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Journal of Organometallic Chemistry 593–594 (2000) 416–420

Journal of Organo metallic Chemistry

Ruthenium sulfophthalocyanine catalyst for the oxidation of chlorinated olefins with hydrogen peroxide

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Received 16 July 1999; accepted 7 October 1999

Dedicated to Professor Fausto Calderazzo.

Abstract

In aqueous solution and at room temperature, various α-chloro-alkenes are effectively dechlorinated by hydrogen peroxide oxidation using a water-soluble ruthenium(II)-tetrasulfophthalocyanine catalyst, RuPcS. The molecular structure of RuPcS has been elucidated by ESI-mass spectroscopy. In the reaction conditions, and specifically in acidic media, the complex rapidly gives rise to a novel species, most likely catalytically active, whose nature is investigated. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Aqueous organometallic catalysis; Chlorinated organics; Hydrogen peroxide; Ruthenium phthalocyanine; Oxidation

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1. Introduction

Water-soluble metal complexes are close models to the ubiquitous mono-oxygenase or peroxidase enzymes, of principal importance on a global scale for the degradation of xenobiotics in biological systems [1], and could become a gentle alternative method of oxidation of recalcitrant contaminants dissolved in water [2]. Iron- or manganese-sulfophenylporphyrin [3] and –sulfophthalocyanine [4] have been successfully used for the dechlorination of chlorophenols in aqueous acetonitrile in the presence of hydrogen peroxide. We previously reported that dimethylsulfoxide-'solvated' ruthenium(II) ions are able to catalyze the extensive degradation of a variety of halogenated organics, both aromatic and olefinic, in aqueous media and in conjunction with mono-persulfate [5]. A substantial improvement has been more recently achieved by using the water-soluble, strongly complexed ruthenium(II) derivative RuPcS (where PcS is sodium 2,3-tetrasulfophthalocyaninate, Fig. 1) to effect the oxidation of various chlorophenols in the presence of hydrogen peroxide [6]. In this paper we present further results on the catalytic oxidation of α-chloroalkenes, together with details concerning the characterization of RuPcS and its transformations in the presence of hydrogen peroxide.

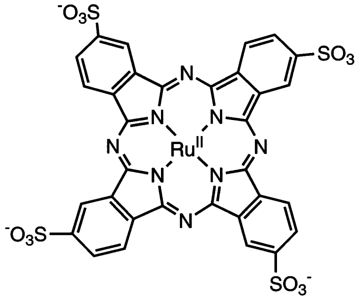

Fig. 1. RuPcS.

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PII: S0022-328X(99)00606-3

2. Experimental

2.1. Preparation of RuPcS

RuPcS was prepared by template synthesis starting from $RuCl_3 \cdot 3H_2O$, sodium 4-sulfophthalate and urea, following the early general procedures for the synthesis of metal-sulfophthalocyanines [7]. The deep-green compound was isolated in the solid by salting out the aqueous reaction mixtures with concentrated NaCl. The ^{15}N–RuPcS derivative was similarly prepared, starting from commercially available ^{15}N–urea ($\geq 99\%$ isotopic purity, Isotec). Anal. Found: C, 35.41; H, 1.64; N, 10.64; S, 11.85%. Anal. Calc. for $RuPcS \cdot 3H_2O$, $RuC_{32}H_{18}N_8O_{15}S_4Na_4$: C, 35.72; H, 1.68; N, 10.41; S, 11.92%. Electronic spectra (400–1500 nm, in water): 630 nm (ε_M, 25 000). Magnetic susceptibility, 20°C. $\chi_g = -0.25 \times 10^{-6}$ emu (solid state, Gouy's method); in 4:1 water–D_2O solutions (20 mM), no detectable shift of the indicator compound (*tert*-butyl alcohol) was measured, following Evans method [8].

