

Redox stability of Re(V)–amine complexes

María Fernanda Cerdá ^{a,*}, Eduardo Méndez ^a, Jorge S. Gancheff ^b,
Carlos Kremer ^b, Ana María Castro Luna ^c

^a *Laboratorio de Electroquímica, Facultad de Ciencias, Iguá 4225, 11400 Montevideo, Uruguay*

^b *Cátedra de Química Inorgánica, Facultad de Química, CC 1157 Montevideo, Uruguay*

^c *INIFTA, Universidad Nacional de La Plata, Sucursal 4-CC 16, 1900 La Plata, Argentina*

Received 10 August 2002; accepted 26 October 2002

Abstract

The complete electrochemical characterization of three amine-related complexes containing the $[\text{ReO}_2]^+$ core was achieved by the use of three different electrode materials. The $[\text{Re}^{\text{V}}\text{O}_2]^+$ core, the amine group and iodide were characterized based on the voltammetric behavior on glassy carbon, nickel and gold, respectively.

© 2002 Elsevier Science B.V. All rights reserved.

Keywords: Rhenium; Dioxo complexes; Electrochemistry; Gold; Glassy carbon; Nickel

1. Introduction

The recent advent of ^{186}Re and ^{188}Re agents in radiotherapy and the use of this metal as a model to mimic the reactivity of $^{99\text{m}}\text{Tc}$ radiopharmaceuticals still offer challenges to study Re coordination compounds [1]. In this context, the most extensively developed chemistry is that of Tc and Re complexes of the metal(V)–oxo core. The chemical reactivity of these complexes determines the in vivo behavior, especially the reactivity towards redox agents.

In previous work [2], we reported the electrochemical behavior of the complex $[\text{ReO}_2(\text{en})_2]^+$ (en = ethylenediamine) characterized by the couple $[\text{Re}^{\text{V}}\text{O}_2(\text{en})_2]^+ / [\text{Re}^{\text{IV}}\text{O}_2(\text{en})_2]$. The voltammetric profile depends on the nature of the electrode material, which in turn determines the adsorptivity of the counter ion. Thus, for the electrochemical behavior of Re(V)-complexes on Au it was shown that I^- counter ion almost completely dominates the voltammetric profile, due to its strong adsorption on the electrode surface [2,3].

The synthesis of new $[\text{ReO}_2(\text{amine})_2]^+$ compounds (amine = dien, diethylenetriamine; trien, triethylene-

tetramine; tren, *N*-tris(2-aminoethyl)amine), which include iodide and chloride as counter ions, has recently been reported [4]. The presence of free amino tails (not bonded to rhenium atom) enhances the reactivity of these complexes. This particular structure envisages three different centres with redox activity: the $[\text{ReO}_2]^+$ core, the free amino group and the counter ion. In order to assess the redox reactivity of such groups, a new approach is presented, which is based on the use of different electrode materials. Thus, free amino groups are redox active on Ni [5,6], iodide is adsorbed on Au electrodes giving a characteristic voltammetric profile [7] and $[\text{ReO}_2]^+$ core can be studied on glassy carbon electrodes, for which halide adsorption is negligible [8].

In this work, the results of this new approach used for the characterization of Re(V)–amine complexes are presented, and the capability of this multi-electrode study is discussed.

2. Materials and methods

Complexes were prepared as previously described [4]. A glassy carbon disk (0.28 cm² geometric area) and polycrystalline (pc) Ni and Au wires (0.16 cm² geomet-

* Corresponding author. Fax: +598-2-525-8617.
E-mail address: fcerd@fcien.edu.uy (M.F. Cerdá).

ric area) were used as working electrodes. Modified Au electrodes towards preferentially oriented planes, i.e., (100) and (111), were prepared according to [9]. A gold flag (4 cm²) and Ag/AgCl (1 M KCl, $E = 0.195$ V–ENH) were used as counter and reference electrodes, respectively. Aqueous 0.1 M LiClO₄, pH=7.5 (supporting electrolyte) was used in the preparation of the following solutions: 1 mM [ReO₂(amine)₂]I (amine = dien, trien, tren) complexes and 1 mM KI. Potential sweep rates ν within the range 10–500 mV/s were employed.

