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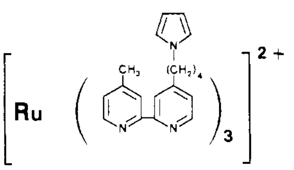
Communications

A Poly[tris(*N*-(bipyridylylbutyl)pyrrole)ruthenium(II)]-RuO_2 Catalytic Modified Electrode for Organic Oxidations

Sir:

Ruthenium tetraoxide species such as RuO_4 and RuO_4^{2-} are recognized as convenient, powerful oxidizing agents in organic chemistry.[1,2] Further, some investigations on the indirect electrooxidation of organic compounds by using these oxides as electrogenerated mediators from RuO_2 oxidation have been described.[3,4] In this communication we report the behavior and the catalytic properties toward the oxidation of benzyl alcohol in acetonitrile of electrodes coated by a polypyrrole film bonded to a tris(bipyridyl)ruthenium(II) complex,[5] denoted poly$[Ru(L)_3]^{2+}$, containing dispersed RuO_2 particles.[6]



$[Ru(L)_3]^{2+}$

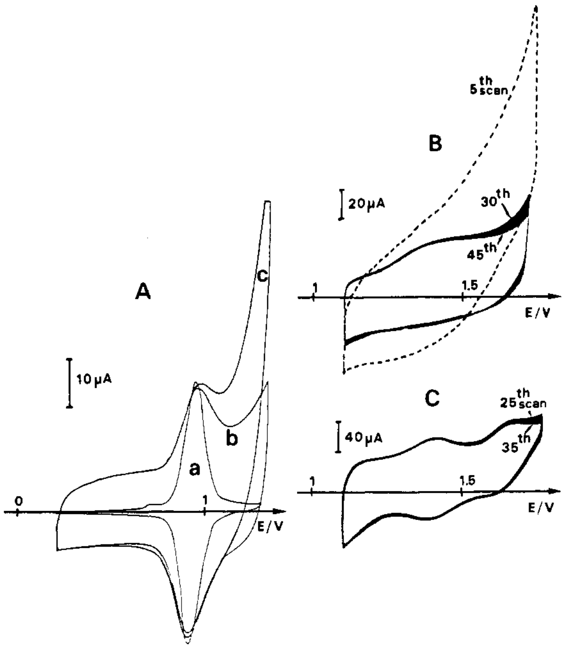


Figure 1. Cyclic voltammograms in CH_3CN containing 0.1 M Et_4NClO_4: (A) Pt (diameter 5 mm)/poly$[Ru(L)_3]^{2+}$–RuO_2 modified electrode (a) without RuO_2 and with 4.4×10^{-9} mol $[Ru(L)_3]^{2+}$, (b) with 4.3×10^{-9} mol of RuO_2, and (c) with 4.3×10^{-9} mol of RuO_2 + 2.2×10^{-4} mol of benzyl alcohol + 7×10^{-4} mol of Na_2CO_3 (scan rate 0.01 V s^{-1}); (B) Pt/poly$[Ru(L)_3]^{2+}$–RuO_2 modified electrode between 1.1 and 1.7 V; (C) Pt/poly$[Ru(L)_3]^{2+}$–RuO_4^{2-} modified electrode between 1.1 and 1.8 V (scan rate 0.1 V s^{-1}).

The behavior of the modified electrode Pt/poly$[Ru(L)_3]^{2+}$–RuO_2 was investigated by cyclic voltammetry curves recorded before and after the incorporation of RuO_2 in CH_3CN containing 0.1 M Et_4NClO_4. The voltammogram of the Pt/poly$[Ru(L)_3]^{2+}$ electrode (Figure 1A, curve a) exhibits the regular redox peaks of the $[Ru(L)_3]^{3+/2+}$ couple ($E_{1/2}$ = 0.86 V)[7] while the small prepeak at the foot of this system depicts, as previously reported,[5] the electroactivity of the polypyrrolic chain itself. If the electroactivity of the $[Ru(L)_3]^{3+/2+}$ system remains unchanged, the presence of RuO_2 particles induces large capacitive currents and a continuous increase of the anodic current above 1.1 V as seen in Figure 1A, curve b. However, repeatedly scanning the potential over the range 1.1–1.7 V results in a continuous decrease in this anodic current while a quasi-reversible couple appears at around 1.45 V (Figure 1B). This couple is attributed to the $RuO_4^{2-} \rightleftarrows RuO_4^-$ process by comparison with the cyclic voltammogram of a Pt/poly$[Ru(L)_3]^{2+}$–RuO_4^{2-} modified electrode.[8] For this

