathway, with formation of products of radical coupling, such as tetrachloro-dihydroxy-biphenyl, and definite ESR evidence for dichlorophenoxyl radicals [21].

Replacement of the dmso-'solvated' ruthenium ions by the water-soluble RuPcS derivative results in a definite improvement of the reaction course with hydrogen peroxide: dismutation of the oxidant is significantly lowered, thus making possible an effective oxidation of the substrates (Table 3 and Fig. 4). Freshly prepared solutions of $[RuCl_2(dmso)_4]$ are scarcely active, not only in terms of oxidation of the substrates, but also for the dismutation of hydrogen peroxide, thus suggesting that the complex is a precursor for the true catalytic species, likely a 'naked' ruthenium ion in high oxidation state. Aged solutions of dmso-derivatives of ruthenium are instead extremely active for the oxidation, also leading to extensive dismutation of hydrogen peroxide. It is also possible that these aged solutions

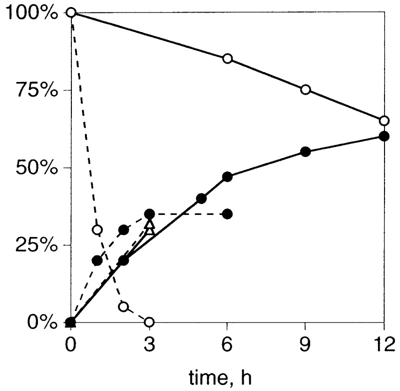

Fig. 4. Time course for the oxidation of 2,4,6-trichlorophenol, 10 mM, by H_2O_2, 300 mM, in water, pH 7.5 (phosphate buffer); RuPcS (——) or $[Ru(H_2O)_2(dmso)_4](BF_4)_2$ (– – – –) catalysts 0.2 mM; 20°C. Cl (●), H_2O_2 (○), CO_2 (△).

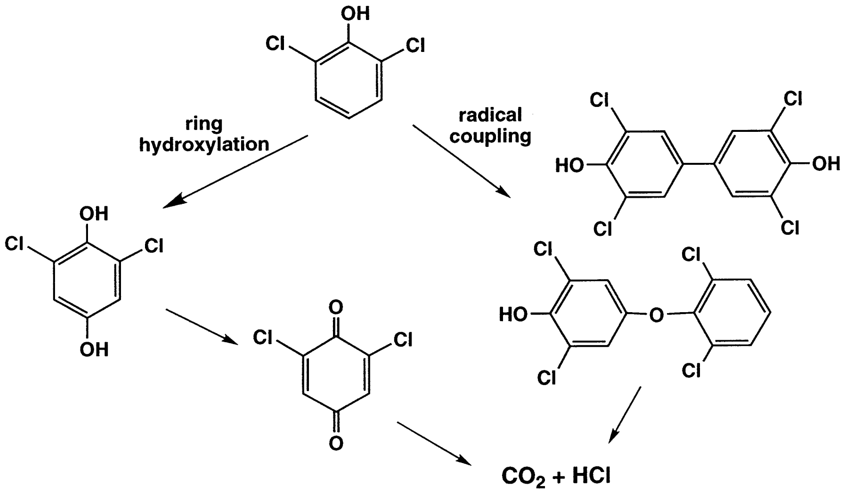

Fig. 5. Hydrogen peroxide oxidation of 2,4-dichlorophenol by RuPcS.

contain colloidal ruthenium, which was recently reported to be formed by the decomposition in water of various ruthenium complexes and proved to be an effective oxidation (and dismutation) catalyst in the presence of ter-BuOOH [22].

RuPcS promotes the oxidation of chlorophenols with various inorganic peroxides, in addition to hydrogen peroxide. Dechlorination yields are in the order: mono-persulfate $\approx$ hydrogen peroxide $\gg$ percarbonate $\approx$ perborate (in the reaction conditions, percarbonate and perborate indeed suffer extensive and fast dismutation, which leads to modest dechlorination, Table 4).