3. Results and discussion

Four anodic contributions are observed in the voltammetric profile of 1 mM KI on pc-Au (Fig. 1a): $I_{ad}/I_{(aq)}^-$ and $I_{2(aq)}/I_{(aq)}^-$ couples at 0.50 V (I_{ad} stands for adsorbed iodine); $IO_{3(aq)}^-/I_{2(aq)}$ couple at 0.95 V; $IO_{3(aq)}^-/I_{ad}$ couple at 1.23 V overlapped to O-electroadsorption on Au; and finally another O-electroadsorption contribution at 1.33 V [2,3,7].

On a glassy carbon electrode, only $I_{2(aq)}/I_{(aq)}^-$ and $IO_{3(aq)}^-/I_{2(aq)}$ redox couples are observed at 0.54 and 0.97

V, respectively (Fig. 1b). This is in agreement with the fact that iodine does not adsorb on this electrode surface [8].

The cyclic voltammogram of [ReO₂(amine)₂]I at pH=7.5 on pc-Au is completely dominated by current peaks ascribed to I species, in accordance with our previous works involving iodide complexes with the [ReO₂]⁺ and [ReO]³⁺ cores [2,3]. Three anodic contributions at ca. 0.5, 1.25 and 1.4 V are related to the oxidation of I-species and to O-electroadsorption (Fig. 2a). A broad fourth anodic current peak centred at 0.86–0.90 V was studied by graphic deconvolution, and two overlapped contributions were found: one ascribed to the oxidation of [Re^VO₂]⁺ to [Re^{VI}O₂]²⁺ (0.84–0.88 V), and the other to the oxidation of $I_{2(aq)}$ to $IO_{3(aq)}^-$ (0.95 V). The anodic current peak related to the Re^{VI}/Re^V couple varies linearly with $\nu^{1/2}$, whereas the peak potential increases with ν . No cathodic peak is detected, so it can be concluded that [Re^VO₂]⁺ oxidation takes place through a one-electron irreversible process under linear diffusion control [10,11].

Under the same conditions, but on a glassy carbon electrode, a Re^{VI}/Re^V couple centred at 0.85 V can be isolated for dien (Fig. 2b). A slight dependence between the potential value and the amine was observed: 0.88 V

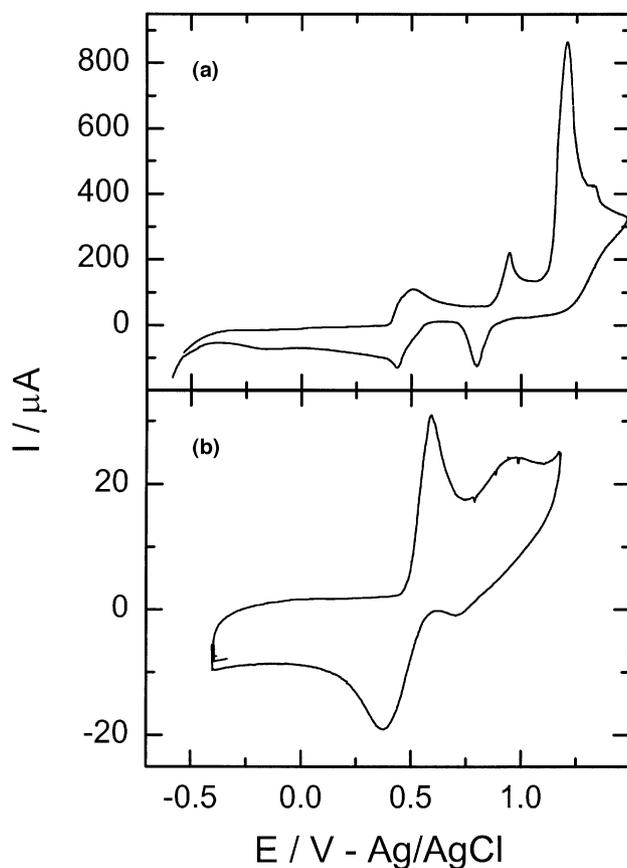


Fig. 1. Cyclic voltammogram of 1 mM KI in 0.1 M LiClO₄, pH=7.5, $\nu = 100$ mV/s, $T = 25$ °C, on (a) polycrystalline Au and (b) glassy carbon electrodes.