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(1) Lee, D. G.; Congson, L. N.; Spitzer, U. A.; Olson, M. E. *Can. J. Chem.* **1984**, *62*, 1835–1839 and references therein.

(2) See for example: Mijs, W. J.; De Jonge, C. R. H. I. *Organic Synthesis by Oxidation with Metal Compounds*; Plenum: New York, London, 1986; pp 445–467.

(3) (a) Burke, L. D.; Murphy, O. J. *J. Electroanal. Chem. Interfacial Electrochem.* **1979**, *101*, 351–361. (b) Burke, L. D.; Healy, J. F. *J. Electroanal. Chem. Interfacial Electrochem.* **1981**, *124*, 327–332. (c) Laule, G.; Hawk, R.; Miller, D. *J. Electroanal. Chem. Interfacial Electrochem.* **1986**, *213*, 329–332.

(4) (a) Torii, S.; Inokuchi, T.; Yukawa, T. *Chem. Lett.* **1984**, 1063–1066. (b) Torii, S.; Inokuchi, T.; Sugiura, T. *J. Org. Chem.* **1986**, *51*, 155–161.

(5) Synthesis and purification of the ligand L were reported previously (Cosnier, S.; Deronzier, A.; Moutet, J. C. *J. Electroanal. Chem. Interfacial Electrochem.* **1986**, *207*, 315–321). $[Ru(L)_3]^{2+}(BF_4^-)_2$ was prepared and purified by following a known procedure (Cosnier, S.; Deronzier, A.; Moutet, J. C. *J. Electroanal. Chem. Interfacial Electrochem.* **1985**, *193*, 193–204). FAB MS (*m/e*, positive mode): C^{2+}·BF_4^-, 1062; C^+, 975. Thin films of poly$[Ru(L)_3]^{2+}$ were prepared by controlled-potential oxidation at 0.83 V (vs the Ag/10 mM Ag^+ in CH_3CN reference electrode) of 1 mM $[Ru(L)_3]^{2+}$ in CH_3CN containing 0.1 M Et_4NClO_4 on a platinum disk (5 mm diameter). The electrochemical behavior of the Pt/poly$[Ru(L)_3]^{2+}$ electrode is quite similar to those of our other thin films of polypyrrole functionalized with Ru tris(bipyridyl) complexes (see the above-mentioned reference).

(6) Incorporation of RuO_2 was made by a procedure close to that of the RuO_2 incorporation in polypyrrole films (Noufi, R. *J. Electrochem. Soc.* **1983**, *130*, 2126–2127): the poly$[Ru(L)_3]^{2+}$ modified electrode was dipped into an aqueous solution containing 0.05 M K_2RuO_4 for 20 min. The resulting film was removed, washed several times with distilled water, and transferred to a cell containing 0.1 M $LiClO_4$ in water. The RuO_4^{2-} ions incorporated in the film were reduced to RuO_2 by potentiostating the electrode at 0.2 V vs SCE. The amount of RuO_2 in the poly$[Ru(L)_3]^{2+}$ film was estimated from the charge passed for this reduction. The modified electrode was then washed several times with CH_3CN and dried under vacuum.

(7) All potentials are referenced vs the Ag/10 mM Ag^+ system in CH_3CN, unless otherwise noted.