Catalytic H_2O_2 (and $KHSO_5$)-oxidation of chlorophenols by RuPcS in water results in all cases in the complete and rapid disappearance of the substrates. Inspection of the reaction mixtures by GC–MS and NMR indicates the early conversion of dichlorophenols into the corresponding biphenyl (and/or O-bridged dimers) derivatives via radical coupling, together with substantial amounts of products of further ring hydroxylation and their oxidized counterparts (Fig. 5). At prolonged times, the above derivatives disappear progressively, with formation of massive amounts of HCl and CO_2, finally accounting for almost complete mineralization of the substrates. Oxidation of 2,4,6-trichlorophenols and pentachlorophenol (Table 5) yields no products of radical coupling nor hyperhydroxylation products, presumably because of the lack of activated ring positions: when all the starting substrate has disappeared from the reaction mixtures, the products only detected were HCl and CO_2. In order to speed up the reaction, we also perform the oxidation in the presence of larger amounts of the catalyst: under these conditions we observed that HCl is almost quantitatively formed quite rapidly, whereas the formation of CO_2 follows slower kinetics, by being produced dominantly only after dechlorination is completed (Fig. 6). Mass balance indicates the presence of significant amounts of organic derivatives, other than the substrate, and indeed

Table 4
Oxidation of 2,4-dichlorophenol catalyzed by RuPcS in water; 20°C

Substrate (mM)	pH	Catalyst/substrate (mol/mol) (%)	Oxidant/substarte (equiv/mol)	Time (h)	Oxidant consumed (%)	HCl (%)	CO_2 (%)
25	5	1	35 (H_2O_2)	24	25	21	28
25	12	2	60 (H_2O_2)	24	90	22	18
20	2	2	30 ($KHSO_5$)	14	100	42	29
30	9	2	30 ($KHSO_5$)	14	100	40	26
30	11	0.5	15 (percarbonate)	4	100	2	n.d.[a]
30	11	0.5	10 (perborate)	4	100	4	n.d.[a]

[a] n.d. = non detected.

Table 5
Oxidation of chlorophenols by H_2O_2 catalyzed by RuPcS (usually 0.2 mM) in water; 20°C[a]

				HCl		
Substrate (mM)	pH	Catalyst/substrate (mol/mol) (%)	Oxidant/substrate (equiv/mol)	(6 h) (%)	(24 h) (%)	(48 h) (%)
2,6-DCP						
10	5[b]	2	60	6	20	30
10	7.5	2	60	17 (4 h)	34	37
10	8.5	2	60	12 (4 h)	26	37
10	13	2	60	5 (4 h)[c]		
2,4,6-TCP						
10	5[b]	2	60	9	13	24
10	7.5	0.2	60	5	10	21 (96 h)
10	7.5	2	60	47	69	
10	7.5	10	60	98 (3 h) (CO_2, 31%)		
20	7.5	0.25	30	10 (CO_2, 12%)	17 (CO_2, 18%)	23 (CO_2, 26%)
10	8.5	0.2	60	3	8	18 (96 h)
10	8.5	2	60	27	46	
20	8.5	0.25	30		14	33 (96 h)
10	13	2	60	4[c]		
PCP						
3[d]	5[b]	7	200	7	9	12
4[d]	7.5	5	150	16	30	67 (96 h)
10	8.5	2	60	10	19	39 (96 h)
10	13	2	60	3[c]		

[a] Runs at pH 7.5 and 8.5 in phosphate buffer (0.1 M); runs at pH 13 and 12 in NaOH 0.1 and 0.01 M, respectively.

[b] Acetonitrile: water 1:3 (acidic solution, ca. pH 5).

[c] Oxidant completely consumed.

[d] Saturated solutions.

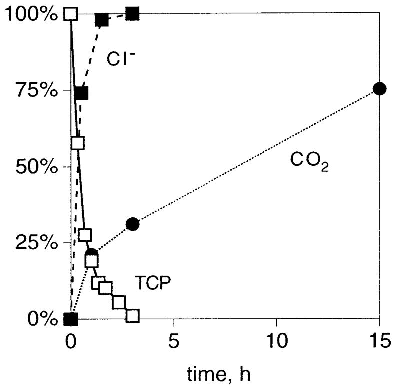

Fig. 6. Time course for the oxidation of 2,4,6-trichlorophenol (TCP), 10 mM, by H_2O_2, 300 mM, in water pH 7.5 (phosphate buffer); RuPcS catalyst (1 mM); 20°C.