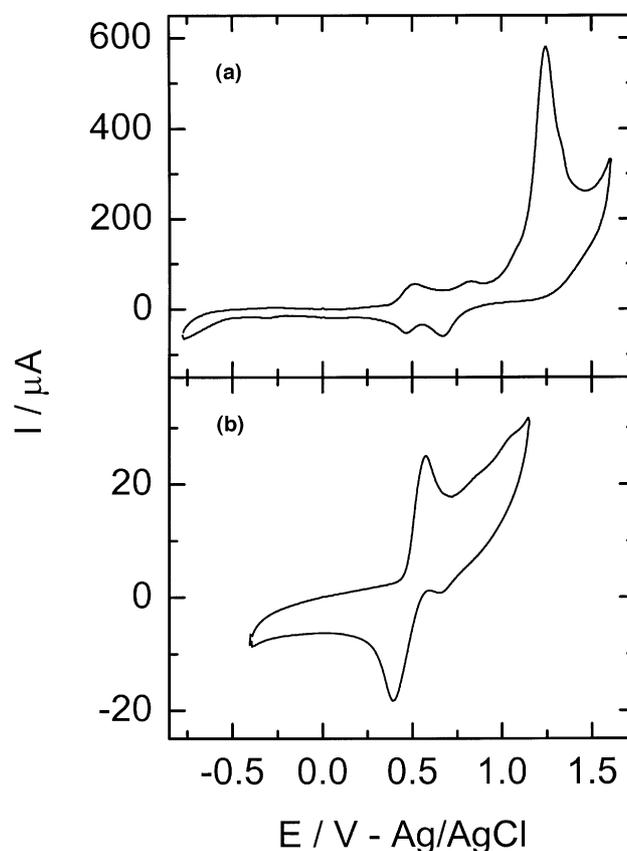


Fig. 2. Cyclic voltammogram of 1 mM [ReO₂(dien)₂]I in 0.1 M LiClO₄, pH=7.5, $\nu = 100$ mV/s, $T = 25$ °C, on (a) polycrystalline Au and (b) glassy carbon electrodes.

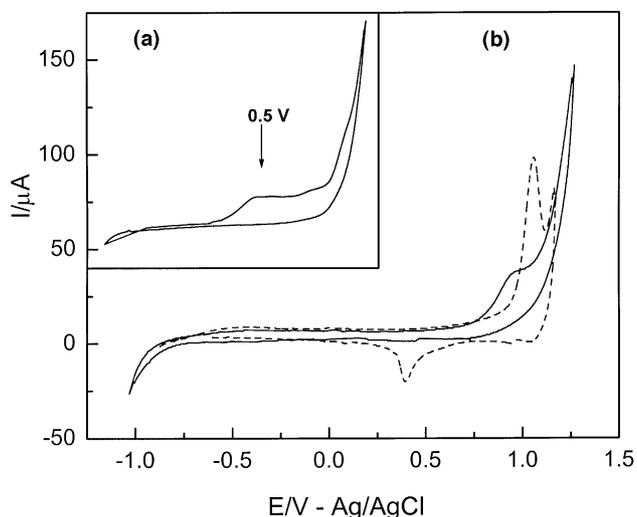


Fig. 3. (a) Cyclic voltammogram of 0.1 M LiClO₄, pH = 7.5, $\nu = 100$ mV/s, $T = 25$ °C on polycrystalline Ni (dashed line) and 1 mM [ReO₂(dien)₂]I in 0.1 M LiClO₄ (solid line). (b) Cyclic voltammogram of 1 mM [ReO₂(dien)₂]I after cathodic polarization at -1.0 V for 2 min.

for trien and 0.86 V for tren. The anodic peak potentials are in accordance with those obtained by graphical deconvolution on pc-Au. The current peak increases linearly with $\nu^{1/2}$, the anodic and cathodic current peak values are the same, and the anodic peak potential moves with $\log \nu$ by 33 mV/decade. All these features are in accordance with a one-electron transfer-controlled process [10,11].

The influence of the IO_{3(aq)}⁻/I_{2(aq)} redox couple depends on the surface configuration. By using electrofaceted surfaces oriented towards the (111) planes for Re–dien, extended iodine oxidation was observed, as can be deduced from the shift in the peak potential to 0.90 V. On the contrary, on a (100)-type electrofaceted surface, the peak potential shifts to 0.80 V, i.e., it is closely related to the Re^{VI}/Re^V couple.