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Table I. Preparative-Scale Electrolysis at 1 V of Benzyl Alcohol (0.2 mmol) on Different Modified Electrodes

entry	modified carbon-felt electrode	amt of electroactive species, 10^7 mol	Q, C[e]	amt of benzaldehyde produced, 10^3 mol
1	C/poly$[Ru(L)_3]^{2+}$–RuO_2	$[Ru(L)_3]^{2+}$, 6.6[a] RuO_2, 6.0[b]	29.3	0.131
2	C/poly$[Ru(L)_3]^{2+}$–Pd(0)	$[Ru(L)_3]^{2+}$, 8.3[a] Pd, 9.5[c]	1.5	0.006
3	C/poly(v^{2+})–RuO_2	v^{2+}, 6.6[d] RuO_2, 7[b]	16.9	0.072

[a] Estimated from the charge under the anodic peak (Ru(II) → Ru(III)). [b] Estimated from the charge obtained for the reduction ($RuO_4^{2-} \rightarrow RuO_2$). [c] Estimated from the charge obtained for the reduction ($Pd^{2+} \rightarrow$ Pd(0)). [d] Estimated from the charge under the first reduction peak ($v^{2+} \rightarrow v^{\bullet +}$). [e] Total number of coulombs passed after 340 min.

electrode two successive quasi-reversible redox couples emerge at 1.41 and 1.65 V (Figure 1C), corresponding probably to the two successive one-electron transfers $RuO_4^{2-} \rightleftarrows RuO_4^- \rightleftarrows RuO_4$.[9] These observations seem to indicate that potentiostating the Pt/poly$[Ru(L)_3]^{2+}$–RuO_2 electrode to 1.1–1.2 V produces in the film RuO_4^{2-} from RuO_2. The addition of benzyl alcohol (8 mM) induces a marked increase in the anodic current of the Pt/poly-$[Ru(L)_3]^{2+}$–RuO_2 electrode above 1.1 V (Figure 1A, curve c). It should be noted that the same experiment conducted with Pt/poly$[Ru(L)_3]^{2+}$ without RuO_2 exhibits only the regular direct oxidation of the alcohol on Pt at 2 V,[10] indicating a good diffusion of the substrate through the film. A preparative-scale electrolysis of a solution containing 0.2 mmol of benzyl alcohol and 0.7 mmol of Na_2CO_3 as a basic agent was carried out at 1.16 V on a carbon-felt electrode (20 × 9 × 4 mm, 47 mg of carbon), coated by 6.3×10^{-7} mol of poly$[Ru(L)_3]^{2+}$ and 6.4×10^{-7} mol of RuO_2. The electrooxidation was stopped when the initial amount of electricity needed to oxidize all the alcohol was reached. The oxidation produced benzaldehyde with 76% current efficiency. No benzoic acid was detected.[11]

In order to specify the respective roles of $[Ru(L)_3]^{3+}$ and RuO_4^{2-} in this oxidative process, we have carried out preparative-scale electrolysis at a less positive potential (1 V) close to the redox potential of the $[Ru(L_3)]^{3+/2+}$ couple, on carbon-felt electrodes modified by three kinds of films: (1) poly$[Ru(L)_3]^{2+}$–RuO_2, (2) poly$[Ru(L)_3]^{2+}$–Pd(0),[12] and (3) poly(v^{2+})–RuO_2, where the polypyrrole film is bonded to a viologen group which is nonelectroactive in the anodic region.[13] Electrolysis of 0.2 mmol of benzyl alcohol in the presence of 0.7 mmol of Na_2CO_3 was stopped after 340 min. At this point the catalytic currents dropped to less than 20% of their initial values. Results are summarized in Table I. It appears that, for the C/poly$[Ru(L)_3]^{2+}$–RuO_2 electrode, the oxidation occurs with a rate markedly slower than that observed at 1.16 V. The comparison between entries 1 and 2 demonstrates that RuO_2 is needed to obtain a significant catalysis at 1 V. This indicates that, in contrast with the case for Pd(0), RuO_2 does not act only as an electronic conductor. The difference between entries 1 and 3 of Table I shows that the use of v^{2+} instead of $[Ru(L)_3]^{2+}$ as the pendant substituent group of the polypyrrole decreases appreciably the efficiency of the electrocatalysis. Since polypyrrole films are known to lose their conductivity and adherence at too high an overpotential (1–1.2 V),[14] the presence of the electroactive $[Ru(L)_3]^{2+}$ group makes the film more conductive and stable at 1 V than the v^{2+} film. The $[Ru(L)_3]^{3+}$ species probably acts as an electron relay for the oxidation of RuO_2.