The catalytic reactions were typically carried out at 20°C in a 5 ml vial, by stirring magnetically 2 ml of an aqueous solution containing the catalyst (RuPcS, 0.2 mM) and the oxidant (H_2O_2, 2 N), to which 50 µl of the chlorinated substrate were added, either as neat, to give a saturated aqueous solution, or, alternatively, dissolved in 2 ml of an organic solvent (hexane, chloroform), to perform the reactions in a double phase system. Chloride ions were analyzed spectrophotometrically by the mercury thiocyanate method. Carbon dioxide and carbon monoxide analyses were made by passing a moderate flow of nitrogen through the reaction mixtures, previously acidified with H_2SO_4 1 N, which was captured first by aqueous $Ba(OH)_2$ 0.1 M and finally by a dichloromethane solution of the violet $RuCl(DPP)_2]PF_6$ complex (10 mM). Aliquots from the filtered $Ba(OH)_2$ solution were back-titrated with HCl 0.1 N for CO_2, whereas the dichloromethane solutions were spectrophotometrically analyzed for the formation of the colorless mono-carbonyl adduct (ν_{CO} at 1930 cm^{-1}) [9].

Organic analyses were performed on a HP 6890 GLC instrument equipped with a flame ionization detector (FID), using a 30 m HP-5 capillary columns (0.32 mm i.d.; 0.25 film thick) with the injection port thermostatted at 250°C (carrier gas: He) on aliquots withdrawn with a microsyringe from the aqueous reaction mixtures either as such or diluted 1:10 with acetone. The reaction mixtures were also treated by standard procedures with a 10:1 excess 2-methyl-1-butanol to analyze the possibly formed dicarboxylic acids as their isobutyl-esters. NMR spectra were measured on a Bruker Avance 300 MHz, IR spectra on a Bio-Rad FTS-7 PC and vis–NIR spectra on a Cary instrument.

A Sciex API 365 triple-quadrupole mass spectrometer was used to obtain ESI-mass spectra. Instrument control and data acquisition were performed with a Macintosh System 7600/132 using MASSCHROM 1.0 software. Calibration was carried out using polypropylene glycol and the resolution was set in the range 0.6–0.9 amu. Analyses were performed by direct infusion of aqueous solution of the sample containing ammonium formate 50 mM (or formic acid 1%, ammonia 50 mM or NaOH 50 mM), which was delivered by a model 11 syringe pump at the flow rate of 5 µl min^{-1}. The infusion pump was connected to a Sciex ion-spray interface through a 1 m fused silica capillary (0.75 mm i.d.). Q1 scan mass spectra were acquired with a mass range 200–2000 amu using a step size of 0.1 amu and a dwell time of 0.250 ms. The nebulizer gas (air) and the curtain gas (N_2) flows were set at 1.8 l and 2.4 l min^{-1}, respectively. The ionization voltage was set at +4600 V, and the orifice and ring potentials were set at +75 and +280 V, respectively. In product ion scan experiments, spectra were acquired with a mass range of 30–1200 amu using a step size of 0.1 amu and a dwell time of 0.500 ms. The collision-activated dissociation (CAD) gas pressure (N_2) was maintained at 2.84×10^{-3} torr.

3. Results

To our knowledge RuPcS is the first water-soluble phthalocyanine derivative of ruthenium so far reported, whereas variously substituted ruthenium-phthalocyanines are known, both with Ru(II) and Ru(III) [10]. The vis–NIR spectra (400–1500 nm) of RuPcS in water only show the diagnostic Q band at 630 nm, arising from the $\pi \rightarrow \pi^*$ transition within the heteroaromatic ring; the spectra are insensitive to the acidity of the media in the 1–13 pH range. The complex is attributed a monomeric structure on the basis of the ESI-mass spectra (positive patterns: in all examined cases no results were obtained with negative patterns), which exhibit six complex signals of various intensities, each showing the isotopic pattern of ruthenium diagnostic for a monomeric form and spaced by 22 amu ($AW_{Na} - AW_H$), corresponding to the RuPcS molecular ion in the form of the penta-protonated tetra-sulfonic acid and the tetra-protonated mono-, the tri-protonated di-, the di-protonated tri-, the mono-protonated tetra- and the penta-sodium sulfonate ions, respectively (Fig. 2). Mass spectra of the ^{15}N-enriched RuPcS compound again show the diagnostic six signals only shifted to higher molecular weight by 8 amu. No evidence for ^{14}N–RuPcS is detected, thus indicating a isotopic enrichment close to 100%. The compound is diamagnetic both in the solid state and in aqueous solution (see Section 2), as expected for a d^6 metal ion