TOC analysis data substantially agree with the calculated mass balance. Nevertheless, we were not able to detect by GC and HPLC measurements any low-molecular weight organics in the aqueous reaction mixtures, deriving from the oxidative fission of the aromatic nuclei. We also attempted derivatization of the reaction mixtures by standard diazomethane treatments, but GC measurements on the ethereal extracts only showed the presence of residual 1,3,5-trichloro-2-methoxybenzene; careful inspection of ^1H- and ^{13}C-NMR spectra of both the crude aqueous reaction mixtures and of their methoxyl-derivatized counterparts in ether, was equally unsuccessful. Whereas it is possible that transient C1 and/or C2 fragments are in fact formed, which are difficult to detect, the experimental data allow us to rule out significant formation of stable, heavy organic intermediates ($\geq$ C3) deriving from the fragmentation of the aromatic nuclei.

Dechlorination is strongly dependent upon the pH of the media, by following a more or less bell-shaped trend with a maximum around the neutrality for all the

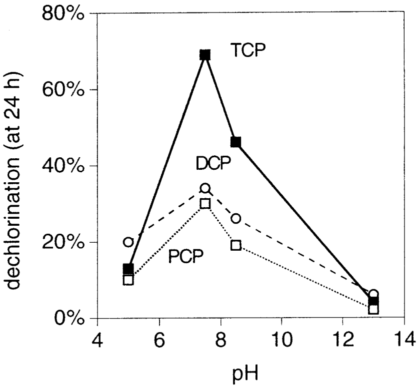

Fig. 7. Dechlorination of 2,4,6-trichlorophenol (TCP), 2,6-dichlorophenol (DCP) and pentachlorophenol (PCP) by H_2O_2, 300 mM, in water at various pH; 20°C. Substrate, 10 mM; RuPcS catalyst, 0.2 mM.

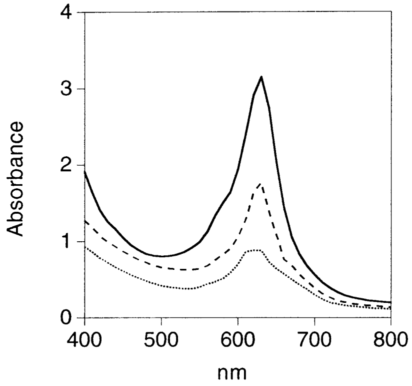

Fig. 8. Time course of visible spectra of 0.2 mM RuPcS in water, ——; with H_2O_2 (300 mM) added, after 15 min, – – – –; after 1 and 6 h, ······. pH 7.5 (phosphate buffer); 20°C.

chloro-phenols examined (Fig. 7). The observed trend is somewhat unexpected, since H_2O_2 is known to be more reactive in alkaline media, moreover the phenolic substrates might be more sensitive to the oxidation in the form of the phenolate anions: therefore we were expecting increasing oxidation with pH (even if disproportionation of hydrogen peroxide is intrinsically favoured in alkaline media, thus limiting the overall oxidation yields). We noticed that whereas the RuPcS catalyst is considerably stable in aqueous solutions in the 3–13 range of pH, as shown by the persistence of the diagnostic $\pi \rightarrow \pi^*$ band at 630 nm), it is affected by the addition of H_2O_2, especially in neutral or acidic media, giving rise to a novel, colorless species, whose nature is under investigation, but is likely responsible for the catalytic activity (Fig. 8). Indeed, the reduced activity of the catalytic system in alkaline media appears to be related to the stability of RuPcS at pH 13 (Fig. 9).

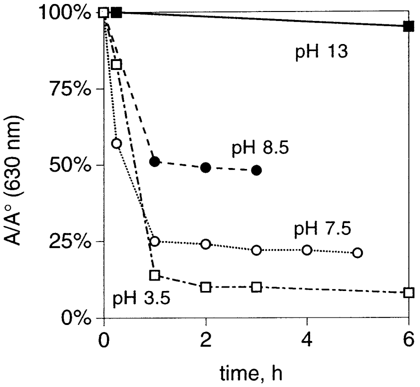

Fig. 9. Relative intensity of the band at 630 nm at various pHs; RuPcS, 0.2 mM, in water and in the presence of H_2O_2, 300 mM; 20°C.