At pH = 7.5, the Ni electrode surface is covered by Ni(OH)₂ that oxidizes to NiOOH at ca. 1 V, the reduction of NiOOH taking place at 0.4 V (Fig. 3a) [5,6]. Re(V)–amine complexes are oxidized by a mechanism involving a chemical reaction between NiOOH and the amine moiety at 0.95 V. After cathodic polarization in the hydrogen evolution domain, the reductive decomposition of [ReO₂(amine)₂]⁺ to ReO₂ is verified [3,12], which in turn oxidizes to ReO₄⁻ at ca. 0.5 V [12] (Fig. 3b).

4. Conclusions

- The voltammetric profile of the complexes on Au electrodes is strongly influenced by iodide. However, it is possible to study the oxidation of the [Re^VO₂]⁺

core after graphic deconvolution, from which an irreversible one-electron process under linear diffusion control can be deduced.

- Preferentially oriented Au surfaces are useful to discriminate the attributed Re^{VI}/Re^V redox couple.
- The redox couple Re^{VI}/Re^V can be isolated on glassy carbon electrodes, with no interference of adsorbed I-species. The peak potentials were the same as those obtained on Au after graphic deconvolution.
- On Ni, the free amino group oxidizes at 0.95 V. In addition, the reductive decomposition of the complex takes place in the hydrogen evolution potential region, yielding ReO₂ as the stable product.
- The analysis of Re(V)–amine dioxo complexes with the new approach proposed in this work allows studying all the redox reactive centres of the molecule independently.
- When comparing the voltammetric behavior of Re–dien and related complexes with that of other amine-containing compounds such as [ReO₂(en)₂]I, it is possible to conclude that Re–dien and related complexes are less stable towards oxidation than the Re–en complex. As mentioned above, the Re–en complex shows a [Re^{IV}O₂]/[Re^VO₂]⁺ oxidation peak potential value at ca. 0.8 V, while Re–dien and related complexes show a current contribution attributed to Re^{VI}/Re^V at nearly the same potential value. This accounts for the presence of the free amino tail, which enhances the redox reactivity of the Re–dien complexes. Moreover, Re–dien complexes result more stable towards reduction than Re–en compounds, as the reductive decomposition of the Re–dien and related complexes to ReO₂ are verified only under strongly reductive conditions on nickel.

Acknowledgements

Financial support from CONICYT-FCE No. 6015, PEDECIBA-Química (Uruguay) and CIC (Argentina) is acknowledged.

References

- [1] K. Schwochau, *Technetium, Chemistry and Radiopharmaceutical Applications*, Wiley-VCH, Weinheim, 2000.
- [2] M.F. Cerdá, G. Obal, E. Méndez, C.F. Zinola, C. Kremer, M.E. Martins, A.M. Castro Luna, *J. Colloid Interf. Sci.* 236 (2001) 104.
- [3] M.F. Cerdá, E. Méndez, L. Malacrida, C.F. Zinola, C. Melián, M.E. Martins, A.M. Castro Luna, C. Kremer, *J. Colloid Interf. Sci.* 249 (2002) 366.
- [4] J. Gancheff, C. Melián, C. Kremer, S. Domínguez, A. Mederos, O.N. Ventura, E. Kremer, *J. Coord. Chem.* 54 (2001) 285.
- [5] M. Fleischmann, K. Korinek, D. Plechter, *J. Chem. Soc. Perkin Trans. II* (1972) 1396.
- [6] R.S. Schebler, J.R. Vilche, A.J. Arvía, *J. Electrochem. Soc.* 125 (1978) 1578.

- [7] J.F. Rodríguez, M.P. Soriaga, J. Electrochem. Soc. 135 (1988) 616.
- [8] G.E. Cabaniss, A.A. Diamantis, W.R. Murphy, R.W. Linton, T.J. Meyer, J. Am. Chem. Soc. 107 (1985) 1845.
- [9] C.L. Perdriel, M. Ipohorski, A.J. Arvía, J. Electroanal. Chem. 215 (1986) 317.
- [10] A.J. Bard, L.R. Faulkner, in: *Electrochemical Methods*, Wiley, New York, 1980, pp. 215–227.
- [11] R.N. Adams, in: *Electrochemistry at Solid Electrodes*, Dekker, New York, 1969, p. 115.
- [12] J. Zerbino, A.M. Castro Luna, C.F. Zinola, E. Méndez, M.E. Martins, J. Electroanal. Chem. 521 (2002) 763.