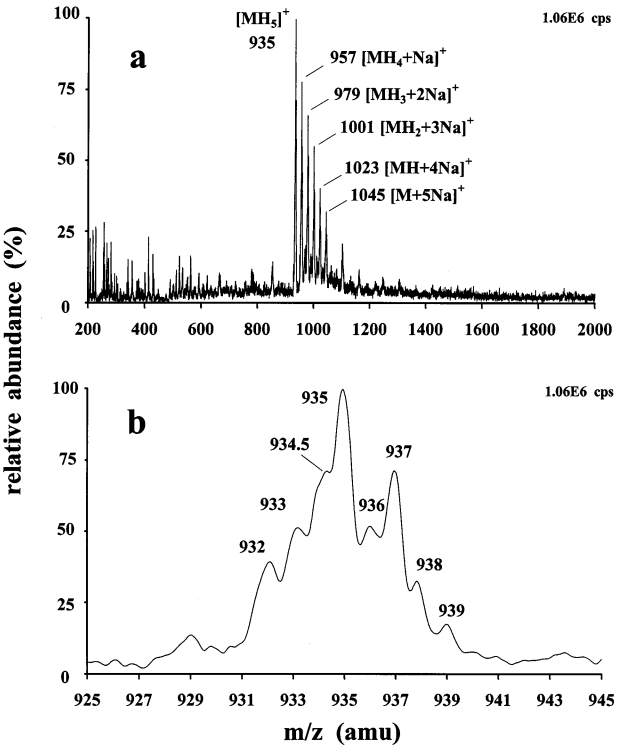

Fig. 2. (a) ESI-mass spectra (positive patterns) of RuPcS in aqueous $HCOONH_4$ 50 mM. (b) Fine structure of the $RuPcSH_5^+$ ion peak at $m/z = 635$.

Table 1
Oxidation of chlorinated organics by hydrogen peroxide catalyzed by RuPcS [a]

Substrate	Oxidation [b]	Products
2-Chloro-2-butene	50	3-Chloro-2-butanone, acetic acid, chloride, 3-hydroxy-2-butanone (13:12:8:1 molar ratio)
1,2-*cis*-Dichloroethylene	5	Chloride, formic acid (1:1 molar ratio)
Trichloroethylene	8	Chloride, formic acid (3:1 molar ratio) [c]

[a] 2 ml of aqueous H_2O_2, 2 N, containing the RuPcS catalyst, 0.2 mM (non buffered solutions, pH ca. 5) and 2 ml of hexane or $CDCl_3$, to which 50 μl of the substrates are added; 20°C.

[b] Turnovers at 8 h.

[c] Smaller amounts of carbon dioxide are also detected.

in an octahedral geometry (since square-planar structures give rise to paramagnetic species, it is likely that two water molecules are coordinated in apical positions, even if no evidence has been obtained from mass spectra). However, ^{1}H-NMR spectra of RuPcS (ca. 10 mM in D_2O) exhibit only a broad and unresolved signal in the 8 ppm region of benzene protons of the phthalocyanine ring, most likely due to the strong intermolecular interactions (stacking) commonly found in phthalocyanine complexes.

