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Electrocatalytic oxidation of organic substrates with molecular oxygen using tetradentate ruthenium(III)-Schiff base complexes as catalysts

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ABSTRACT

Three complexes Ru(III)ClL^n involving different tetradentate Schiff base ligands L^n (see L^1, L^2 and L^3 in Chart 1) were used as catalysts in the oxidation of cyclooctene and tetraline in the presence of molecular dioxygen associated with benzoic anhydride. The efficiency of this oxidation reaction was tested in the presence of two apical bases: 1- or 2-methylimidazole. All complexes exhibit a quasi-reversible redox system. The electrolysis experiments were carried out at controlled potential for each complex, using different substrates such as cyclooctene and tetraline. The oxidized products are cyclooctene oxide (turnover 6.7), a mixture of 1-tetralol and 1-tetralone (turnover 7.6) respectively.

1. Introduction

The activation of molecular oxygen using transition metals as catalysts in the oxidation reactions such as hydrocarbons or olefins epoxidation is of great interest particularly when the ligands involved in the electrocatalytic systems are Schiff bases. So, tetradentate Schiff base complexes of transition metals have been extensively studied mainly with manganese, iron, cobalt, copper and nickel [1–5] while those of ruthenium are relatively less studied [6]. It was demonstrated that such complexes might be involved in several applications namely in catalysis [7] or electrocatalysis [8] by activating small molecules like carbon dioxide [9] or molecular oxygen [10]. Here, we focus on the electrocatalytic study of the activation of molecular oxygen using tetradentate ruthenium-Schiff base complexes in order to reduce substantially their reduction potential leading to electrocatalytic systems operating at lower potential values. The metabolic role of cytochrome P450 is well known [11] and its metabolic cycle established [12]. This involves several steps: molecular dioxygen fixation, water elimination, and peroxo high oxidation state metal (*i.e.*, Fe^{IV}). In all cases, the active form of the coordinated iron ion is axially linked to a sulfur protein. However, a large number of cytochrome P450 oxo-complexes including ligands such as Schiff base complexes have been tested for their catalytic activity [13,14,7,15–18] and their electrocatalytic properties [6,8,19,20,10,21–25]. New catalysts deriving from symmetrical tetradentate ruthenium-Schiff base complexes seem to be more and more attractive and efficient in catalysis [26,27]. Though these new electrocatalytic systems have been less studied. They can be advantageously better used than those currently applied in chemical catalysis [28–38] where oxygen atom sources are iodosylbenzene [28–31], hypochlorites [32–34], tBuOOH [35,36], amine oxides [37] or hydrogen peroxide [38].

This work is a continuation of our recent papers describing olefin epoxidations using manganese(III) complexes [22,39]. Three ruthenium(III) complexes Ru(III)ClL^1 (**1**), Ru(III)ClL^2 (**2**), and Ru(III)ClL^3 (**3**) (Chart 1) were synthesized according to literature [23,40] and then used as catalysts in the presence of molecular oxygen, benzoic anhydride and 1- or 2-methylimidazole to oxidize substrates such as cyclooctene and tetraline.

2. Experimental

2.1. Chemicals

The three complexes Ru(III)ClL^1 (**1**), Ru(III)ClL^2 (**2**) and Ru(III)ClL^3 (**3**) (Chart 1) used in this study were prepared as reported by some of us [40]. Salicylaldehyde, 2-hydroxyacetophenone, 3,5-dibromosalicylaldehyde, ruthenium chloride ($RuCl_3 \cdot H_2O$), cyclooctene, and tetraline were purchased from Aldrich and used without any further purification.

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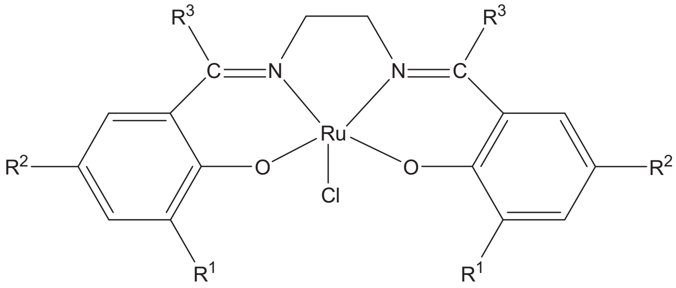

(L^1) $R^1 = R^2 = R^3 = H$
(L^2) $R^1 = R^2 = H$, $R^3 = CH_3$
(L^3) $R^1 = R^2 = Cl$, $R^3 = H$

Chart 1.

The supporting electrolyte, tetra-*n*-butylammonium perchlorate (TBAP) was crystallized in ethyl acetate and dried at 80 °C in vacuum for 72 h. Traces of benzoic acid contained in the commercial benzoic anhydride were removed by simple washing by an aqueous solution (10%, w/w) of sodium hydrogenocarbonate ($NaHCO_3$). Benzoic anhydride was then crystallized in a mixture of toluene/petroleum ether (40–60). After one night in refrigerator, the solid was recovered by filtration, followed by some washings using petroleum ether. Acetonitrile (analytical grade) was distilled over potassium permanganate ($KMnO_4$) and the distillate was kept over 4 Å molecular sieves. Water was twice distilled. Methanol, purity HPLC, obtained from Aldrich was used as received.