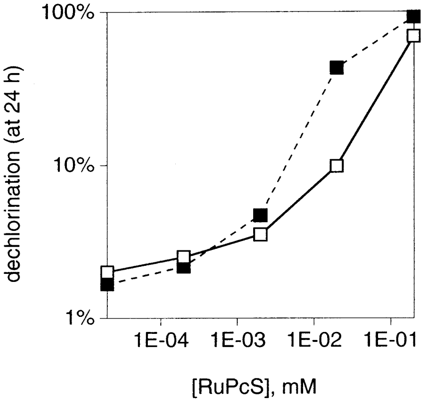

Fig. 10. Dechlorination (at 24 h) of 2,4,6-trichlorophenol (TCP) by H_2O_2, in water, pH 7.5 (phosphate buffer), and in the presence of RuPcS catalyst; 20°C. TCP 10 mM, H_2O_2 600 mN, ——; TCP 1 mM, H_2O_2 100 mN, – – – –.

The rate of dechlorination depends linearly upon the amount of catalyst dissolved (0.1–0.01 mM concentration range, Fig. 10 and Table 6), indicating a reaction order of one in the catalyst (and also, indirectly, in the substrate). When very low amounts of the catalyst are used (below 1 μM), we observe a relative enhancement of the reactivity and consequently of the turnover frequency. A likely explanation, also confirmed by preliminary NMR data (see Section 3.3.2) is the formation of intermolecular aggregates of the catalyst, which significantly dissociate only on dilution; stacking is a well known behaviour of phthalocyanine derivatives [23].

3.3. Fate of ruthenium catalysts during the oxidation

3.3.1. Persulfate oxidation by Ru-dmso derivatives

During the catalytic oxidation with mono-persulfate, quantitative transformation of the starting ruthenium catalysts into ruthenium tetroxide (absorptions at 310 and 385 nm) occurs rapidly (Fig. 11) [24]. When the reaction runs out of oxidant, a sharp chromatic 'end point' is observed, with formation of intensely coloured species with distinctive absorptions at 305 and 500 nm, which, on addition of fresh monopersulfate rapidly re-forms the yellow ruthenium tetroxide. Redox titrations of the violet solutions with potassium monopersulfate and the yellow ruthenium tetroxide with sodium sulfite constantly indicate a four-electron jump and therefore an average oxidation state IV for the violet ruthenium species (the resting state of the catalyst) dissolved in the acidic sulfate medium.

The outstanding oxidising power of the monopersulfate–ruthenium system is not due to the markedly acidic character of the aqueous phase, since no dramatic differences were observed between uncontrolled acidic and NaH_2PO_4/Na_2HPO_4 buffered solutions. We propose that the performances of these systems may be ascribed to the formation of a very active peroxometal-species [$M{-}O{-}O{-}SO_3^-$], as

Table 6
Oxidation of 2,4,6-trichlorophenol (1 mM) by H_2O_2 catalyzed by RuPcS in water; 20°C. Runs at pH 7.5 and 8.5 in phosphate buffer (0.1 M)

				HCl		
pH	Catalyst/substrate (mol/mol) (%)	Oxidant/substrate (equiv/mol)	(1 day) (%)	(2 days) (%)	(4 days) (%)	(7 days) (%)
8.5	2	200	19	25	33	49
8.5	2	600	22	38	49	78
7.5	20	200	92			
7.5	2	200	43 (6 h, 27%)			
7.5	0.2	200		14 (3 days)		36

proposed for a number of oxidation catalysts based on iron- and manganese-porphyrins, when monopersulfate was used in place of conventional oxo reagents [25].