The apical positions are nevertheless available for further coordination, as demonstrated by the slow addition of carbon monoxide to RuPcS in aqueous solution (ca. 5 mM). After 7 days stirring under $p_{CO} = 50$ atm a solid material could be isolated after evaporation in vacuo. The IR spectra exhibit a strong absorption at 1960 cm^{-1}, attributable to the ν_{CO} of the monocarbonyl adduct, together with a very weak band at 2064 cm^{-1}, which, on the basis of its higher energy, could be tentatively attributed to small amounts of the corresponding *trans*-dicarbonyl adduct. However, mass spectra (ESI, positive pattern) of the carbonylated solid, redissolved in water, only show the diagnostic pattern of the parent RuPcS compound, while no peaks at + 28 amu, corresponding to the mono-carbonylated adduct, are detected. Early loss of CO is likely to occur in the mass spectra measurement conditions.

RuPcS (0.2 mM) promotes the oxidation of a series α-chloro-alkenes, i.e. 2-chloro-2-butene, *cis*- and *trans*-1,2-dichloroethylene and trichloroethylene, in the aqueous–organic double-phase and in the presence of excess hydrogen peroxide (Table 1). The aqueous phase becomes slightly acidic, with a measured pH value of ca. 5. Monitoring the reactions by GC–MS and ^{1}H-NMR indicates slow oxidation of the substrates (5–50 turnovers within 8 h) with formation of aqueous chloride ions and various organic products, which were found both in the aqueous and in the organic phase and whose nature depends upon a combination of oxidation and hydrolysis reactions. Oxidation of tetrachloroethylene also takes place, but the reaction is much slower. As evidenced by the ^{1}H-NMR spectra, 2-chloro-2-butene gives rise to the early formation of a number of transient intermediates, which are rapidly transformed into 3-chloro-2-butanone, which is the expected product of ketonization (ca. 65% of substrate oxidation), 2-hydroxybutanone, which arises upon epoxidation followed by hydrolysis and dehydrochlorination (ca. 5%) and acetic acid, the final product of the oxidative cleavage of the substrate. No evidence of butanedione, a possible further oxidation product of 3-hydroxy-2-butanone, was obtained (Fig. 3). Chloride ions were also found, in agreement with the measured amounts of dechlorinated products. In the same reaction conditions 1,2-dichloroethylene (*cis* and *trans* isomers) gave only the products from the oxidative cleavage, i.e. formic acid and chloride ions in equimolar amounts, with no evidence of carbon monoxide. Also, trichloroethylene only undergoes oxidative cleavage, with formation of formic acid and chloride ions in a ca. 3:1 molar ratio, even if only ill-measurable amounts of carbon dioxide are detected, which is the other product from the oxidative cleavage of trichloroethylene. Again, no carbon monoxide is evolved.

Oxidations are almost completely inhibited in alkaline media, despite the expected larger reactivity of

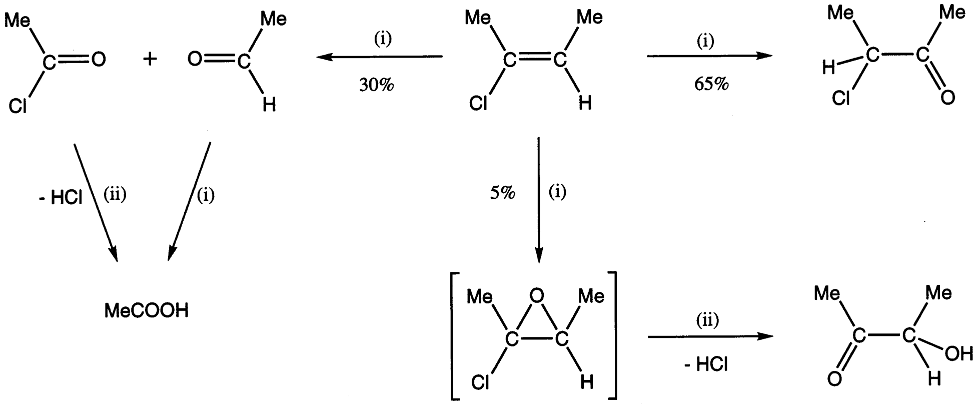

Fig. 3. Proposed pathway for the oxidation of 2-chloro-2-butene by H_2O_2 and RuPcS catalyst; (i) oxidation, (ii) dehydrochlorination and/or hydrolysis.