2.2. Physical measurements

Cyclic voltammograms were performed using a Tacussel PJT Potentiostat Galvanostat, driven by Pilovit-Num and an integrator “Type IG5-LN, Tacussel”. All measurements were performed in a 5 mL Metrohm monocompartment cell equipped with a conventional three electrodes system and an X–Y recorder Sefram. The electrodes were polished with diamond paste and rinsed with large amounts of acetone and finally with the solvent. The working electrode was a piece of carbon felt, RVC 2000 (10 mm × 10 mm × 4 mm) for the electrolyses or a glassy carbon disk ($d = 5$ mm, Metrohm) for voltammetry. The counter electrode was a platinum wire and the reference electrode a glass Y tube, filled with the same electrolytic solution contained in the cell to which was added $AgNO_3$ (10^{-1} mol dm^{-3}). The solvent was acetonitrile containing 10^{-3} mol dm^{-3} concentration of the investigated complexes and a constant ionic strength maintained at 10^{-1} $AgNO_3$ with tetra-*n*-butylammonium perchlorate (TBAP). The electrolyses were carried out at the appropriate controlled potential value for each complex.

2.3. Electrocatalytic oxidation

All experiments for the electrocatalytic oxidation were carried out in 5 mL acetonitrile solutions containing TBAP (10^{-1} mol dm^{-3}), the complex (catalyst) (10^{-3} mol dm^{-3}), the axial base, 1- or 2-methylimidazole (10^{-2} mol dm^{-3}), benzoic anhydride (10^{-1} mol dm^{-3}) and hydrocarbon substrate (10^{-1} mol dm^{-3}). Molecular dioxygen was moderately bubbled into the electrolytic solution during the electrolysis. The selected electrolysis potential value was that of the maximum peak current (i_c^p) at which the ruthenium-oxo species are massively electrogenerated. The electrolysis was then monitored by recording the peak current i_c^p *vs.* time until reaching almost zero. During the electrolysis experiments, the consumption of the electricity was also determined by an integrator giving the charge passed through the cell.

2.4. Products analysis

The starting material cyclooctene and its epoxide were identified by gas chromatography (GC) using a capillary column by 20% carbowax 20 M (diam. 2 mm, length 50 m). These analyses were performed on GC-Shimadzu, equipped by a FID detector and accompanied by program temperature going from 80 to 180 °C with a rate of 10 °C/min. The oxidation products obtained from tetraline were analyzed by HPLC technique employing a column with reverse phase (C_{18} Waters). The mobile phase, composed with methanol/water (50/50, v/v), was preliminary degassed on the porosity glass frit before use and the flow was adjusted to 1.5 mL/mn. The UV-detector used to characterize the oxidized products was again adjusted to 154 nm. The peaks (retention times) of each one of these products were assigned by comparison with their authentic samples, commercially available.

3. Results and discussion

The electrochemical technique used to study the redox properties of the three ruthenium(III) complexes Ru(III)ClL^1 (**1**), Ru(III)ClL^2 (**2**), and Ru(III)ClL^3 (**3**) (Chart 1), was the cyclic voltammetry because it gives evidence for electrochemical species formed in the reaction medium either under nitrogen atmosphere or under electrocatalytic conditions using molecular oxygen.

3.1. Under nitrogen atmosphere

The voltammograms of the ruthenium(III) complexes were focused on the redox system Ru(III)/Ru(II) characteristic of these kind of complexes, as very recently reported by some of us [40]. They indicated that the redox couples Ru(III)/Ru(II) at a glassy carbon disk electrode, obeyed a quasi-reversible diffusion behavior for the three complexes **1**, **2** and **3**. The half potential wave values ($E_{1/2}$) were −585, −530 and −507 mV *vs.* Ag/Ag$^+$/$AgNO_3$/0.1 M, for complexes **1**, **2** and **3** (Fig. 1A) respectively.

The cyclic voltammograms of Ru(III)ClL^3 (Ru^{III}/Ru^{II}) performed under nitrogen in the presence of apical ligands (1-methylimidazole, 2-methylimidazole) are shown in Fig. 1B and C. As observed previously for complexes **1** and **2** [40] the CV was not significantly modified by the presence of the apical ligands.

3.2. Under electrocatalytic conditions with molecular dioxygen

The cyclic voltammetry of Ru(III)ClL^3 was then performed in the presence of 1- or 2-methylimidazole and molecular dioxygen, leading to current enhancement and lost of reversibility (Fig. 2). The reduction of dioxygen alone took place at a more negative potential: $E_{\mathrm{red}}^{p} = -0.92$ *vs.* (Ag/$AgNO_3$) *V* (Fig. 3). Its direct reduction was therefore not involved in the investigated process. The metallic center of the ruthenium complex was first attacked by a nitrogen base (apical ligand) like 1- or 2-methylimidazole in order to extract it from its plane to facilitate the following attack by molecular oxygen leading to the formation of ruthenium superoxo species [Ru(III)—O—O]$^-$ as shown in Fig. 2 (curve A with 1-methylimidazole, curve B with 2-methylimidazole).

The superoxo species can be generated from two different species Ru(II)ClL^n and Ru(III)ClL^n ($n = 1$, 2 and 3) as indicated in Scheme 1 (route a or b) and in Fig. 2 (*vide supra*).

The ruthenium superoxo species were characterized by a reduction wave (i_c^p) appearing at the same potential as that of the Ru(II) species, produced under nitrogen atmosphere [6]. Moreover, these