Another remark deals with the nature of the inorganic chlorine during the monopersulfate-oxidation of the chlorinated organics. With excess oxidant, dichlorine is the dominant species, clearly because of the higher reduction potential for the HSO_5^-/HSO_4^- couple (1.8 V [26]). However, analysis of the reaction mixtures when oxidant was exhausted gave evidence only of hydrochloric acid: this is likely due to the strong reducing power of the Ru(IV)–RuO_4 couple, for which an $E° = 1.1$ V has been previously measured in the same reaction conditions, i.e. in dilute sulfuric acid [27].

3.3.2. Hydrogen peroxide oxidation by RuPcS

Intermediate and acidic pH conditions dramatically favor the oxidative dechlorination of the substrates by RuPcS, while at the same time limiting to a reasonable level the dismutation of hydrogen peroxide. The fact that the deep green solutions of RuPcS fade irreversibly, and to a degree dependent upon pH, suggests that under these conditions a catalytically active species is formed, which, on the basis of the general oxidation chemistry of ruthenium, can be an oxo- or a hydroperoxo-metal derivative in a higher oxidation state (Fig. 12). It is also likely that at alkaline pHs, where the catalytic activity is rather low, the dominant ruthenium species are 'protected' hydroxo- or oxo-bridged derivatives, stable towards hydrolysis and oxidative attack by hydrogen peroxide, and therefore catalytically inactive. ^{1}H-NMR spectra of the diamagnetic RuPcS complex (> 10 mM in D_2O or H_2O/D_2O) were however poor and substantially independent of pH and exhibit the phthalocyanine protons in the 6–8 ppm region as broad signals; although definite ^{1}H-NMR spectral changes are observed upon addition of hydrogen peroxide. Further investigation is necessary in order to have a comprehensive explanation.

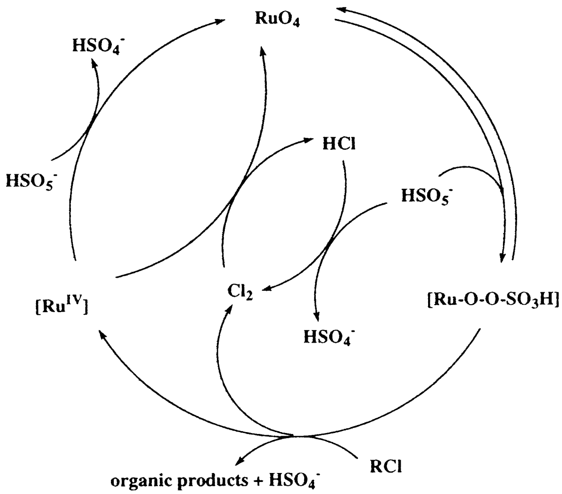

Fig. 11. Persulfate oxidation by Ru-dmso catalysts.

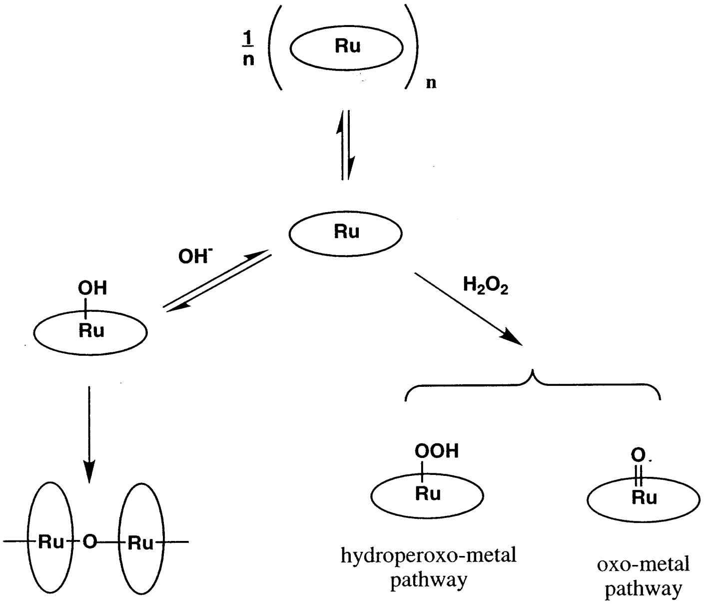

Fig. 12. Proposed pathways for the RuPcS-oxidation.

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