hydrogen peroxide. In these conditions ($pH \geq 13$) the green RuPcS complex, or its hydroxo- and/or oxo-bridged derivatives, is the overwhelmingly dominant species, as indicated by the persistence (and intensity) of the 630 nm band. In acidic media ($pH \leq 5$), where the catalytic processes take place satisfactorily, RuPcS undergoes an irreversible transformation in the presence of hydrogen peroxide, with the fast formation (30 min) of yellow solutions, whose electronic spectra show the complete disappearance of the distinctive 630 nm band and no other absorption up to 1500 nm (which represents the upper wavelength detectable for aqueous hydrogen peroxide solutions). UV spectra of an organic phase added to the aqueous reaction mixtures do not exhibit the two distinctive absorptions of ruthenium tetroxide, at 310 and 385 nm, thus indicating that no release of free metal occurs during the transformation, and indeed upon simple demetallation, a fairly uncommon event for phthalocyanine complexes, with no disappearance of the $\pi \rightarrow \pi^*$ band expected [11]. However, no mass spectral data could be obtained for the yellow compound, most likely a polymeric species, present in these solutions. Accordingly, evaporation under vacuum results in aqueous irreducible concentrates, from which only intractable waxy solids were obtained after drastic treatments with refluxing methyl orthoformate.

Definite changes in the ^1H-NMR spectra accompany the dramatic change in the visible spectra, described above. The yellow solutions are still diamagnetic, therefore indicating either persistence of ruthenium in the same oxidation state (+2), or, alternatively its oxidation to diamagnetic species, such as a ruthenium(VI) (d^2 ion) in a tetragonally distorted geometry with apical ligand(s), for which a spin-paired electronic configuration is expected. However, and unlike the starting RuPcS complex, the yellow acidic solutions exhibit well-resolved signals in the 8 ppm region (aromatic protons), a clear indication that stacking has been extensively removed. An ABX pattern is observed, with multiplets at 7.9 ppm (six peaks) corresponding to the X proton (positions 1 of the phthalocyanine ring; positions 2 are occupied by the sulfonate moieties) and at 8.1 ppm corresponding to the AB portion of the spectrum (protons in positions 3 and 4), thus pointing to the integrity of the benzene ring substituted at positions 2, 5 and 6, as in the starting phthalocyanine complex.

In H_2O–D_2O (4:1) mixtures and at pH ca. 1, three signals of equal intensity also appear at 7.0 ppm, separated by 51 Hz, attributable to hydrogen atoms coupled to one nitrogen atom (^{14}N). The ^1H-NMR spectra of the corresponding ^{15}N–RuPcS derivative nicely confirm the attribution, with the same signal appearing at 7.0 ppm as a doublet separated by 74 Hz (Fig. 4). The values of both $J(^1H–^{14}N)$ and $J(^1H–^{15}N)$ coupling constants are distinctive of protons directly bound to nitrogen (^1J), whereas the measured $J(^1H–^{15}N)/J(^1H–^{14}N)$ ratio is in full agreement with the expected value of -1.4027 [12]). In increasingly D_2O enriched media the signals at 7.0 ppm progressively loose intensity because of extensive replacement of the nitrogen-bonded protons by deuterium. At higher pH values the signals disappear suddenly, indicating fast exchange with water protons. The ^{15}N-NMR spectra (DEPT-45 experiments) of the ^{15}N enriched compound in pure water show a neat quintuplet at -360 ppm, with the same $J(^1H–^{15}N)$ observed in the ^1H-NMR spectra, clearly attributable to the ammonium ion. The intensity ratio between benzene and ammonium protons is close to 3:1 in aqueous media and this leads one to conclude that ammonium arises upon cleavage of one of the nitrogen atoms of the phthalocyanine ring, most likely from the *meso*-position. Oxidative cleavage of amines to ammonia is known to be catalyzed by the copper-containing enzymes amine oxidases and has been recently reported to occur also in the presence of a synthetic copper complex mimicking the above enzyme [13]. Nevertheless, the observed reaction is rather unexpected and deserves further investigation.