On the other hand, we found that addition of water up to a percentage of about 4% to the anolyte induced a strong increase of the catalytic current, while a pseudoplateau was reached for higher percentages and improved the stability of the electrode. An electrolysis of a large amount of alcohol (10 mmol), in a 9/1 CH_3CN–H_2O mixture, carried out to the total loss of electroactivity of the C/poly$[Ru(L)_3]^{2+}$–RuO_2 electrode, leads to 4.47 mmol of aldehyde after 490 min with a current efficiency of 96%. No benzoic acid was detected. The turnover (moles of benzaldehyde formed divided by the moles of RuO_2 in the film) was close to 5000. The strong increase of the rate of the catalysis could be due to an easier formation of RuO_4^{2-} in the water–CH_3CN mixture since the potential of the RuO_4^{2-}–RuO_2 system depends on the basicity[3b] of the medium.

In summary this preliminary study demonstrates that a modified electrode based on $[Ru(L)_3]^{2+}$ as an electron relay associated with RuO_2 as an oxidizing agent is useful to the electrooxidation of benzyl alcohol to benzaldehyde. Further investigations are currently being made, in order to improve the lifetime of this type of electrode and to extend its utilization to activate less oxidizable organic compounds.

Acknowledgment. We are grateful to Professor G. Cauquis for his interest in this work and PIRSEM (ARC "Electrodes modifiées") for partial financial support.

Registry No. RuO_2, 12036-10-1; RuO_4^{2-}, 14333-22-3; Pt, 7440-06-4; Pd, 7440-05-3; poly($V^{2+} \cdot 2BF_4^-$), 100779-25-7; benzyl alcohol, 100-51-6; benzaldehyde, 100-52-7.

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(8) The preparation of this electrode was similar to that of poly[Ru-$(L)_3]^{2+}$–RuO_2 except that the incorporated RuO_4^{2-} was not reduced. The electrode was washed several times with CH_3CN and dried under vacuum before its use in dry CH_3CN in a controlled-atmosphere glovebox.

(9) Potentials of these transformations are found to be respectively 1.45–1.35 and 1.80–1.68 V vs NHE in aqueous solutions. Burke, L. D.; Whelan, D. P. *J. Electroanal. Chem. Interfacial Electrochem.* **1979**, *103*, 179–187.

(10) Cano-Yelo, H.; Deronzier, A. *Nouv. J. Chim.* **1987**, *11*, 479–485.

(11) Product analysis was performed by HPLC vs authentic samples.

(12) The impregnation of the film with Pd(0) was accomplished by incorporation of $PdCl_4^{2-}$ followed by reduction to Pd(0) at −0.1 V vs SCE in aqueous medium. The impregnation procedure was repeated twice to obtain ~1 mol of Pd/mol of $[Ru(L)_3]^{2+}$ units.

(13) The preparation of the poly(v^{2+}) electrode was described previously. Coche, L.; Deronzier, A.; Moutet, J. C. *J. Electroanal. Chem. Interfacial Electrochem.* **1986**, *198*, 187–193. The procedure of RuO_2 incorporation into the poly(v^{2+}) polymer was similar to that used for the poly$[Ru(L)_3]^{2+}$ electrode.

(14) See for example: Daire, F.; Bedioui, F.; Devynck, J.; Bied-Charreton, C. *J. Electroanal. Chem. Interfacial Electrochem.* **1987**, *224*, 95–110.

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Crystal and Molecular Structure, Magnetic Properties, and EPR Spectra of a Trinuclear Copper(II) Complex with Bridging Nitronyl Nitroxides

Sir:

Transition-metal ions and stable organic radicals, such as the nitroxides, can form clusters containing variable numbers of spins.[1] For instance finite clusters containing from 2 to 12 spins have been reported, as well as infinite arrays.[2] The nitronyl nitroxides are

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(1) Eaton, S. S.; Eaton, G. R. *Coord. Chem. Rev.* **1978**, *26*, 207.