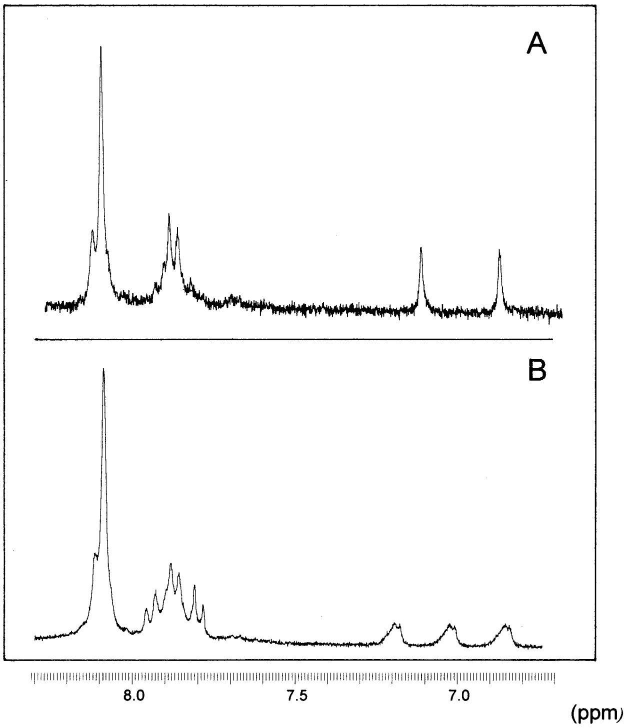

Fig. 4. ^{1}H-NMR spectra of RuPcS (10 mM) in aqueous H_2O_2 (0.2 M) at pH 1 (H_2SO_4), after 6 h, 20°C: ^{15}N–RuPcS, ≥ 99% isotopic purity (A); ^{14}N–RuPcS (B).

4. Conclusion

The ruthenium(II) derivative RuPcS undergoes rapid and irreversible transformation to a yellow species when in the presence of excess hydrogen peroxide in acidic or neutral aqueous media, which seems to be the catalytically active species for the oxidation of recalcitrant substrates, such as α-chloro-alkenes, via conventional and most likely non-radical oxidation pathways (oxidative cleavage, ketonization and epoxidation/dihydroxylation). The nature of the yellow species is elusive, although a dioxo-ruthenium(VI) derivative could be proposed on the basis of the well documented reactivity of ruthenium(II) complexes with many oxidizing agents, including hydrogen peroxide [14]. However, the most intriguing feature is the absence of absorptions in the visible spectra. These strong bands are indeed diagnostic of the π-conjugated aromatic system of phthalocyanine, unless an unprecedented bathochromic shift to very low energies has occurred. The absence of absorptions in the visible spectra of the yellow species must be related to the other two surprising features: the definite reduction of stacking and the formation of ammonia. It seems therefore likely that substantial chemical modifications of the phthalocyanine ligand must have occurred, akin, for instance, to those reported for the celebrated oxidative degradation of heme to biliverdin and recently observed also in relevant iron-porphyrin model compounds [15].

Acknowledgements

The authors thank A. Ravazzolo, C.N.R., Padova, for technical assistance, and M.U.R.S.T., Cofin98 funding, for financial support.

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